

COMISION NACIONAL DE ENERGIA ATOMICA
PRESIDENCIA DE LA NACION

PROGRAMA MULTINACIONAL DE METALURGIA
(Programa Regional de Desarrollo Científico y Tecnológico-OEA)

ATAQUE LOCALIZADO DE METALES. PARTE I

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Tercer Seminario Latinoamericano en el Nivel de Postdoctorado
Tema: CORROSION

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MECHANISM OF INTERGRANULAR CORROSION OF Al-Cu ALLOYS*

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Abstract—The anodic behaviour of pure Al and some specially prepared Al-Cu alloys has been studied to check the mechanism of intergranular corrosion of aged Al-4%Cu. A clear relationship between pitting and intergranular corrosion has been found. Intergranular corrosion only occurs in the presence of certain anions, and over a narrow range of potentials. Difference in pitting potentials, rather than difference in electrode potentials, is the main factor in producing intergranular corrosion of Al-4%Cu. The conditions of heat treatment, solution composition, and potential, at which intergranular corrosion appears, have been established.

Résumé—On a étudié le comportement de Al et de quelques alliages Al-Cu spécialement préparés afin de vérifier le mécanisme de la corrosion intergranulaire de Al-4% Cu vieilli. On a trouvé une relation nette entre piqûration et corrosion intergranulaire. Celle-ci n'a lieu qu'en présence de certains anions et dans un intervalle étroit de potentiel. La différence des potentiels de piqûration, plus que celle des potentiels d'électrode, est le facteur essentiel de la corrosion intergranulaire de Al-4% Cu. On a établi les circonstances de traitement thermique, de composition de solution et de potentiel de l'apparition de la corrosion intergranulaire.

Zusammenfassung—Das anodische Verhalten von reinem Aluminium und einigen, besonders aufbereiteten Al-Cu Legierungen ist untersucht worden, um den Mechanismus von Korngrenzenkorrosion von gealtertem Al-4%Cu zu prüfen. Es wurde ein deutliches Verhältnis zwischen Lochfrass und Korngrenzenkorrosion gefunden. Korngrenzenkorrosion erfolgt nur bei Vorhandensein von bestimmten Anionen und über einen engen Potentialbereich. Unterschied in Lochfrass Potentialen zu einem grösseren Grade als Unterschied in Elektroden Potentialen ist die Hauptursache, Korngrenzenkorrosion von Al-4%Cu hervorzurufen. Die Bedingungen für Wärmebehandlung, Lösungszusammensetzung und Potential, bei welchem Korngrenzenkorrosion erscheint, wurden festgelegt.

INTRODUCTION

THE INTERGRANULAR corrosion of aged Al-4%Cu alloys has been the subject of numerous investigations.¹⁻⁷ It is generally agreed that the microstructure of the aged Al-Cu alloy is the one represented in Fig. 1. At this stage of heat treatment the changes in the structure of the grain bodies are not yet detectable by common metallographic techniques, and for the present purposes are usually considered as a single phase. At the grain boundaries, on the other hand, the precipitation rate is higher, and two phases can be observed, the θ phase, or Al_2Cu , surrounded by the other phase, a Cu-depleted zone, which, according to the equilibrium diagram⁽⁸⁾, should approximate to Al-0.2%Cu. Consequently in the generally accepted mechanism of intergranular corrosion¹⁻⁷ the aged Al-4%Cu alloy is described as a three-phase system having anodic and cathodic zones. The copper-depleted zone along the grain boundaries is

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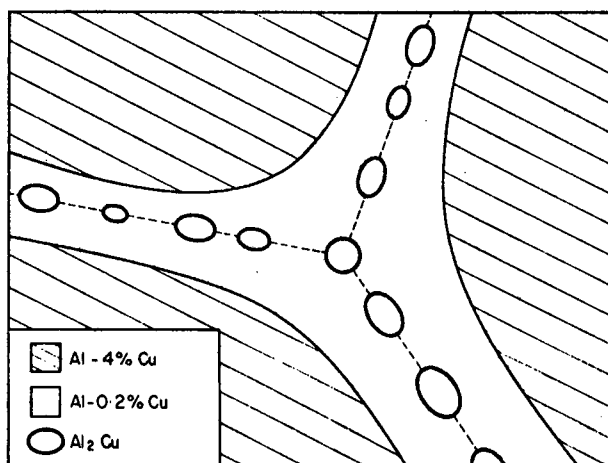


FIG. 1. Schematic representation of the microstructure of an aged Al-4%Cu alloy.

the anode (phase I), whilst the grain bodies (phase II) and the intermetallic Al_2Cu (phase III) are cathodes. The intergranular corrosion of Al-Cu would then be a process in which a very small anode is in contact with a large cathode. In support of this mechanism measurements made by various authors²⁻⁵ showed that during corrosion there was a difference in potentials of the order of 100 mV between the grain boundaries and the grain bodies. Nevertheless, a mechanism of anodic and cathodic zones does not explain why the presence of Cl^- is necessary to get intergranular corrosion, and intergranular corrosion should occur in almost any corrosive medium. Therefore any mechanism of intergranular corrosion of aged Al-4%Cu must explain the action of the Cl^- ions.

The purpose of the present work was to find out the function of the Cl^- in the intergranular corrosion of Al-Cu alloys. Specimens of each of the three phases present in the aged Al-4%Cu alloy were studied in Cl^- solutions. It has been found that the intergranular corrosion of the aged Al-4%Cu alloy appears only over a certain potential range, and that it is related to the process of pitting of Al.

EXPERIMENTAL

Specimens of solubilized Al-4%Cu were used to simulate the behaviour of the grain bodies of aged Al-4%Cu. For the study of the other two phases the intermetallic Al_2Cu and Al-0.2%Cu alloy were used.

Measurements were performed on alloys prepared with Al 99.99% and Cu 99.999%. The analytical composition of the nominal alloy was, for Al-4%Cu, 4.07%Cu; for Al-0.2%Cu, 0.27%Cu; and for the intermetallic Al_2Cu , 56.1%Cu. Several potentiostatic measurements on Al 99.99% and Al 99.9999% were also performed.

The specimens were prepared by cutting coupons of 10×30 mm from a 1 mm thick cold-rolled sheet of the alloys. The solubilized Al-4%Cu was prepared by heating the specimens for 2 h at 550°C and water quenching. The aged specimens were prepared by heating the solubilized specimens for 3 h at 176°C; and the over-aged

specimens were obtained by heating the solubilized material for 1 h at 430°C. The Al-0.2%Cu and the pure Al specimens were annealed for 2 h at 600°C and water quenched. The edges and the surface of the specimens were covered with a cured-epoxy resin, leaving an uncovered area of about 1 cm². The specimens were electro-polished in a HClO₄ acetic anhydride bath, and stored in a desiccator for a few days before the experiments.

The specimens of the intermetallic Al₂Cu were cast rods of about 6 mm dia. The surface of the rods was covered with the cured-epoxy resin, and one end was mechanically taper polished with diamond powder, leaving an exposed area of about 1 cm².

The solutions were prepared with analytical grade reagents and were deaerated⁹ with purified N₂.

The potential was controlled with a Tacussel PRT 20-2-M potentiostat. All the measurements were made at 25°C in a Pyrex glass cell, with a platinum counter electrode. The potentials were measured, through a Luggin capillary, with a saturated calomel electrode, and referred to the normal hydrogen electrode scale (nhe).

RESULTS

Anodic polarization curves in NaCl

Polarization curves were obtained for each of the three phases, in solutions containing various concentrations of NaCl. The measurements were made in steps of 10 mV, waiting at each point until a stationary current was observed. Figure 2 shows a typical example of the polarization curves obtained. The results with pure Al were similar to the ones reported by Kaesche¹⁰ and Bond *et al.*,¹¹ and the same type of anodic polarization curve was obtained with solubilized Al-4%Cu, Al-0.2%Cu, and Al₂Cu. In all cases the specimens showed a passive range, where no attack was observed. But, as the potential was increased to the critical potential, there was a

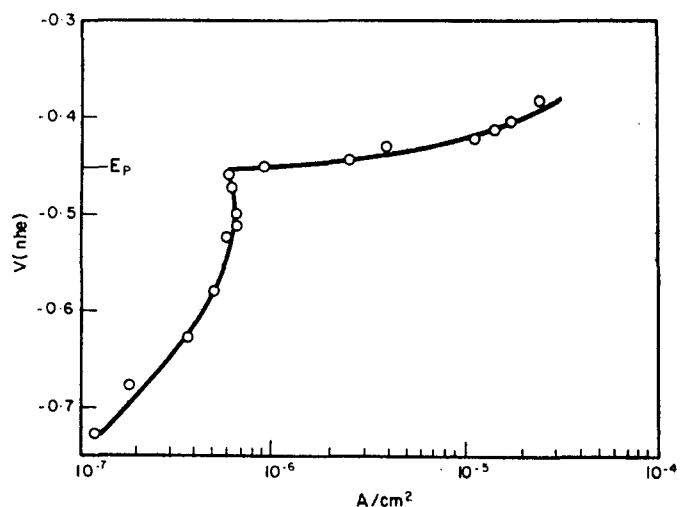


FIG. 2. Anodic polarization curve of 99.99%Al in deaerated 0.1M NaCl solution.
E_p: potential at which pitting starts.

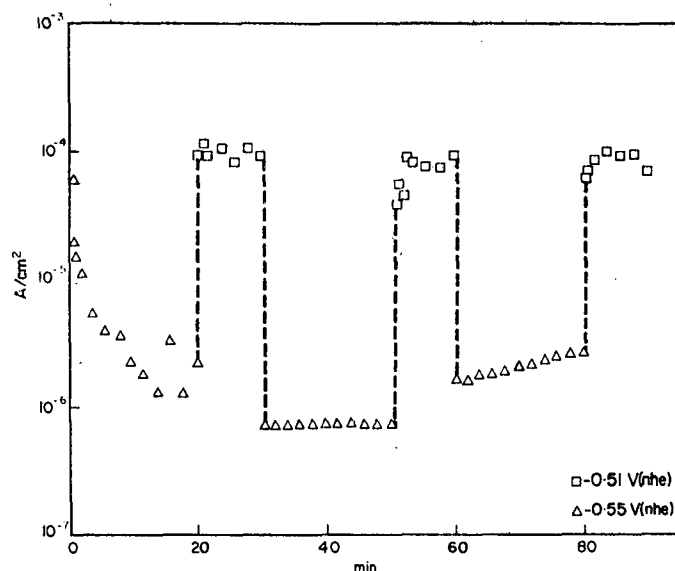


FIG. 3. Behaviour of 99.99%Al in deaerated 1M NaCl solution when the potential is switched from the passive range to the pitting range. The pitting potential was -0.53 V(nhe).

marked increase in the current, and pitting was then detected on the surface. Although the existence of critical potentials for pitting is supported by various authors,¹⁰⁻¹⁵ recent work has thrown doubts on the existence of such potentials,¹⁶⁻¹⁸ since pitting does not occur until after an induction period.

In view of this discrepancy of opinions, two types of experiments were made to study the pitting of Al in Cl^- solutions.

In a first series of experiments 99.99%Al was immersed in deaerated 1M NaCl and the potential of the specimen was switched every 10 to 20 min from the passive range to the pitting range (Fig. 3). When the specimen is held at a low potential the current decreases to very small values, but if the potential is then switched to a higher value, which is in the pitting range, the current increases by two or more orders of magnitude, and pits form on the surface of the metal. If the potential is switched back to the low initial value, the pitting stops and the metal repassivates. This experiment can be repeated several times on the same specimen with the same results. If pitting of Al in Cl^- solutions is a time-dependent process, independent of the potential, once pitting has started it would not be expected to stop when the potential is decreased.

A second series of experiments consisted in recording the changes in the anodic current for 5 h when specimens of 99.99%Al were held at various constant potentials in 1M deaerated NaCl (Fig. 4). When the potential was maintained in the range -0.76 V(nhe) and -0.53 V(nhe) the c.d. after 5 h remained below $1 \mu\text{A}/\text{cm}^2$, and no pitting was observed. But with a potential only 10 mV higher than -0.53 V the c.d. increased by more than three orders of magnitude and pitting commenced. These experiments showed that if there is an induction time for pitting of Al, a change in potential of 10 mV should decrease the induction time by at least four orders of

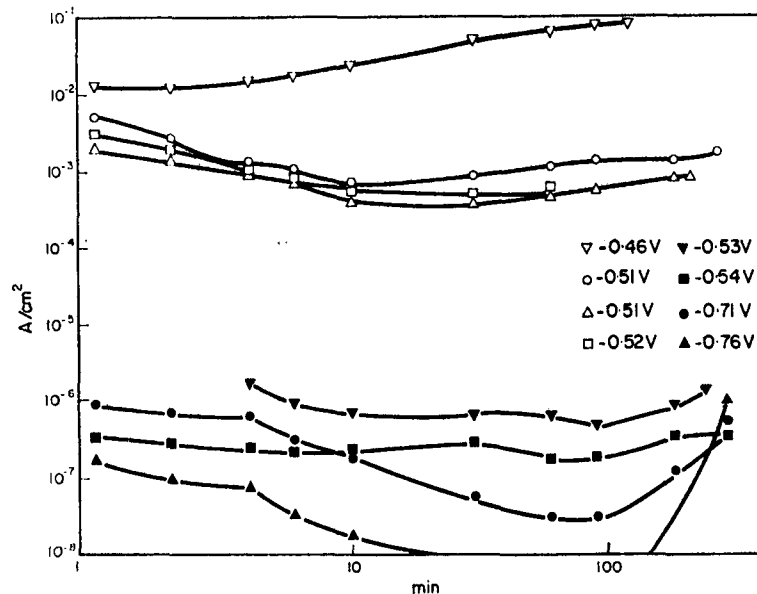


FIG. 4. Current-time curves for 99.99% Al in deaerated 1M NaCl solution at various potentials.

magnitude. It can be concluded therefore that pitting of Al is related to a critical potential which does not depend on an induction period.

Pitting potentials

The critical pitting potentials of the three phases and of pure Al in various concentrations of deaerated NaCl are shown in Fig. 5. The pitting potential for all the three phases is linearly related to logarithm of the activity of NaCl, and in the range 0.01 to 5M NaCl the following relations were obtained:

Phase I, and high purity Al:

$$Ep_I = -0.536 - 0.073 \log (\alpha_{\text{NaCl}})$$

where Ep_I is the breakdown potential in V(nhe).

Phase II:

$$Ep_{II} = -0.404 - 0.046 \log (\alpha_{\text{NaCl}}), \text{ and}$$

Phase III:

$$Ep_{III} = -0.420 - 0.055 \log (\alpha_{\text{NaCl}}).$$

In all the cases studied the breakdown potentials for the Cu-rich phases were about 100 mV higher than the values for specimens with lower Cu content. The pitting potentials of the solubilized Al-4%Cu were similar to those of the intermetallic Al_2Cu , and no difference was observed in the pitting potentials of the Al-0.2%Cu and high purity Al.

Influence of heat treatment on intergranular corrosion

With the results shown in Fig. 5 it should be possible to predict the behaviour of heat-treated Al-4%Cu alloys in Cl^- solutions at different potentials. As shown in this

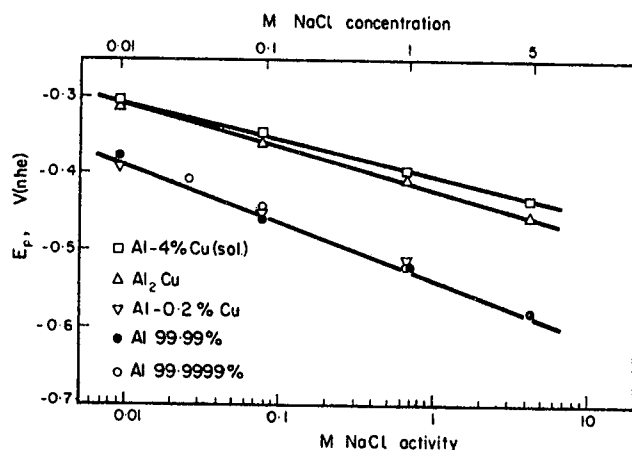


FIG. 5. Effect of the chloride concentration on the pitting potential of pure aluminium and various Al-Cu alloys in deaerated NaCl solutions.

figure, there is a range of potentials where an alloy with a Cu-depleted zone will show attack in such zone while the two others remain passive. This sort of behaviour should be expected in a wide range of Cl^- concentrations. For example, an aged Al-4%Cu alloy (Fig. 1) will corrode along the grain boundaries over a range of 100 mV while the grain bodies remain passive. In this case corrosion will concentrate in the few-microns-thick Cu-depleted zone.

The results for aged Al-4%Cu confirm such prediction, and Fig. 6 shows a typical example of an anodic polarization curve in deaerated 1M NaCl; in this particular experiment the potential was changed in steps of 10 mV every minute. The values of the expected breakdown potentials of the grain boundaries and of the grain bodies

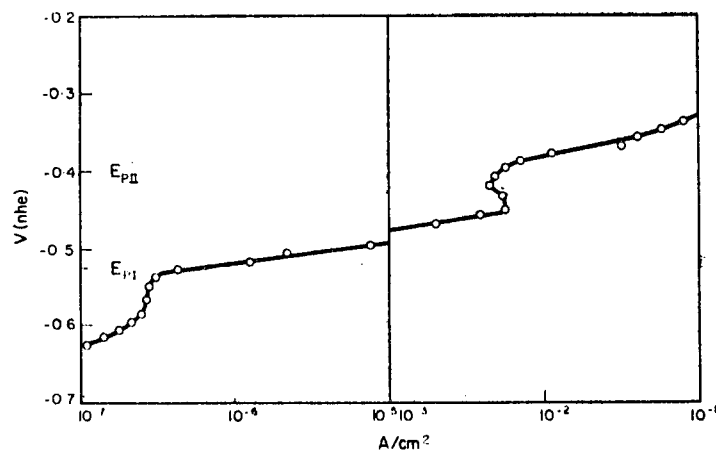


FIG. 6. Anodic polarization curve of aged Al-4%Cu in deaerated 1M NaCl solutions. Measurements made in steps of 10 mV/min. E_{pI} : pitting potential measured for Al-0.2%Cu. E_{pII} : pitting potential of solubilized Al-4%Cu.

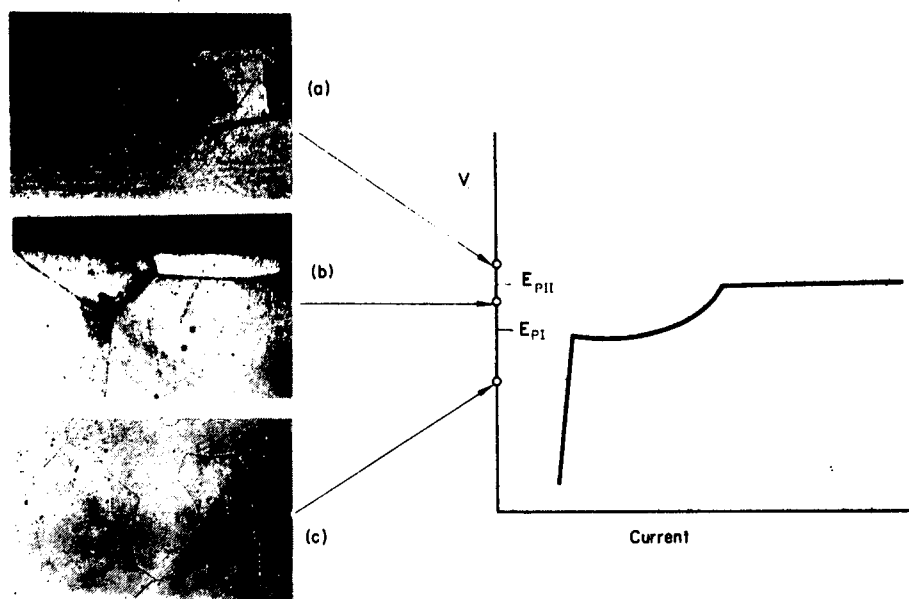


FIG. 7. Anodic polarization curve and type of attack for aged Al-4%Cu in deaerated 1M NaCl solution. Exposure conditions: *a* = 20 min at -0.35 V(nhe), intergranular corrosion plus tunnel-like pitting, section ($120\times$); *b* = 20 min at -0.43 V(nhe), intergranular corrosion, section ($120\times$); *c* = 90 min at -0.66 V(nhe), specimen not corroded, normal view ($30\times$).

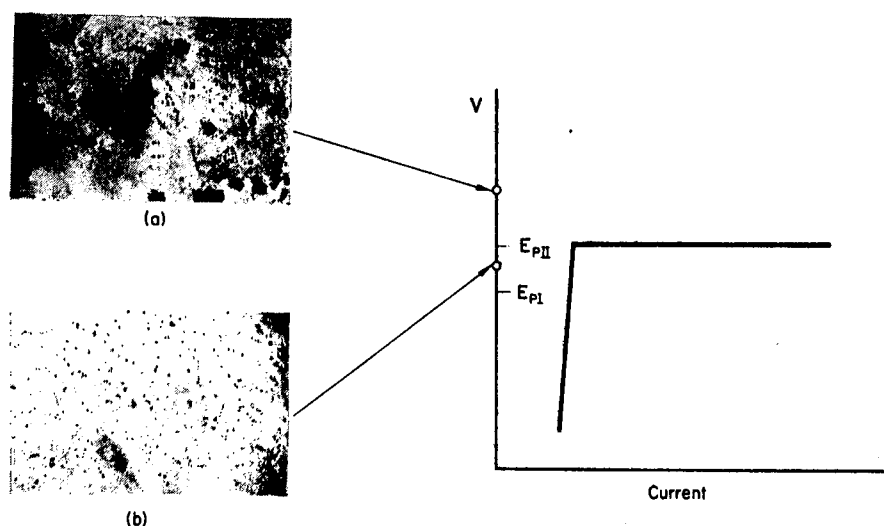


FIG. 9. Polarization curve and type of attack of solubilized Al-4%Cu in deaerated 1M NaCl solution. *a* = 5 min at 0.26 V(nhe), pitting corrosion ($30\times$); *b* = 90 min at -0.46 V(nhe), no corrosion except for the pits produced during electropolishing ($30\times$).

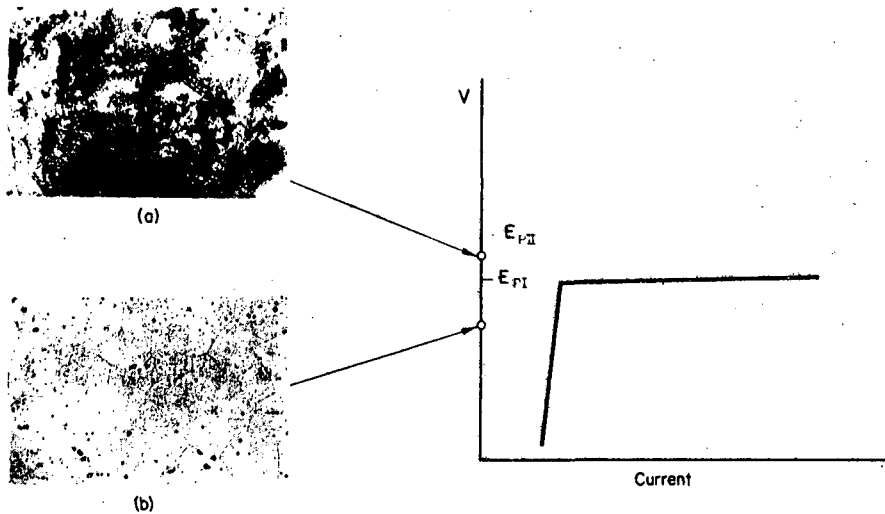


FIG. 11. Polarization curve and type of attack of over-aged Al-4%Cu in deaerated 1M NaCl solution. *a* = 10 min at -0.44 V(nhe), generalized pitting ($30\times$); *b* = 90 min at -0.66 V(nhe), no corrosion except for pits produced during electropolishing ($30\times$).

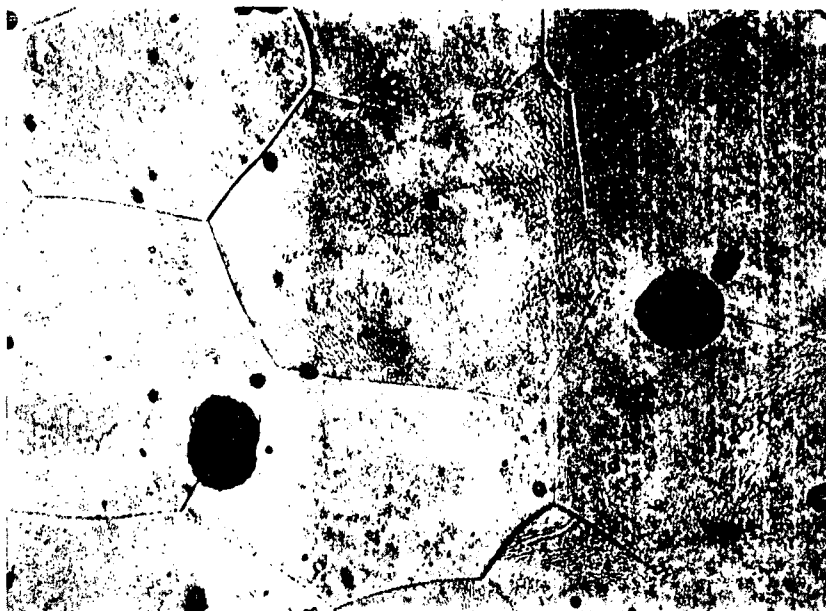


FIG. 13. Type of attack of aged Al-4%Cu in 1M NaNO₃ solution, exposed 1 h at $+1.85$ V(nhe). Pitting nucleates at the grain boundaries but no intergranular corrosion was observed ($100\times$).

are also included. It was found that when the first breakdown potential is reached, an increase in c.d. occurs, and intergranular corrosion begins. Increasing further the potential results in a slowdown in the current increase, probably due to the narrow front in which the attack is taking place, but when the second breakdown potential is reached there is a new increase in current and corrosion of the grain bodies begins.

Similar results were obtained in other experiments where the potential was maintained constant, and Fig. 7 shows the type of corrosion observed for aged Al-4%Cu in 1M deaerated NaCl, under constant potential. Specimen c was exposed for 90 min at a potential of -0.66 V(nhe), and did not show any type of attack. Another specimen b exposed for 20 min at -0.43 V(nhe) showed intergranular corrosion. And a third specimen a exposed for 20 min at -0.35 V(nhe), showed corrosion at the grain boundaries and in the grain bodies. The attack in the grain bodies took the form of tunnels, similar to the ones described by various authors for pure Al.¹⁹⁻²¹ These experiments were repeated with several other specimens of aged Al-4%Cu and the same relation between the potential applied and the type of corrosion was always obtained.

The data in Fig. 5 can also be applied to predict the kind of corrosion for other heat treatments. A solubilized Al-4%Cu, for example, has only one phase (Fig. 8), and in this case localized corrosion should appear at potentials higher than E_{pII} , but the metal should remain passive at lower potentials. This is confirmed in Fig. 9, where 90 min exposure at -0.46 V(nhe) did not produce any attack, except for the small pits produced during electropolishing of the specimens. But after 5 min exposure at -0.26 V(nhe) severe pitting was observed.

In the over-aged condition, on the other hand, the grain bodies show a two-phase structure, as schematically represented in Fig. 10. According to Fig. 5 an alloy with this microstructure should suffer general corrosion at potentials higher than E_{pI} . This was experimentally confirmed (Fig. 11), and a specimen exposed at a potential of -0.44 V(nhe) showed severe pitting, while another specimen exposed for 90 min

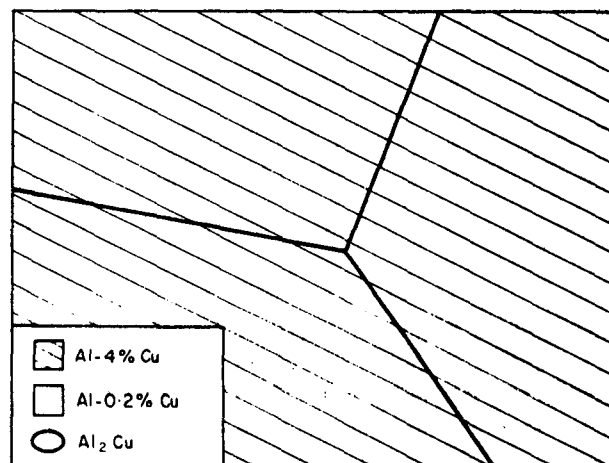


FIG. 8. Schematic representation of the microstructure of solubilized Al-4%Cu alloy. Only one phase is present.

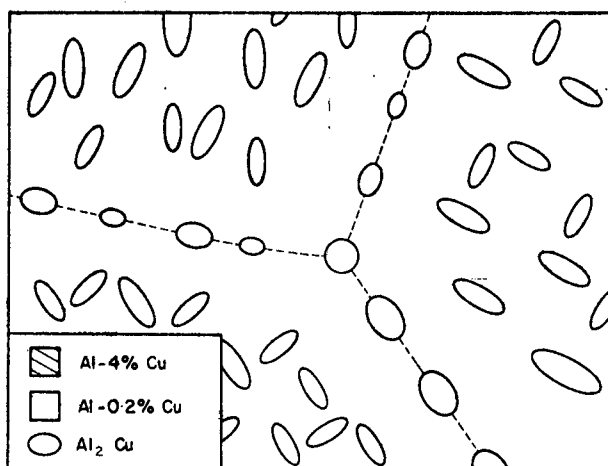


FIG. 10. Schematic representation of the microstructure of over-aged Al-4% Cu alloy. Only Al-0.2% Cu and Al_2Cu are present.

at -0.66 V(nhe) was unattacked. This type of behaviour explains why Farmery and Evans² found that the "light zone" along the grain boundaries was *not always* related to intergranular corrosion. This precipitate-free zone is also present in the over-aged alloy. But the over-aged alloy will suffer corrosion not only in the grain boundaries but also in the grain bodies (Fig. 11). Besides, the increase in the anodic area, and the consequent reduction in the cathodic area, will favor generalized corrosion rather than intergranular attack.

TABLE 1. TYPE OF ATTACK OF AGED Al-4% Cu IN 1M DEAERATED NaCl SOLUTION

Heat treatment	Potential		
	Below -0.52 V(nhe)	Between -0.52 and -0.40 V(nhe)	Over -0.40 V(nhe)
Solubilized	Passive	Passive	Pitting
Aged	Passive	Intergranular	Generalized*
Over-aged	Passive	Pitting	Pitting

*The attack is a mixture of pitting plus intergranular corrosion.

Table 1 summarizes the behaviour of Al-4% Cu alloys with different heat treatments at various potentials in deaerated 1M NaCl solutions. No attack is observed for any heat treatment at potentials below -0.52 V(nhe). Such a behaviour could not be predicted from the mechanism of anodic and cathodic zones. Between -0.52 V(nhe) and -0.40 V(nhe) the behaviour of all heat treatments is the same as that expected from the original anodic-zone mechanism, and above -0.40 V(nhe) a behaviour not predicted by that mechanism is again found.

From a practical point of view, the low potentials are obtained when working in pure Cl^- solutions in the absence of O_2 . The second range of potentials is obtained in O_2 -saturated solutions, and in order to reach the highest range of potentials either a stronger oxidizer or an external current will be required.

Cathodic polarization curves

It is known in practice that O_2 plays an important role in the intergranular corrosion of Al-Cu alloys.²² For this reason the cathodic polarization curves in air-saturated 1M NaCl were determined for pure Al, solubilized Al-4%Cu and Al_2Cu (Fig. 12). It was found that, as already mentioned by Ketcham and Haynie,⁷ the cathodic reaction is kinetically easier in the Cu-rich phases than in pure Al, which is decisive in the behaviour of Al alloys in Cl^- solutions, as discussed later.

Intergranular corrosion in absence of Cl^-

To determine the possibility of pitting in media other than Cl^- solutions, polarization curves were obtained for 99.99%Al and for solubilized Al-4%Cu in various solutions. From what had been observed in Cl^- solutions, pure Al was expected to behave in the same way as the depleted zone of grain boundaries, and the solubilized alloy was used to simulate the behaviour of the grain bodies (Table 2). In 1M NaIO_3 , Na_2SO_4 , H_2SO_4 , and ammonium tartrate no pitting was observed up to +3 V(nhe), the highest potential used in the present work. Furthermore, no intergranular corrosion was detected in aged Al-4%Cu when polarized in those solutions at +3 V(nhe). A similar behaviour is to be expected in all other solutions that produce compact anodic oxide films on Al. On the other hand pitting was observed in Br^- , I^- , ClO_4^- , and NO_3^- solutions. In the first three solutions, as in the case of Cl^- solutions, a difference of 130 to 200 mV was observed between the pitting potentials of pure Al and of the

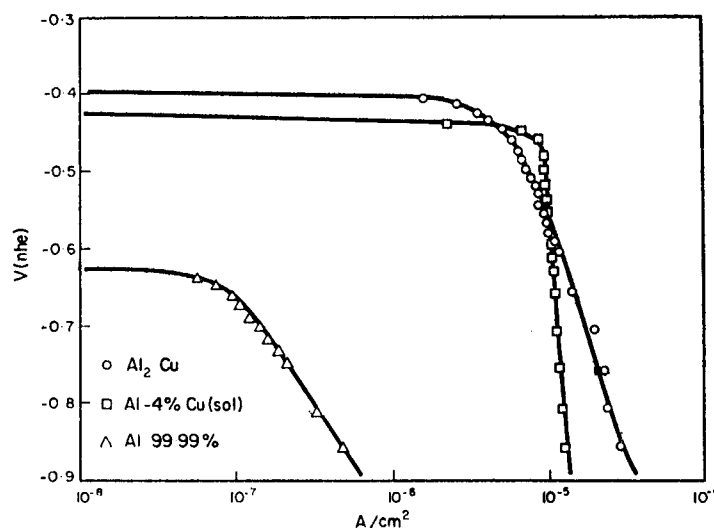


FIG. 12. Cathodic polarization curves in air-saturated 1M NaCl solution of pure aluminium, solubilized Al-4%Cu, and intermetallic Al_2Cu .

TABLE 2. RELATION BETWEEN PITTING POTENTIALS AND INTERGRANULAR CORROSION IN SOLUTIONS OTHER THAN NaCl

Electrolyte	Pitting potentials V(nhe)		Intergranular corrosion*
	99.99%Al	Al-4%Cu (solub.)	Al-4%Cu (aged)
1M KBr	- 0.42	- 0.28	Yes (- 0.40)
1M KI	- 0.26	- 0.13	Yes (- 0.23)
1M NaClO ₄	- 0.17	+ 0.03	Yes (- 0.14)
1M NaNO ₃	+ 1.80	+ 1.85	No (+ 1.85)
1M Na ₂ SO ₄	> + 3.0	> + 3.0	No (+ 3.0)
1M H ₂ SO ₄	> + 3.0	> + 3.0	No (+ 3.0)
0.1M NaIO ₃	> + 3.0	> + 3.0	No (+ 3.0)
1M Ammonium tartrate	> + 3.0	> + 3.0	No (+ 3.0)

*In parentheses, potentials at which the intergranular corrosion susceptibility was tested.

solubilized Al-4%Cu. When the aged Al-4%Cu alloy was exposed to a potential between both pitting potentials intergranular corrosion was detected.

As mentioned above pitting of pure Al and of solubilized Al-4%Cu was observed in NO₃ solutions. No intergranular corrosion of the aged Al-4%Cu was detected. Aged Al-Cu showed pitting along the grain boundaries (Fig. 13), and the reason for this difference in behaviour could lie in the differences in pitting morphology.³³ The pits in Al in NO₃ solutions are hemispherical, while in the other media they were found to be tunnel-like. It seems that in nitrate solutions corrosion starts in the grain boundaries, but cannot spread along the narrow depleted zone as it occurs in ClO₄ and in halide solutions.

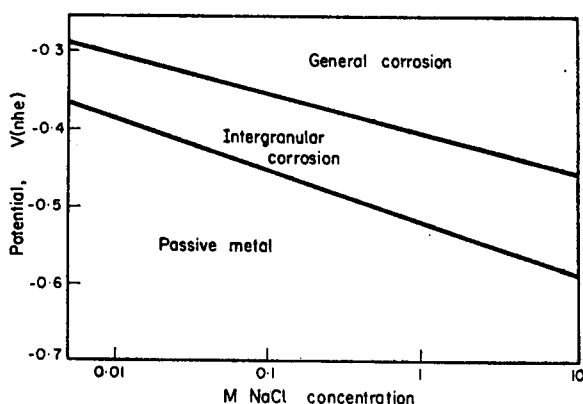


FIG. 14. Simplified potential-concentration diagram showing the type of attack suffered by aged Al-4%Cu.

DISCUSSION AND CONCLUSIONS

The present results show that intergranular corrosion of aged Al-4%Cu occurs only in a narrow range of potentials. Figure 14 summarizes the results obtained with aged Al-4%Cu, showing the type of attack expected at different potentials and Cl⁻ concentrations. If the metal is maintained in the *passive metal* region, no intergranular corrosion will occur and the metal will be cathodically protected, although its potential will be more positive than the potential of immunity in the potential-pH diagram for Al-H₂O. From the old mechanism of intergranular corrosion by anodic and cathodic zones no protection would be expected at potentials higher than about -2.0 V(nhe).²⁴ Nevertheless, it was found in the present work that intergranular corrosion does not occur if the metal is kept in the range -0.4 V(nhe) to -0.6 V(nhe), depending on the Cl⁻ concentration of the media. These results apply only to pure NaCl or KCl solutions. If other anions are present in the solution the zones in Fig. 14 should be displaced to higher potentials, this displacement should be equal to that caused to pitting potentials by the same anions.²³

The behaviour of Al-Cu alloys in natural environments can be explained by the use of the anodic and cathodic polarization curves previously described. Figure 15 shows schematically the anodic and cathodic polarization curves for the Al-Cu system in chloride solutions. A_1 is the anodic polarization curve for pure Al and Al-0.2%Cu, A_2 is the anodic polarization curve for solubilized Al-4%Cu and for Al₂Cu, C_1 is the cathodic polarization curve for the Al-Cu alloy in the absence of O₂, C_2 is the cathodic polarization curve for pure Al and for Al-0.2%Cu in the presence of O₂ and C_3 is the cathodic polarization curve for the Cu-rich phases in the presence of O₂. In the absence of O₂, the corrosion potential of the aged Al-4%Cu alloy will be E_1 , and the

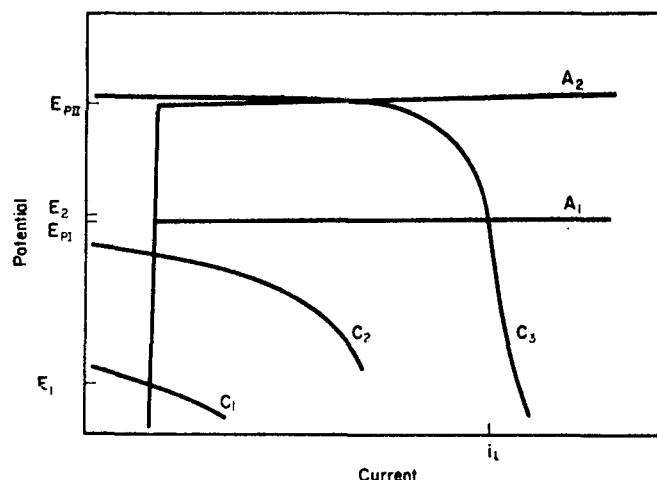


FIG. 15. Current-potential relations for Al and Al-Cu in chloride solutions. A_1 : anodic polarization of Al and Al-0.2%Cu; A_2 : anodic polarization of solubilized Al-4%Cu and of Al₂Cu; C_1 : cathodic polarization of solubilized Al-4%Cu in absence of oxygen; C_2 : cathodic polarization of pure aluminium in air saturated solutions; C_3 : cathodic polarization of solubilized Al-4%Cu in air saturated solution; E_1 : corrosion potential of Al-Cu in deaerated solution; E_2 : corrosion potential of aged Al-Cu in air saturated solution; i_L : limiting current for the cathodic reaction, and dissolution current of the grain boundaries of the aged Al-Cu alloy.

alloy will remain passive. If O_2 is allowed into the system, the corrosion potential will develop to E_2 , a little higher than E_{p1} . Under these conditions the Cu-rich phase will remain passive and the Cu-depleted zone will corrode. The rate of corrosion of the Cu-depleted zone will be equal to the limiting current of the cathodic reaction of O_2 reduction. Hence the higher the O_2 content, or the higher the cathodic area, the higher the corrosion rate of the grain boundaries. This explains the influence of the cathodic area on intergranular corrosion found by Colner and Francis.⁵ As for pure Al, the corrosion potential will be given by the intersection of A_1 and C_2 , but due to the "slowness" of the cathodic reaction on pure Al the metal will not show much corrosion.

Summing up, the results of the present work show that intergranular corrosion of Al-Cu alloys is not due to a difference in potentials between grain boundaries and grain bodies, but to a difference in the breakdown potentials of those phases. The mechanism of intergranular corrosion of Al-Cu is found to be of the same nature as the process of pitting of Al. It is concluded that intergranular corrosion of Al-Cu will occur only under the following conditions:

1. The alloy must have a solute-depleted zone along the grain boundaries.
2. The corrosive medium should contain anions capable of breaking down the passivity of the Al.
3. The breakdown potential of the depleted zone must be lower than that of the grain bodies.
4. The corrosion potential of the alloy must be over the breakdown potential of the depleted zone, and under the breakdown potential of the grain bodies.

When the pitting potential is too high, as in the case of nitrate solutions, other factors, like the morphology of pitting, could be important and are being studied at present.

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**CORROSION BAJO TENSIONES DEL ZIRCALOY-4 EN PRESENCIA
DE CLORUROS . ESTUDIO FRACTOGRAFICO**

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INTRODUCCION

Es un hecho conocido que el Circonio presenta el fenómeno del picado en soluciones acuosas de cloruros (1, 2). En cambio en dichos medios es muy poco lo que se conoce acerca de su susceptibilidad a la corrosión fisurante bajo tensiones mecánicas, ya sean aplicadas o residuales (3, 4).

Como en diversas aleaciones el picado en presencia de cloruros está asociado a la aparición de corrosión bajo tensiones: acero inoxidable, Aluminio-4%, AISI 4340, etc. (5, 6, 7), se comenzó a investigar si el Circonio y algunas de sus aleaciones presentaban una relación similar.

El presente trabajo fué realizado con una aleación de Circonio, el Zircaloid-4, muy empleada en la tecnología nuclear como vaina para los elementos combustibles, tanto de uranio natural como enriquecido, que se emplean en los reactores moderados por agua (H_2O o D_2O) a presión.

Se comprobó que el Zircaloid-4 es susceptible a la corrosión bajo tensiones en soluciones acuosas de cloruro de sodio cuando se lo mantiene a potenciales iguales o superiores al potencial de picado.

Además, la observación de las superficies de fractura reveló que esta aleación, en dichas condiciones, presenta tres modos consecutivos de propagación de las fisuras. La primera etapa es intergranular y estaría íntimamente relacionada con el fenómeno de picado. Posteriormente, a partir de un dado grado de avance de la fisura, la propagación se continúa en forma transgranular, hasta que finalmente el material se fractura en forma dúctil.

DETALLES EXPERIMENTALES

La composición de la aleación empleada es la siguiente: Zr-1,44% Sn-0,22% Fe-0,10% Cr. Aunque su microestructura no es bien conocida, se considera que en una matriz de α -Zr (hc) el Sn se halla disuelto y el Fe y el Cr están precipitados. En el Zircaloid-2, que además de los aleantes mencionados contiene Ni (0,03 a 0,08%), se detectaron intermetálicos $Zr_2Fe_xCr_y$ y $Zr_2Fe_xNi_y$, cuya estequiometría se aproxima a Zr_2Me (8).

Con este material se prepararon probetas de tracción (fig. 1), que fueron recocidas en un vacío del orden de 10^{-6} mm Hg a $750^\circ C$, o sea en fase α , durante dos horas

y enfriadas en el horno. El tamaño promedio de los granos alcanzaba los 10μ y las propiedades mecánicas a la tracción obtenidas en ensayos de tensión vs. deformación arrojaron los siguientes valores: Límite de fluencia (0,2%): 35,3 Kg/mm²; Ductilidad: 31% y Resistencia a la tracción: 42,2 Kg/mm².

Las probetas, previamente tratadas con solución fluorídrica hasta eliminar una capa superficial de aproximadamente 20μ , antes de cada ensayo fueron pulidas electrolíticamente en una solución de Butilcelosolve-10% ClO₄H. Se pulió a 15°C, bajo una tensión de 25 Voltios que correspondió a una densidad de corriente de $1,5 \times 10^{-3}$ A/cm², durante 30 segundos.

En los ensayos se emplearon soluciones acuosas neutras de ClNaIN, preparadas con droga analítica, sin desgasar, efectuándose las determinaciones a temperatura ambiente.

Como método para evaluar la susceptibilidad a la corrosión bajo tensiones se determinó la influencia que tiene el potencial de electrodo que se aplica a la aleación, controlado potencioestáticamente, sobre los tiempos de fractura. En cada ensayo se mantuvo el material a un potencial anódico controlado, sometiéndolo simultáneamente a un esfuerzo de tracción inferior al límite de fluencia mediante la aplicación de una carga constante.

La celda de vidrio Pyrex que se utilizó (fig. 2), permitía el pasaje de barras de acero tanto por su parte superior como por el fondo que sostenían, mediante pernos, a las probetas de tracción. Dicho conjunto fué recubierto con resina epoxi curada en estufa a 70-80°C dejando expuesto al medio corrosivo sólo el cuello de las probetas.

Se empleó un arrollamiento helicoidal de alambre de Platino como contraelectrodo y la medición del potencial se efectuó con un electrodo de calomel saturado, mediante un capilar de Luggin, refiriéndose los valores de potencial a la escala normal de hidrógeno.

Para someter las probetas a una carga constante, que en los ensayos efectuados correspondió a un esfuerzo igual al 80% del límite de fluencia, se usó una balanza de tracción. Las probetas de tracción fueron acopladas a la misma a través de las barras de sostén mediante un doble dispositivo cardánico a fin de evitar cualquier desalineación.

La balanza de tracción fue calibrada para diferentes pesos en su platillo mediante una celda de carga provista de extensómetros (strain gauge).

El tiempo de fractura se midió con un reloj eléctrico, conectado a un sistema de corte, que interrumpía su marcha al producirse la rotura de las probetas.

El potencial se mantuvo controlado mediante un potencióstato LYP Electrónica y se midió con un pH-mVmetro Leeds & Nortrup Modelo 7404. Para el trazado de curvas de polarización se empleó un Registrador Honeywell Modelo Electronik 193.

Las observaciones fractográficas fueron efectuadas con un microscopio electrónico de barrido (SEM) JSM-U3.

MECHANISM OF INTERGRANULAR CORROSION OF Al-Cu ALLOYS*

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Abstract—The anodic behaviour of pure Al and some specially prepared Al-Cu alloys has been studied to check the mechanism of intergranular corrosion of aged Al-4%Cu. A clear relationship between pitting and intergranular corrosion has been found. Intergranular corrosion only occurs in the presence of certain anions, and over a narrow range of potentials. Difference in pitting potentials, rather than difference in electrode potentials, is the main factor in producing intergranular corrosion of Al-4%Cu. The conditions of heat treatment, solution composition, and potential, at which intergranular corrosion appears, have been established.

Résumé—On a étudié le comportement de Al et de quelques alliages Al-Cu spécialement préparés afin de vérifier le mécanisme de la corrosion intergranulaire de Al-4% Cu vieilli. On a trouvé une relation nette entre piqûration et corrosion intergranulaire. Celle-ci n'a lieu qu'en présence de certains anions et dans un intervalle étroit de potentiel. La différence des potentiels de piqûration, plus que celle des potentiels d'électrode, est le facteur essentiel de la corrosion intergranulaire de Al-4% Cu. On a établi les circonstances de traitement thermique, de composition de solution et de potentiel de l'apparition de la corrosion intergranulaire.

Zusammenfassung—Das anodische Verhalten von reinem Aluminium und einigen, besonders aufbereiteten Al-Cu Legierungen ist untersucht worden, um den Mechanismus von Korngrenzenkorrosion von gealtertem Al-4%Cu zu prüfen. Es wurde ein deutliches Verhältnis zwischen Lochfrass und Korngrenzenkorrosion gefunden. Korngrenzenkorrosion erfolgt nur bei Vorhandensein von bestimmten Anionen und über einen engen Potentialbereich. Unterschied in Lochfrass Potentialen zu einem grösseren Grade als Unterschied in Elektroden Potentialen ist die Hauptursache, Korngrenzenkorrosion von Al-4%Cu hervorzurufen. Die Bedingungen für Wärmebehandlung, Lösungszusammensetzung und Potential, bei welchem Korngrenzenkorrosion erscheint, wurden festgelegt.

INTRODUCTION

THE INTERGRANULAR corrosion of aged Al-4%Cu alloys has been the subject of numerous investigations.¹⁻⁷ It is generally agreed that the microstructure of the aged Al-Cu alloy is the one represented in Fig. 1. At this stage of heat treatment the changes in the structure of the grain bodies are not yet detectable by common metallographic techniques, and for the present purposes are usually considered as a single phase. At the grain boundaries, on the other hand, the precipitation rate is higher, and two phases can be observed, the θ phase, or Al_2Cu , surrounded by the other phase, a Cu-depleted zone, which, according to the equilibrium diagram⁽⁸⁾, should approximate to Al 0.2%Cu. Consequently in the generally accepted mechanism of intergranular corrosion¹⁻⁷ the aged Al-4%Cu alloy is described as a three-phase system having anodic and cathodic zones. The copper-depleted zone along the grain boundaries is

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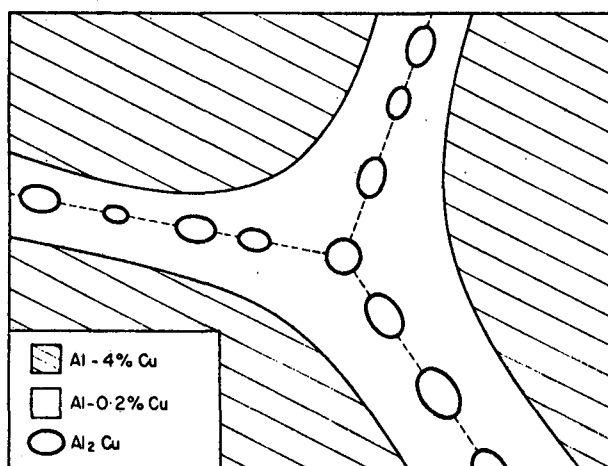


FIG. 1. Schematic representation of the microstructure of an aged Al-4%Cu alloy.

the anode (phase I), whilst the grain bodies (phase II) and the intermetallic Al_2Cu (phase III) are cathodes. The intergranular corrosion of Al-Cu would then be a process in which a very small anode is in contact with a large cathode. In support of this mechanism measurements made by various authors²⁻⁵ showed that during corrosion there was a difference in potentials of the order of 100 mV between the grain boundaries and the grain bodies. Nevertheless, a mechanism of anodic and cathodic zones does not explain why the presence of Cl^- is necessary to get intergranular corrosion, and intergranular corrosion should occur in almost any corrosive medium. Therefore any mechanism of intergranular corrosion of aged Al-4%Cu must explain the action of the Cl^- ions.

The purpose of the present work was to find out the function of the Cl^- in the intergranular corrosion of Al-Cu alloys. Specimens of each of the three phases present in the aged Al-4%Cu alloy were studied in Cl^- solutions. It has been found that the intergranular corrosion of the aged Al-4%Cu alloy appears only over a certain potential range, and that it is related to the process of pitting of Al.

EXPERIMENTAL

Specimens of solubilized Al-4%Cu were used to simulate the behaviour of the grain bodies of aged Al-4%Cu. For the study of the other two phases the intermetallic Al_2Cu and Al-0.2%Cu alloy were used.

Measurements were performed on alloys prepared with Al 99.99% and Cu 99.999%. The analytical composition of the nominal alloy was, for Al-4%Cu, 4.07%Cu; for Al-0.2%Cu, 0.27%Cu; and for the intermetallic Al_2Cu , 56.1%Cu. Several potentiostatic measurements on Al 99.99% and Al 99.9999% were also performed.

The specimens were prepared by cutting coupons of 10×30 mm from a 1 mm thick cold-rolled sheet of the alloys. The solubilized Al-4%Cu was prepared by heating the specimens for 2 h at 550°C and water quenching. The aged specimens were prepared by heating the solubilized specimens for 3 h at 176°C ; and the over-aged

specimens were obtained by heating the solubilized material for 1 h at 430°C. The Al-0.2%Cu and the pure Al specimens were annealed for 2 h at 600°C and water quenched. The edges and the surface of the specimens were covered with a cured-epoxy resin, leaving an uncovered area of about 1 cm². The specimens were electro-polished in a HClO₄ acetic anhydride bath, and stored in a desiccator for a few days before the experiments.

The specimens of the intermetallic Al₂Cu were cast rods of about 6 mm dia. The surface of the rods was covered with the cured-epoxy resin, and one end was mechanically taper polished with diamond powder, leaving an exposed area of about 1 cm².

The solutions were prepared with analytical grade reagents and were deaerated⁹ with purified N₂.

The potential was controlled with a Tacussel PRT 20-2-M potentiostat. All the measurements were made at 25°C in a Pyrex glass cell, with a platinum counter electrode. The potentials were measured, through a Luggin capillary, with a saturated calomel electrode, and referred to the normal hydrogen electrode scale (nhe).

RESULTS

Anodic polarization curves in NaCl

Polarization curves were obtained for each of the three phases, in solutions containing various concentrations of NaCl. The measurements were made in steps of 10 mV, waiting at each point until a stationary current was observed. Figure 2 shows a typical example of the polarization curves obtained. The results with pure Al were similar to the ones reported by Kaesche¹⁰ and Bond *et al.*,¹¹ and the same type of anodic polarization curve was obtained with solubilized Al-4%Cu, Al-0.2%Cu, and Al₂Cu. In all cases the specimens showed a passive range, where no attack was observed. But, as the potential was increased to the critical potential, there was a

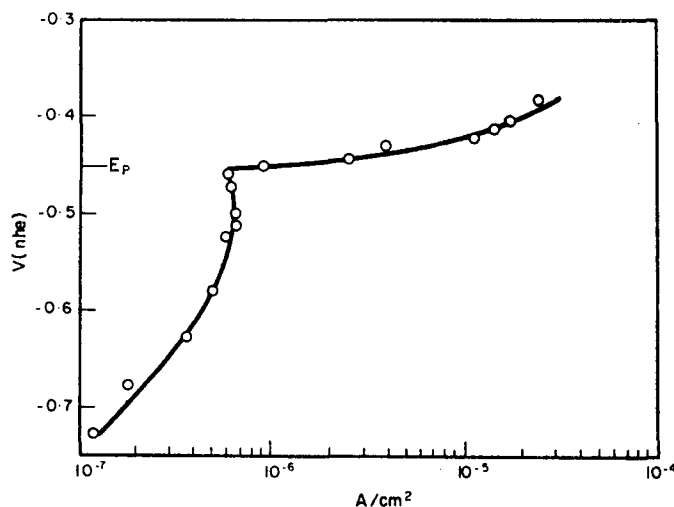


FIG. 2. Anodic polarization curve of 99.99%Al in deaerated 0.1M NaCl solution.
E_p: potential at which pitting starts.

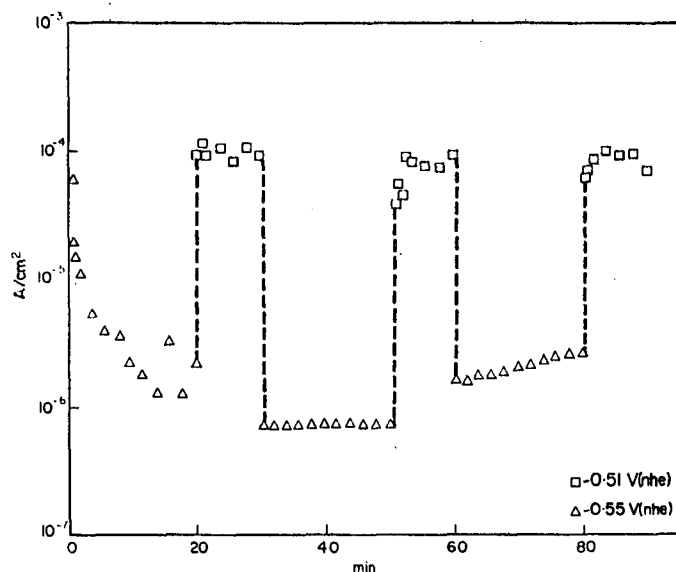


FIG. 3. Behaviour of 99.99%Al in deaerated 1M NaCl solution when the potential is switched from the passive range to the pitting range. The pitting potential was -0.53 V(nhe).

marked increase in the current, and pitting was then detected on the surface. Although the existence of critical potentials for pitting is supported by various authors,¹⁰⁻¹⁵ recent work has thrown doubts on the existence of such potentials,¹⁶⁻¹⁸ since pitting does not occur until after an induction period.

In view of this discrepancy of opinions, two types of experiments were made to study the pitting of Al in Cl^- solutions.

In a first series of experiments 99.99%Al was immersed in deaerated 1M NaCl and the potential of the specimen was switched every 10 to 20 min from the passive range to the pitting range (Fig. 3). When the specimen is held at a low potential the current decreases to very small values, but if the potential is then switched to a higher value, which is in the pitting range, the current increases by two or more orders of magnitude, and pits form on the surface of the metal. If the potential is switched back to the low initial value, the pitting stops and the metal repassivates. This experiment can be repeated several times on the same specimen with the same results. If pitting of Al in Cl^- solutions is a time-dependent process, independent of the potential, once pitting has started it would not be expected to stop when the potential is decreased.

A second series of experiments consisted in recording the changes in the anodic current for 5 h when specimens of 99.99%Al were held at various constant potentials in 1M deaerated NaCl (Fig. 4). When the potential was maintained in the range -0.76 V(nhe) and -0.53 V(nhe) the c.d. after 5 h remained below $1 \mu\text{A}/\text{cm}^2$, and no pitting was observed. But with a potential only 10 mV higher than -0.53 V the c.d. increased by more than three orders of magnitude and pitting commenced. These experiments showed that if there is an induction time for pitting of Al, a change in potential of 10 mV should decrease the induction time by at least four orders of

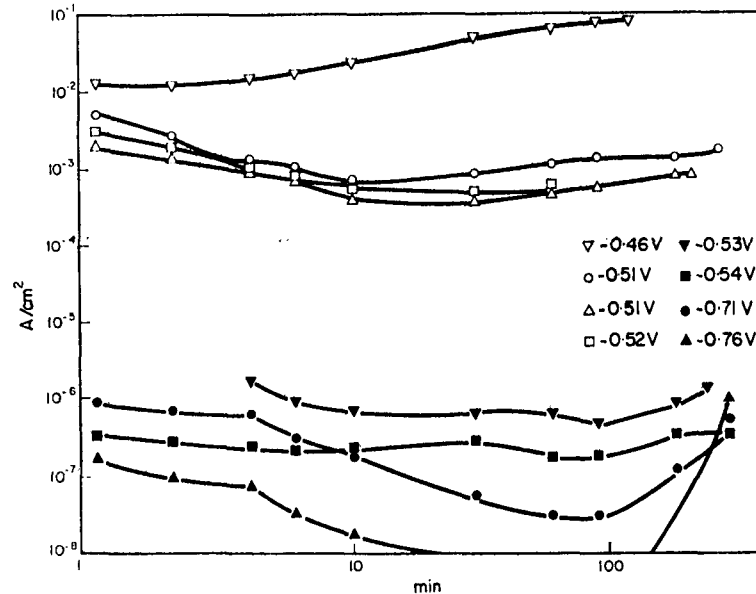


FIG. 4. Current-time curves for 99.99% Al in deaerated 1M NaCl solution at various potentials.

magnitude. It can be concluded therefore that pitting of Al is related to a critical potential which does not depend on an induction period.

Pitting potentials

The critical pitting potentials of the three phases and of pure Al in various concentrations of deaerated NaCl are shown in Fig. 5. The pitting potential for all the three phases is linearly related to logarithm of the activity of NaCl, and in the range 0.01 to 5M NaCl the following relations were obtained:

Phase I, and high purity Al:

$$Ep_I = -0.536 - 0.073 \log(a_{\text{NaCl}})$$

where Ep_I is the breakdown potential in V(nhe).

Phase II:

$$Ep_{II} = -0.404 - 0.046 \log(a_{\text{NaCl}}), \text{ and}$$

Phase III:

$$Ep_{III} = -0.420 - 0.055 \log(a_{\text{NaCl}}).$$

In all the cases studied the breakdown potentials for the Cu-rich phases were about 100 mV higher than the values for specimens with lower Cu content. The pitting potentials of the solubilized Al-4%Cu were similar to those of the intermetallic Al_2Cu , and no difference was observed in the pitting potentials of the Al-0.2%Cu and high purity Al.

Influence of heat treatment on intergranular corrosion

With the results shown in Fig. 5 it should be possible to predict the behaviour of heat-treated Al-4%Cu alloys in Cl^- solutions at different potentials. As shown in this

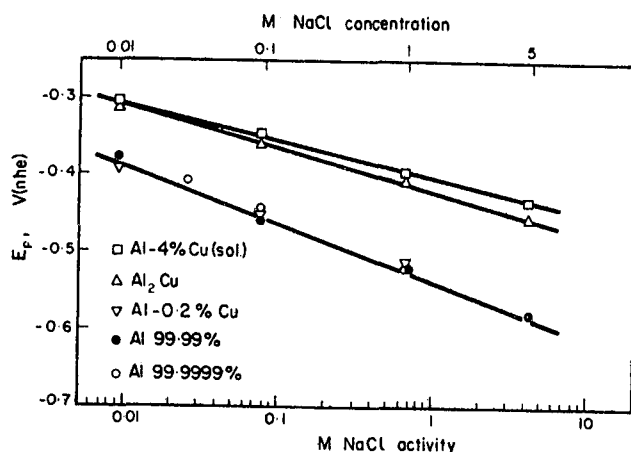


FIG. 5. Effect of the chloride concentration on the pitting potential of pure aluminium and various Al-Cu alloys in deaerated NaCl solutions.

figure, there is a range of potentials where an alloy with a Cu-depleted zone will show attack in such zone while the two others remain passive. This sort of behaviour should be expected in a wide range of Cl^- concentrations. For example, an aged Al-4%Cu alloy (Fig. 1) will corrode along the grain boundaries over a range of 100 mV while the grain bodies remain passive. In this case corrosion will concentrate in the few-microns-thick Cu-depleted zone.

The results for aged Al-4%Cu confirm such prediction, and Fig. 6 shows a typical example of an anodic polarization curve in deaerated 1M NaCl; in this particular experiment the potential was changed in steps of 10 mV every minute. The values of the expected breakdown potentials of the grain boundaries and of the grain bodies

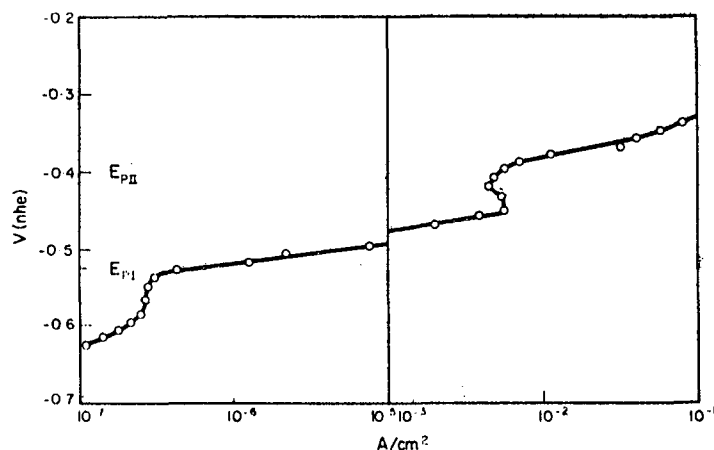


FIG. 6. Anodic polarization curve of aged Al-4%Cu in deaerated 1M NaCl solutions. Measurements made in steps of 10 mV/min. E_{pI} : pitting potential measured for Al-0.2%Cu. E_{pII} : pitting potential of solubilized Al-4%Cu.

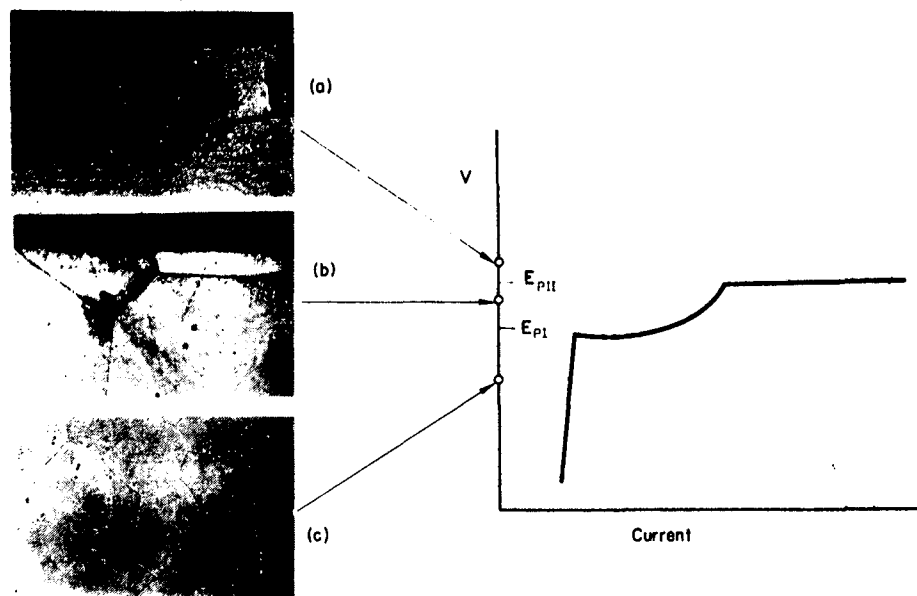


FIG. 7. Anodic polarization curve and type of attack for aged Al-4%Cu in deaerated 1M NaCl solution. Exposure conditions: *a* = 20 min at -0.35 V(nhe), intergranular corrosion plus tunnel-like pitting, section ($120\times$); *b* = 20 min at -0.43 V(nhe), intergranular corrosion, section ($120\times$); *c* = 90 min at -0.66 V(nhe), specimen not corroded, normal view ($30\times$).

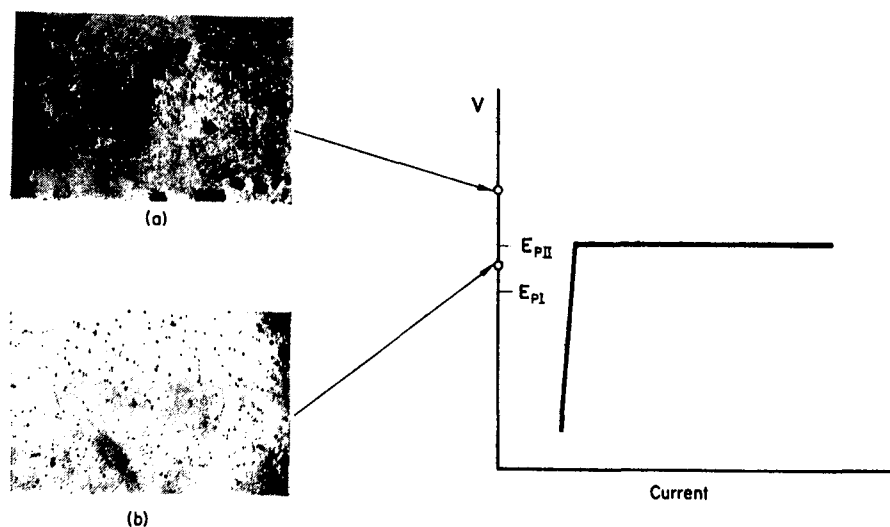


FIG. 9. Polarization curve and type of attack of solubilized Al-4%Cu in deaerated 1M NaCl solution. *a* = 5 min at -0.26 V(nhe), pitting corrosion ($30\times$); *b* = 90 min at -0.46 V(nhe), no corrosion except for the pits produced during electropolishing ($30\times$).

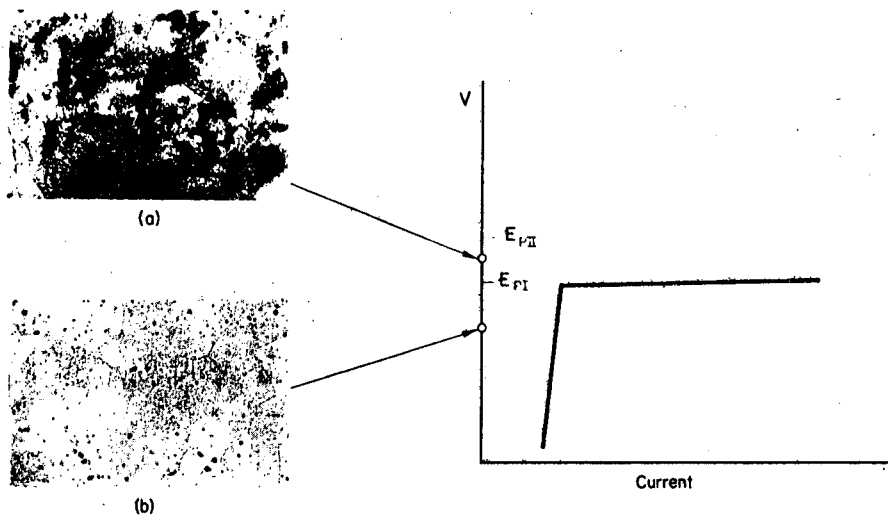


FIG. 11. Polarization curve and type of attack of over-aged Al-4%Cu in deaerated 1M NaCl solution. *a* = 10 min at -0.44 V(nhe), generalized pitting ($30\times$); *b* = 90 min at -0.66 V(nhe), no corrosion except for pits produced during electropolishing ($30\times$).



FIG. 13. Type of attack of aged Al-4%Cu in 1M NaNO₃ solution, exposed 1 h at $+1.85$ V(nhe). Pitting nucleates at the grain boundaries but no intergranular corrosion was observed ($100\times$).

are also included. It was found that when the first breakdown potential is reached, an increase in c.d. occurs, and intergranular corrosion begins. Increasing further the potential results in a slowdown in the current increase, probably due to the narrow front in which the attack is taking place, but when the second breakdown potential is reached there is a new increase in current and corrosion of the grain bodies begins.

Similar results were obtained in other experiments where the potential was maintained constant, and Fig. 7 shows the type of corrosion observed for aged Al-4%Cu in 1M deaerated NaCl, under constant potential. Specimen c was exposed for 90 min at a potential of -0.66 V(nhe), and did not show any type of attack. Another specimen b exposed for 20 min at -0.43 V(nhe) showed intergranular corrosion. And a third specimen a exposed for 20 min at -0.35 V(nhe), showed corrosion at the grain boundaries and in the grain bodies. The attack in the grain bodies took the form of tunnels, similar to the ones described by various authors for pure Al.¹⁹⁻²¹ These experiments were repeated with several other specimens of aged Al-4%Cu and the same relation between the potential applied and the type of corrosion was always obtained.

The data in Fig. 5 can also be applied to predict the kind of corrosion for other heat treatments. A solubilized Al-4%Cu, for example, has only one phase (Fig. 8), and in this case localized corrosion should appear at potentials higher than E_{pH} , but the metal should remain passive at lower potentials. This is confirmed in Fig. 9, where 90 min exposure at -0.46 V(nhe) did not produce any attack, except for the small pits produced during electropolishing of the specimens. But after 5 min exposure at -0.26 V(nhe) severe pitting was observed.

In the over-aged condition, on the other hand, the grain bodies show a two-phase structure, as schematically represented in Fig. 10. According to Fig. 5 an alloy with this microstructure should suffer general corrosion at potentials higher than E_{p1} . This was experimentally confirmed (Fig. 11), and a specimen exposed at a potential of -0.44 V(nhe) showed severe pitting, while another specimen exposed for 90 min

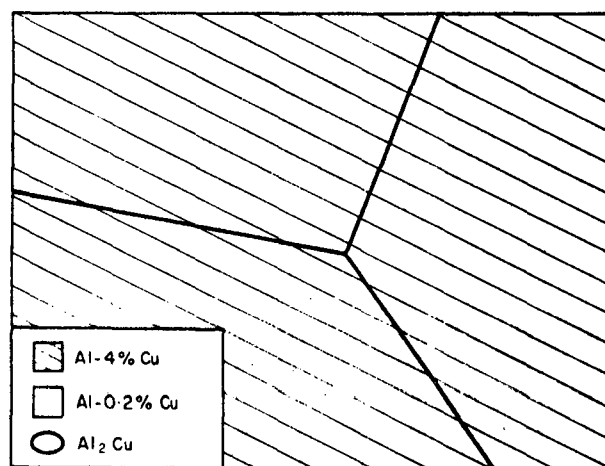


FIG. 8. Schematic representation of the microstructure of solubilized Al-4%Cu alloy. Only one phase is present.

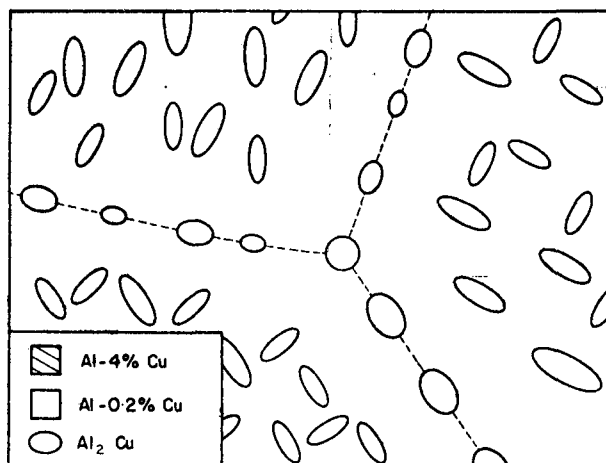


FIG. 10. Schematic representation of the microstructure of over-aged Al-4%Cu alloy. Only Al-0.2%Cu and Al_2Cu are present.

at -0.66 V(nhe) was unattacked. This type of behaviour explains why Farmery and Evans² found that the "light zone" along the grain boundaries was *not always* related to intergranular corrosion. This precipitate-free zone is also present in the over-aged alloy. But the over-aged alloy will suffer corrosion not only in the grain boundaries but also in the grain bodies (Fig. 11). Besides, the increase in the anodic area, and the consequent reduction in the cathodic area, will favor generalized corrosion rather than intergranular attack.

TABLE I. TYPE OF ATTACK OF AGED Al-4%Cu IN 1M DEAERATED NaCl SOLUTION

Heat treatment	Potential		
	Below -0.52 V(nhe)	Between -0.52 and -0.40 V(nhe)	Over -0.40 V(nhe)
Solubilized	Passive	Passive	Pitting
Aged	Passive	Intergranular	Generalized*
Over-aged	Passive	Pitting	Pitting

*The attack is a mixture of pitting plus intergranular corrosion.

Table I summarizes the behaviour of Al-4%Cu alloys with different heat treatments at various potentials in deaerated 1M NaCl solutions. No attack is observed for any heat treatment at potentials below -0.52 V(nhe) . Such a behaviour could not be predicted from the mechanism of anodic and cathodic zones. Between -0.52 V(nhe) and -0.40 V(nhe) the behaviour of all heat treatments is the same as that expected from the original anodic-zone mechanism, and above -0.40 V(nhe) a behaviour not predicted by that mechanism is again found.

From a practical point of view, the low potentials are obtained when working in pure Cl^- solutions in the absence of O_2 . The second range of potentials is obtained in O_2 -saturated solutions, and in order to reach the highest range of potentials either a stronger oxidizer or an external current will be required.

Cathodic polarization curves

It is known in practice that O_2 plays an important role in the intergranular corrosion of Al-Cu alloys.²² For this reason the cathodic polarization curves in air-saturated 1M NaCl were determined for pure Al, solubilized Al-4%Cu and Al_2Cu (Fig. 12). It was found that, as already mentioned by Ketcham and Haynie,⁷ the cathodic reaction is kinetically easier in the Cu-rich phases than in pure Al, which is decisive in the behaviour of Al alloys in Cl^- solutions, as discussed later.

Intergranular corrosion in absence of Cl

To determine the possibility of pitting in media other than Cl^- solutions, polarization curves were obtained for 99.99%Al and for solubilized Al-4%Cu in various solutions. From what had been observed in Cl^- solutions, pure Al was expected to behave in the same way as the depleted zone of grain boundaries, and the solubilized alloy was used to simulate the behaviour of the grain bodies (Table 2). In 1M NaIO_3 , Na_2SO_4 , H_2SO_4 , and ammonium tartrate no pitting was observed up to + 3 V(nhe), the highest potential used in the present work. Furthermore, no intergranular corrosion was detected in aged Al-4%Cu when polarized in those solutions at + 3 V(nhe). A similar behaviour is to be expected in all other solutions that produce compact anodic oxide films on Al. On the other hand pitting was observed in Br^- , I^- , ClO_4^- , and NO_3^- solutions. In the first three solutions, as in the case of Cl^- solutions, a difference of 130 to 200 mV was observed between the pitting potentials of pure Al and of the

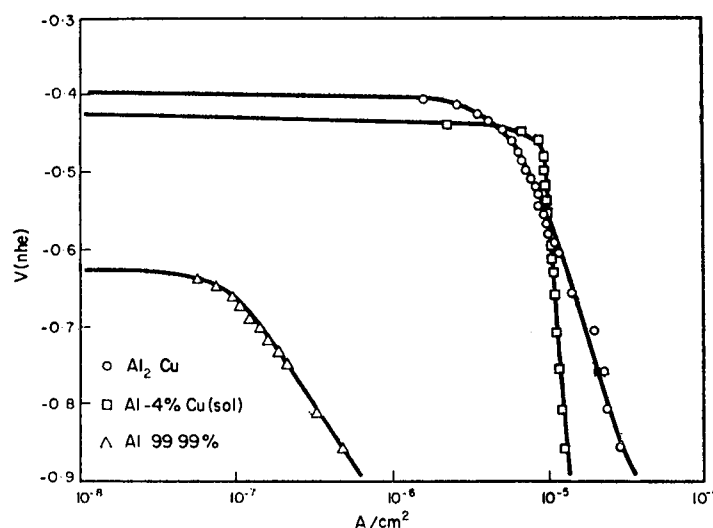


FIG. 12. Cathodic polarization curves in air-saturated 1M NaCl solution of pure aluminium, solubilized Al-4%Cu, and intermetallic Al_2Cu .

TABLE 2. RELATION BETWEEN PITTING POTENTIALS AND INTERGRANULAR CORROSION IN SOLUTIONS OTHER THAN NaCl

Electrolyte	Pitting potentials V(nhe)		Intergranular corrosion*
	99.99%Al	Al-4%Cu (solub.)	Al-4%Cu (aged)
1M KBr	- 0.42	- 0.28	Yes (- 0.40)
1M KI	- 0.26	- 0.13	Yes (- 0.23)
1M NaClO ₄	- 0.17	+ 0.03	Yes (- 0.14)
1M NaNO ₃	+ 1.80	+ 1.85	No (+ 1.85)
1M Na ₂ SO ₄	> + 3.0	> + 3.0	No (+ 3.0)
1M H ₂ SO ₄	> + 3.0	> + 3.0	No (+ 3.0)
0.1M NaIO ₃	> + 3.0	> + 3.0	No (+ 3.0)
1M Ammonium tartrate	> + 3.0	> + 3.0	No (+ 3.0)

*In parentheses, potentials at which the intergranular corrosion susceptibility was tested.

solubilized Al-4%Cu. When the aged Al-4%Cu alloy was exposed to a potential between both pitting potentials intergranular corrosion was detected.

As mentioned above pitting of pure Al and of solubilized Al-4%Cu was observed in NO₃ solutions. No intergranular corrosion of the aged Al-4%Cu was detected. Aged Al-Cu showed pitting along the grain boundaries (Fig. 13), and the reason for this difference in behaviour could lie in the differences in pitting morphology.²³ The pits in Al in NO₃ solutions are hemispherical, while in the other media they were found to be tunnel-like. It seems that in nitrate solutions corrosion starts in the grain boundaries, but cannot spread along the narrow depleted zone as it occurs in ClO₄ and in halide solutions.

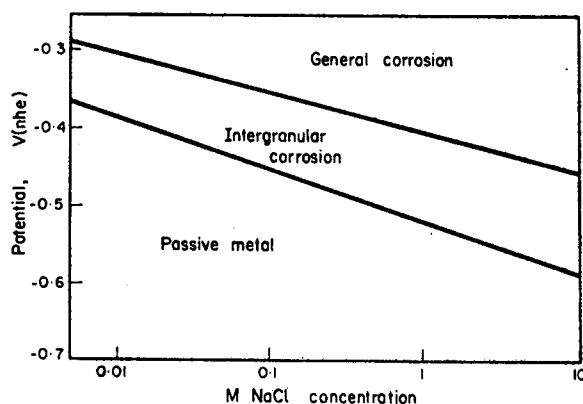


FIG. 14. Simplified potential-concentration diagram showing the type of attack suffered by aged Al-4%Cu.

DISCUSSION AND CONCLUSIONS

The present results show that intergranular corrosion of aged Al-4%Cu occurs only in a narrow range of potentials. Figure 14 summarizes the results obtained with aged Al-4%Cu, showing the type of attack expected at different potentials and Cl⁻ concentrations. If the metal is maintained in the *passive metal* region, no intergranular corrosion will occur and the metal will be cathodically protected, although its potential will be more positive than the potential of immunity in the potential-pH diagram for Al-H₂O. From the old mechanism of intergranular corrosion by anodic and cathodic zones no protection would be expected at potentials higher than about -2.0 V(nhe).²⁴ Nevertheless, it was found in the present work that intergranular corrosion does not occur if the metal is kept in the range -0.4 V(nhe) to -0.6 V(nhe), depending on the Cl⁻ concentration of the media. These results apply only to pure NaCl or KCl solutions. If other anions are present in the solution the zones in Fig. 14 should be displaced to higher potentials, this displacement should be equal to that caused to pitting potentials by the same anions.²³

The behaviour of Al-Cu alloys in natural environments can be explained by the use of the anodic and cathodic polarization curves previously described. Figure 15 shows schematically the anodic and cathodic polarization curves for the Al-Cu system in chloride solutions. A_1 is the anodic polarization curve for pure Al and Al-0.2%Cu, A_2 is the anodic polarization curve for solubilized Al-4%Cu and for Al₂Cu, C_1 is the cathodic polarization curve for the Al-Cu alloy in the absence of O₂, C_2 is the cathodic polarization curve for pure Al and for Al-0.2%Cu in the presence of O₂ and C_3 is the cathodic polarization curve for the Cu-rich phases in the presence of O₂. In the absence of O₂, the corrosion potential of the aged Al-4%Cu alloy will be E_1 , and the

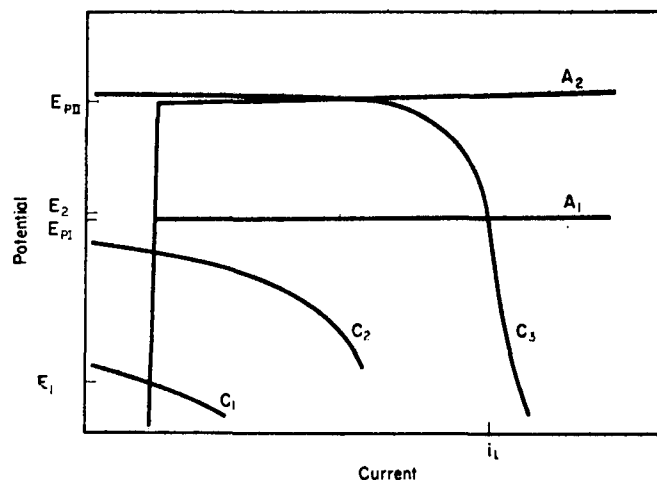


FIG. 15. Current-potential relations for Al and Al-Cu in chloride solutions. A_1 : anodic polarization of Al and Al-0.2%Cu; A_2 : anodic polarization of solubilized Al-4%Cu and of Al₂Cu; C_1 : cathodic polarization of solubilized Al-4%Cu in absence of oxygen; C_2 : cathodic polarization of pure aluminium in air saturated solutions; C_3 : cathodic polarization of solubilized Al-4%Cu in air saturated solution; E_1 : corrosion potential of Al-Cu in deaerated solution; E_2 : corrosion potential of aged Al-Cu in air saturated solution; i_L : limiting current for the cathodic reaction, and dissolution current of the grain boundaries of the aged Al-Cu alloy.

alloy will remain passive. If O_2 is allowed into the system, the corrosion potential will develop to E_2 , a little higher than E_{p1} . Under these conditions the Cu-rich phase will remain passive and the Cu-depleted zone will corrode. The rate of corrosion of the Cu-depleted zone will be equal to the limiting current of the cathodic reaction of O_2 reduction. Hence the higher the O_2 content, or the higher the cathodic area, the higher the corrosion rate of the grain boundaries. This explains the influence of the cathodic area on intergranular corrosion found by Colner and Francis.⁶ As for pure Al, the corrosion potential will be given by the intersection of A_1 and C_2 , but due to the "slowness" of the cathodic reaction on pure Al the metal will not show much corrosion.

Summing up, the results of the present work show that intergranular corrosion of Al-Cu alloys is not due to a difference in potentials between grain boundaries and grain bodies, but to a difference in the breakdown potentials of those phases. The mechanism of intergranular corrosion of Al-Cu is found to be of the same nature as the process of pitting of Al. It is concluded that intergranular corrosion of Al-Cu will occur only under the following conditions:

1. The alloy must have a solute-depleted zone along the grain boundaries.
2. The corrosive medium should contain anions capable of breaking down the passivity of the Al.
3. The breakdown potential of the depleted zone must be lower than that of the grain bodies.
4. The corrosion potential of the alloy must be over the breakdown potential of the depleted zone, and under the breakdown potential of the grain bodies.

When the pitting potential is too high, as in the case of nitrate solutions, other factors, like the morphology of pitting, could be important and are being studied at present.

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PROGRAMA MULTINACIONAL DE METALURGIA

(Programa Regional de Desarrollo Científico y Tecnológico - OEA)

**CORROSION BAJO TENSIONES DEL ZIRCALOY-4 EN PRESENCIA
DE CLORUROS . ESTUDIO FRACTOGRAFICO**

G. Cragnolino y J.R. Galvela

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1973

CORROSION BAJO TENSIONES DEL ZIRCALOID-4 EN PRESENCIA DE CLORUROS. ESTUDIO FRACTOGRAFICO

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INTRODUCCION

Es un hecho conocido que el Circonio presenta el fenómeno del picado en soluciones acuosas de cloruros (1, 2). En cambio en dichos medios es muy poco lo que se conoce acerca de su susceptibilidad a la corrosión fisurante bajo tensiones mecánicas, ya sean aplicadas o residuales (3, 4).

Como en diversas aleaciones el picado en presencia de cloruros está asociado a la aparición de corrosión bajo tensiones: acero inoxidable, Aluminio-4%, AISI 4340, etc. (5, 6, 7), se comenzó a investigar si el Circonio y algunas de sus aleaciones presentaban una relación similar.

El presente trabajo fué realizado con una aleación de Circonio, el Zircaloid-4, muy empleada en la tecnología nuclear como vaina para los elementos combustibles, tanto de uranio natural como enriquecido, que se emplean en los reactores moderados por agua (H_2O o D_2O) a presión.

Se comprobó que el Zircaloid-4 es susceptible a la corrosión bajo tensiones en soluciones acuosas de cloruro de sodio cuando se lo mantiene a potenciales iguales o superiores al potencial de picado.

Además, la observación de las superficies de fractura reveló que esta aleación, en dichas condiciones, presenta tres modos consecutivos de propagación de las fisuras. La primera etapa es intergranular y estaría íntimamente relacionada con el fenómeno de picado. Posteriormente, a partir de un dado grado de avance de la fisura, la propagación se continúa en forma transgranular, hasta que finalmente el material se fractura en forma dúctil.

DETALLES EXPERIMENTALES

La composición de la aleación empleada es la siguiente: Zr-1,44% Sn-0,22% Fe-0,10% Cr. Aunque su microestructura no es bien conocida, se considera que en una matriz de α -Zr (hc) el Sn se halla disuelto y el Fe y el Cr están precipitados. En el Zircaloid-2, que además de los aleantes mencionados contiene Ni (0,03 a 0,08%), se detectaron intermetálicos $Zr_2Fe_xCr_y$ y $Zr_2Fe_xNi_y$, cuya estequiometría se aproxima a Zr_2Me (8).

Con este material se prepararon probetas de tracción (fig. 1), que fueron recocidas en un vacío del orden de 10^{-6} mm Hg a $750^\circ C$, o sea en fase α , durante dos horas

y enfriadas en el horno. El tamaño promedio de los granos alcanzaba los 10μ y las propiedades mecánicas a la tracción obtenidas en ensayos de tensión vs. deformación arrojaron los siguientes valores: Límite de fluencia (0,2%): 35,3 Kg/mm²; Ductilidad: 31% y Resistencia a la tracción: 42,2 Kg/mm².

Las probetas, previamente tratadas con solución fluonítrica hasta eliminar una capa superficial de aproximadamente 20μ , antes de cada ensayo fueron pulidas electrolíticamente en una solución de Butilcelosolve-10% ClO₄H. Se pulió a 15°C, bajo una tensión de 25 Voltios que correspondió a una densidad de corriente de $1,5 \times 10^{-3}$ A/cm², durante 30 segundos.

En los ensayos se emplearon soluciones acuosas neutras de ClNa1N, preparadas con droga analítica, sin desgasar, efectuándose las determinaciones a temperatura ambiente.

Como método para evaluar la susceptibilidad a la corrosión bajo tensiones se determinó la influencia que tiene el potencial de electrodo que se aplica a la aleación, controlado potencioestáticamente, sobre los tiempos de fractura. En cada ensayo se mantuvo el material a un potencial anódico controlado, sometiéndolo simultáneamente a un esfuerzo de tracción inferior al límite de fluencia mediante la aplicación de una carga constante.

La celda de vidrio Pyrex que se utilizó (fig. 2), permitía el pasaje de barras de acero tanto por su parte superior como por el fondo que sostenían, mediante pernos, a las probetas de tracción. Dicho conjunto fué recubierto con resina epoxi curada en estufa a 70-80°C dejando expuesto al medio corrosivo sólo el cuello de las probetas.

Se empleó un arrollamiento helicoidal de alambre de Platino como contraelectrodo y la medición del potencial se efectuó con un electrodo de calomel saturado, mediante un capilar de Luggin, refiriéndose los valores de potencial a la escala normal de hidrógeno.

Para someter las probetas a una carga constante, que en los ensayos efectuados correspondió a un esfuerzo igual al 80% del límite de fluencia, se usó una balanza de tracción. Las probetas de tracción fueron acopladas a la misma a través de las barras de sostén mediante un doble dispositivo cardánico a fin de evitar cualquier desalineación.

La balanza de tracción fue calibrada para diferentes pesos en su platillo mediante una celda de carga provista de extensómetros (strain gauge).

El tiempo de fractura se midió con un reloj eléctrico, conectado a un sistema de corte, que interrumpía su marcha al producirse la rotura de las probetas.

El potencial se mantuvo controlado mediante un potencióstato LYP Electrónica y se midió con un pH-mVmetro Leeds & Nortrup Modelo 7404. Para el trazado de curvas de polarización se empleó un Registrador Honeywell Modelo Electronik 193.

Las observaciones fractográficas fueron efectuadas con un microscopio electrónico de barrido (SEM) JSM-U3.

RESULTADOS EXPERIMENTALES

1) Determinación del potencial de picado

En la Fig. 3 está representada una curva típica correspondiente a la polarización anódica del Zircaloy-4 en solución desgasada de ClNa 1N a temperatura ambiente, trazada potencioestáticamente.

El potencial de corrosión hallado fue aproximadamente $-0,5 V_H$ y se pudo observar la existencia de un extenso rango de potenciales, aproximadamente 800 mV, donde no se registró ninguna variación significativa de la densidad de corriente estacionaria (j) que aumentaba continuamente desde 10^{-8} A/cm² hasta aproximadamente 2×10^{-7} A/cm². En estas condiciones el Zircaloy-4 permanece pasivado en presencia de iones cloruro, hecho que fue corroborado por observaciones con el microscopio óptico

Sin embargo, cuando se alcanzó un potencial de aproximadamente $0,34 V_H$ se observó un aumento significativo de la densidad de corriente. Así, un incremento adicional de 20 mV aumentaba la densidad de corriente en más de dos órdenes de magnitud. Este hecho fue asociado a la aparición de picado sobre la superficie pasivada de la probeta, confirmando también por microscopía óptica. La morfología del ataque se determinó mediante el microscopio electrónico de barrido. Se forman picaduras aproximadamente circulares, con bordes irregulares y el fondo aparentemente cubierto por productos de corrosión, tal como puede observarse en la Fig. 4.

En estas experiencias se notó que el sistema Zircaloy-4 / ClNa 1 N evolucionaba muy lentamente hacia el estado estacionario, tanto en la zona pasiva como en la de picado. En la zona de pasividad la probeta se mantuvo en cada potencial durante tiempos del orden de los 30 minutos, al cabo de los cuales la densidad de corriente prácticamente se estabilizaba. Sin embargo, si se la mantenía al mismo potencial durante las siguientes 24 horas la densidad de corriente continuaba descendiendo muy lentamente hasta alcanzar valores inferiores en un orden de magnitud a los mencionados precedentemente. Como ejemplo, una probeta sometida a un potencial de $0,34 V_H$ después de 24 horas alcanzó una densidad de corriente de $1,29 \times 10^{-8}$ A/cm².

En la zona de picado, además de requerirse un cierto tiempo de inducción para que se inicie el ataque, transcurría bastante tiempo antes que se pudiesen alcanzar corrientes estacionarias.

Este tipo de dificultades con la consiguiente irreproducibilidad en la determinación del potencial de picado, condujo a efectuar las experiencias mediante técnicas intensificadas.

Aplicando una intensidad de corriente constante y utilizando en cada ensayo una probeta diferente se registró la variación del potencial con el tiempo, obteniéndose las curvas de la Fig. 5. Se pudo observar que el potencial estacionario se alcanzaba tanto más rápidamente cuanto mayor era la corriente que se aplicaba. Dichos valores aparecen representados en función de la densidad de corriente en el gráfico de la Fig. 6 y permitieron determinar el potencial de picado que resultó ser $0,34 V_H$.

Sin embargo este tipo de ensayos presentaban un inconveniente. Consistía en la oscilación del potencial, alrededor del valor estacionario, con una amplitud que aumentaba a medida que disminuía la densidad de corriente aplicada, llegando a ser ± 15 mV para 1×10^{-6} A/cm², tal como se indica en el mismo gráfico.

2) Ensayos de tracción a velocidad de deformación constante

La incertidumbre mencionada anteriormente con respecto al verdadero valor del potencial de picado planteó la posibilidad de emplear la técnica del electrodo en deformación, controlado potencioestáticamente, bajo una velocidad de tracción constante a fin de corroborar el dato anterior, teniendo en cuenta los resultados obtenidos en nuestro laboratorio con Aluminio en ClNa 1N (5).

En la Fig. 7 aparece una familia de curvas típicas para el sistema Zircaloy-4/ClNa 1N, donde se representó la densidad de corriente en función del tiempo, tomando como parámetro el potencial aplicado. Corresponden a una velocidad de deformación de 9,35%/minuto y se observa la existencia de un potencial crítico a partir del cual la densidad de corriente, a medida que se produce la tracción, aumenta en varios órdenes de magnitud con respecto a lo que sucede para potenciales inferiores. El valor de dicho potencial fue -0,33 VH y no difiere más que en 10 mV del potencial de picado hallado en las determinaciones intensiostáticas, estando por lo tanto comprendido en el rango de fluctuación que presentaba el potencial estacionario en dichos ensayos. En la Fig. 8, puede observarse la representación de j máxima = $f(E)$ donde se evidencia claramente la diferencia de comportamiento entre la zona pasiva y la de picado.

Las probetas ensayadas bajo tracción a velocidad de deformación constante fueron observadas al microscopio óptico, confirmándose que en la zona pasiva no había ninguna señal de ataque. Por otra parte, aquellas deformadas al potencial de picado o a potenciales superiores presentaban un ataque localizado en los límites de grano, que a medida que el potencial se hacía más anódico tendía a ramificarse, penetrando y extendiéndose en los granos según ciertas direcciones preferenciales. Esa morfología del ataque, que difiere sensiblemente de la hallada en los ensayos de polarización anódica en ausencia de un esfuerzo de tracción, puede apreciarse en la Fig. 9 obtenida también con el microscopio electrónico de barrido.

3) Ensayos de tracción bajo carga constante y determinación de tiempos de fractura

En estos ensayos, una vez alcanzado el valor estacionario del potencial de corrosión, se potencioestató durante 2 horas a un potencial correspondiente al rango de pasividad (-0,15 VH) a fin de obtener reproducibilidad en la formación de la película pasivante. Se aplicó luego el potencial de interés y casi simultáneamente las probetas fueron cargadas, computándose el tiempo a partir de ese instante.

Al representar el tiempo de fractura (t_f) en función del potencial aplicado (E) se obtuvo el gráfico de la Fig. 10. Se puede observar que para potenciales iguales e in-

feriores a $0,30 V_H$ no se produjo la fractura de las probetas luego de casi cinco días de exposición. En cambio para potenciales iguales y superiores a $0,33 V_H$ las probetas se fracturaron en menos de una hora, disminuyendo a pocos minutos el tiempo de fractura a medida que se aplicaron potenciales más positivos.

Con el objeto de correlacionar estos resultados con el comportamiento anódico del Zircaloy-4 en soluciones de $ClNa$ 1N, en ausencia de una tensión mecánica aplicada, en el mismo gráfico se superpuso una curva de polarización, construída a partir de los ensayos potenciostáticos e intensiostáticos. Comparando las representaciones gráficas de $j = f(E)$ y $t_f = f(E)$ se comprueba que el Zircaloy-4 es susceptible a la corrosión bajo tensiones en soluciones acuosas de cloruro de sodio para potenciales iguales y superiores al potencial de picado.

4) Observaciones fractográficas

La topografía de las superficies de fractura se puede observar con bajo aumento en la Fig. 11. De acuerdo al modo con que se propaga la fisura se pueden distinguir tres zonas que son sucesivamente en el sentido de avance de la misma: a) Zona de propagación intergranular; b) Zona de propagación transgranular; c) Zona de fractura dúctil.

En la Fig. 12 aparecen esquematizadas dichas zonas de acuerdo a lo que se observaría si fuera posible hacer un corte, según una sección perpendicular a la superficie de fractura, a medida que la fisura se propaga.

Empleando aumentos mayores se pueden revelar los aspectos más significativos de cada zona:

a) Zona de propagación intergranular: tal como se observa en la Fig. 13, está caracterizada por la propagación de la fisura entre los granos. Aparecen como fenómenos secundarios cierta ramificación de la fisura principal apartándose de la superficie de fractura y el ataque localizado de los granos adyacentes a la fisura, siguiendo ciertas direcciones o planos cristalinos, como se observa con más detalle en la Fig. 14. Esto último corresponde a la ramificación del ataque intergranular observado sobre la superficie de las probetas ensayadas a velocidad de tracción constante. A medida que la fisura se acerca a la zona de transición con el ulterior modo de propagación, Fig. 15, el ataque de los granos se hace menos evidente tal como lo muestra la Fig. 16.

b) Zona de propagación transgranular: es una región donde la fractura es típicamente transcristalina como se observa en la Fig. 17. La fractura muestra cierta tendencia hacia la formación de facetas planas, aunque muy afectadas por la deformación plástica, Fig. 18. La ausencia de planos de clivaje definidos impide considerarla como fractura "frágil".

c) Zona de fractura dúctil: Como se observa en la Fig. 19, también está separada de la anterior por una zona de transición. Se caracteriza por la presencia de "dimples" (hoyuelos), Fig. 20. Este tipo de fractura la presentan los materiales, forma-

dos por una matriz dúctil con partículas metálicas precipitadas que pueden clivar o separarse de la matriz en la interfase por efecto del esfuerzo mecánico aplicado y la rotura se produce por la coalescencia de las micro cavidades así originadas. Se comprobó que la fractografía de esta zona es idéntica a la que presenta el Zircaloy-4 cuando se lo fractura en aire, como se evidencia en la Fig. 21. Además, una estimación aproximada del área de fractura dúctil, que fué prácticamente constante en todas las probetas ensayadas, da una idea de la sección efectiva que debería soportar toda la carga aplicada cuando la fisura hubiera alcanzado el límite entre zona transgranular y zona dúctil. El valor del esfuerzo así calculado, en promedio para todas las probetas ensayadas, alcanza a superar la resistencia a la tracción con un error de $\pm 10\%$.

DISCUSION Y CONCLUSIONES

De las experiencias y observaciones efectuadas se concluye que el Zircaloy-4 permanece pasivado en presencia de iones cloruro para un extenso rango de potenciales. Se requiere superar un cierto potencial, correspondiente al potencial de picado en ese medio, para iniciar una disolución preferencial de la superficie pasiva.

Dicho ataque se localiza en los límites de grano cuando se tracciona la aleación a velocidad constante, como se puede observar en la Fig. 9 o cuando se la somete a un esfuerzo de tracción bajo carga constante, como lo evidencia la Fig. 22, probablemente inducido por cierta deformación plástica allí localizada.

Lamentablemente existe muy poca información acerca de la microestructura de esta aleación. Aunque se considera que precipitan tanto el Fe como el Cr no se conoce la composición precisa de las fases intermetálicas presentes ni su distribución a lo largo de los límites de grano. Esto impide discriminar si el camino preferido para la disolución anódica intergranular está dado por una zona empobrecida en dichos solutos o si es a través de las partículas intermetálicas precipitadas del tipo Zr_2Me ($Zr_2Fe_xCr_y$).

Las condiciones de oclusión bajo las cuales se propaga la fisura determinan que se produzcan dentro de la misma importantes cambios en la composición del electrolito. La acidificación, así como el aumento en la concentración de iones cloruro originarían el ataque lateral que se observa en los granos durante la propagación intergranular.

Luego de un cierto avance de la fisura, ésta se transforma de intergranular a transgranular. No es posible explicar las razones de esta transición aunque posteriormente se discutirán algunas ideas al respecto.

Por comparación con fractografías obtenidas por Scully (9) para Titanio hidruado y fracturado en aire (Fig. 23) se puede suponer que la fractura transgranular está asociada a la precipitación de hidruros en ciertos planos cristalinos.

Por otra parte, en aleaciones de Titanio, que también sufren corrosión bajo tensiones en soluciones acuosas neutras de $ClNa$, Brown y col. (10) hallaron que el pH en

el fondo de las fisuras descendía hasta 1,6-1,8, siendo en esas condiciones termodinámicamente posible la reducción del ion hidrógeno que ocurriría simultáneamente con la disolución anódica del vértice de las fisuras. En el caso del Circonio la corrosión bajo tensiones se presenta a potenciales mucho más altos ($> 0,33 V_H$). Para que en el vértice de las fisuras se produzca desprendimiento de hidrógeno la caída mínima de potencial que se requiere sería relativamente grande ($> 400 \text{ mV}$). Si se cumpliesen esas condiciones el hidrógeno formado por reducción podría difundir en la aleación y sobrepasada su solubilidad a temperatura ambiente (10 ppm) precipitar en ciertos planos cristalinos. Los hidruros así precipitados podrían originar ruptura transgranular en presencia de tensiones mecánicas aplicadas. De todos modos es evidente que el caso del Circonio requiere mucho más estudio.

En todos los ensayos la fractura dúctil se presentó prácticamente para la misma penetración de las fisuras. Esta observación concuerda con un hecho conocido: la velocidad de propagación de este tipo de fractura es muy alta (aproximadamente la mitad de la velocidad del sonido) de manera que su contribución al tiempo de fractura es prácticamente despreciable.

Por otra parte la velocidad de propagación transgranular es mayor que la velocidad de propagación intergranular ya que en caso contrario no se presentaría la zona transgranular, excepto que algún otro factor detenga la propagación intergranular. Los valores relativos de ambas no se conocen pero si se considera que en la zona transgranular opera un mecanismo asociado a la precipitación de hidruros similar al propuesto para Titanio (9), su contribución al tiempo de fractura también podría ser muy pequeña, ya que la velocidad de propagación hallada en Titanio es del orden de 10 mm./minuto.

Este análisis aproximado revela que la etapa controlante de la corrosión bajo tensiones del Zircaloy-4 en soluciones acuosas de cloruros sería la propagación intergranular, disminuyendo el tiempo de fractura para potenciales más positivos respecto del potencial de picado al aumentar la velocidad de disolución intergranular.

Además, la etapa de propagación intergranular sería un requisito para la propagación transgranular ya que crearía las condiciones electroquímicas en una zona muy localizada que permiten la reducción del ion hidrógeno, con la consiguiente penetración de hidrógeno y por otra parte incrementaría la intensidad del campo de tensiones mecánicas en el vértice de la fisura.

Las observaciones efectuadas, tanto con el microscopio óptico como con el microscopio electrónico de barrido, revelaron la ausencia de fisuras en las superficies laterales de las probetas de tracción, excepto de aquella que propagándose da lugar a la fractura. Este hecho sugiere que también la nucleación del ataque en los bordes de granos es un proceso relativamente difícil o sea que también sería una etapa controlante que precede a la propagación intergranular.

En resumen, el presente trabajo permitió alcanzar las siguientes conclusiones:

1) El Zircaloy-4 es susceptible a la corrosión bajo tensiones en soluciones acuosas de cloruro de sodio. Dicha susceptibilidad se presenta a potenciales iguales o su-

periores al potencial de picado, disminuyendo sensiblemente el tiempo de fractura a medida que el potencial es más positivo con respecto al potencial de picado.

2) Existen por lo menos tres procesos consecutivos en la propagación de este fenómeno: a) Corrosión intergranular; b) Fractura transgranular; c) Fractura dúctil, siendo el primero la etapa que controla la velocidad total del mismo.

AGRADECIMIENTOS

En la realización del presente trabajo se contó con la valiosa colaboración del Servicio de Microscopía Electrónica de Barrido del Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), y fue parcialmente financiado por el Programa Multinacional de Metalurgia.

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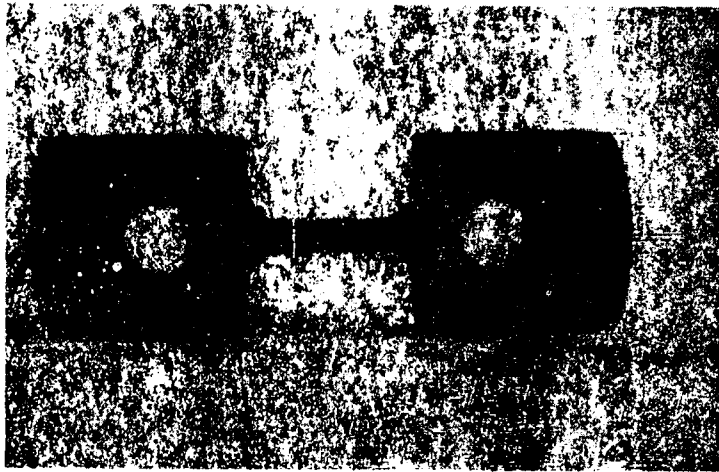


Fig. 1. Probeta de tracción para ensayos a carga constante



Fig. 2. Celda empleada en ensayos de tracción a carga constante

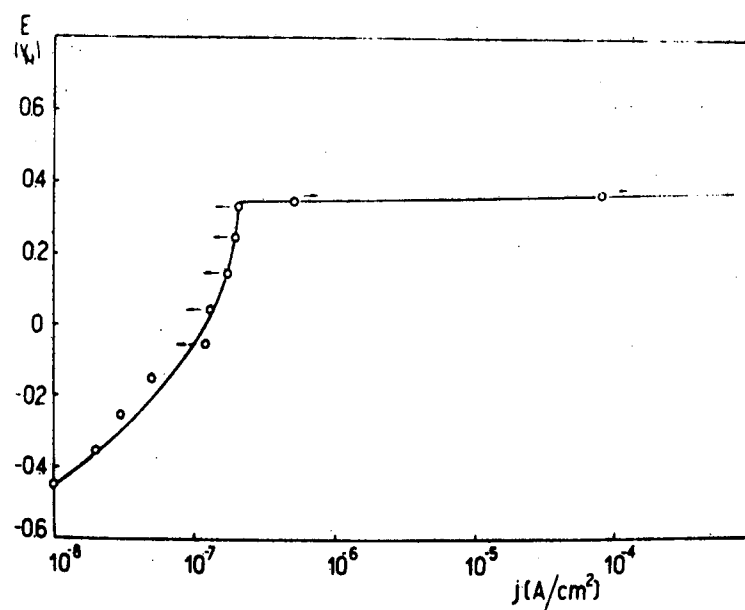


Fig. 3. Curva de polarización anódica, potencioestática, de Zry-4 en ClNa 1N desgasado, a temperatura ambiente

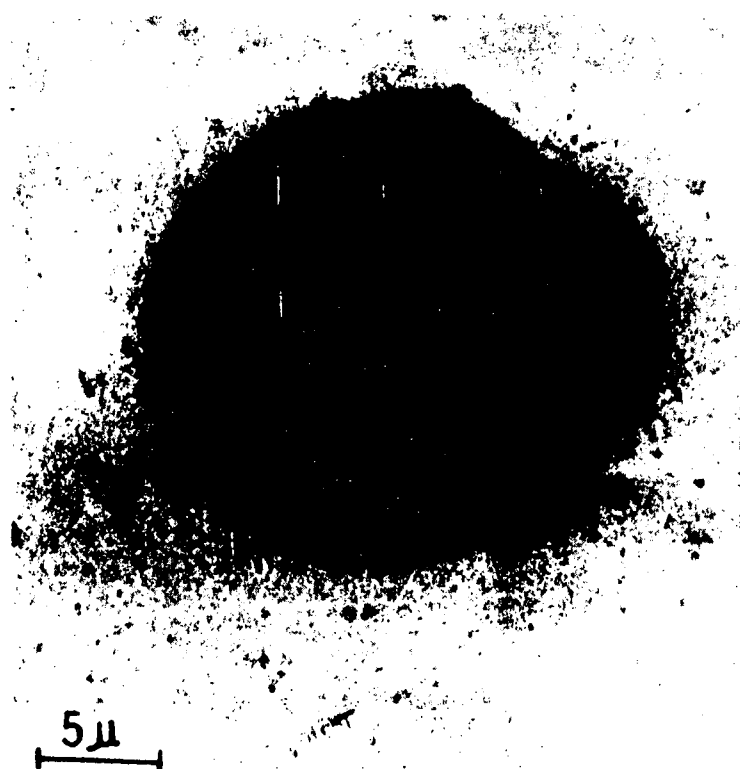


Fig. 4. Morfología del picado de Zry-4 en ClNa 1N

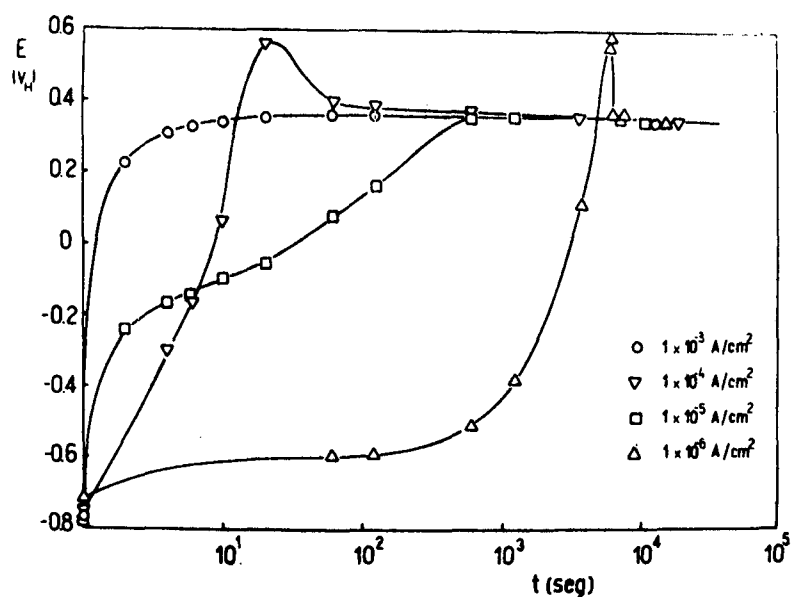


Fig. 5. Curvas potencial vs. tiempo del Zry-4 en ClNa 1N obtenidos para diferentes intensidades de corriente aplicadas.

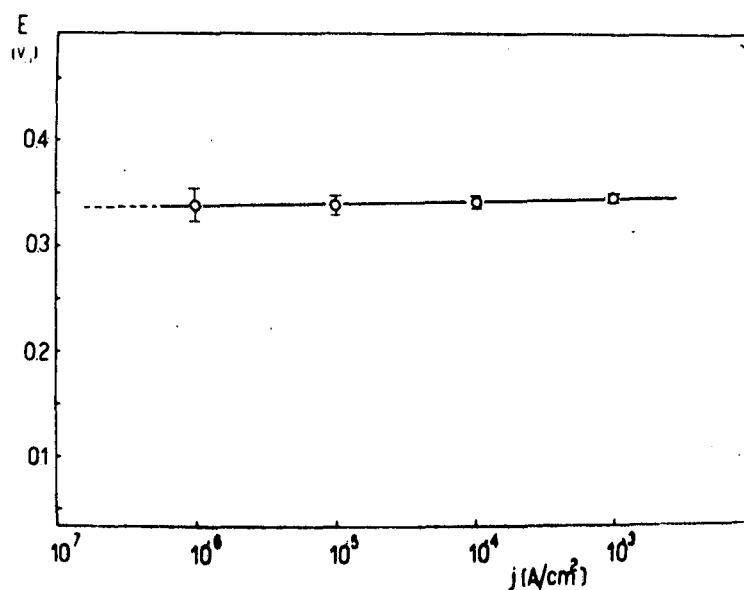


Fig. 6. Curva de potencial vs. densidad de corriente, obtenida a partir de mediciones intenciosas en Zry-4 / ClNa 1N

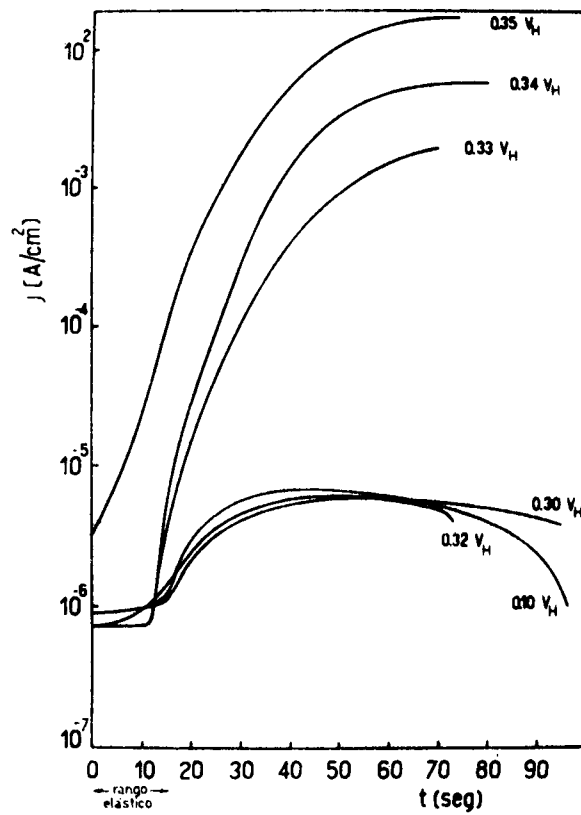


Fig. 7. Curvas densidad de corriente instantánea vs. tiempo, obtenidas potencioestáticamente durante la tracción de Zry-4 en ClNa 1N desgasado, a temperatura ambiente. Velocidad de deformación 9,35%/minuto.

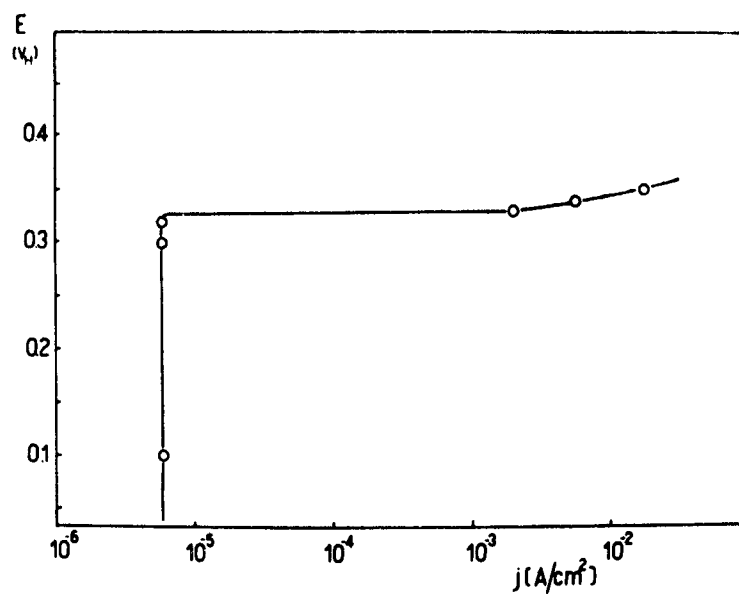


Fig. 8. Curvas de densidad de corriente máxima vs. potencial, para la tracción de Zry-4 en ClNa 1N desgasado, a temp. ambiente.



Fig. 9. Morfología del ataque intergranular del Zry-4 traccionado en ClNa 1N a $E = 0,34 V_H$

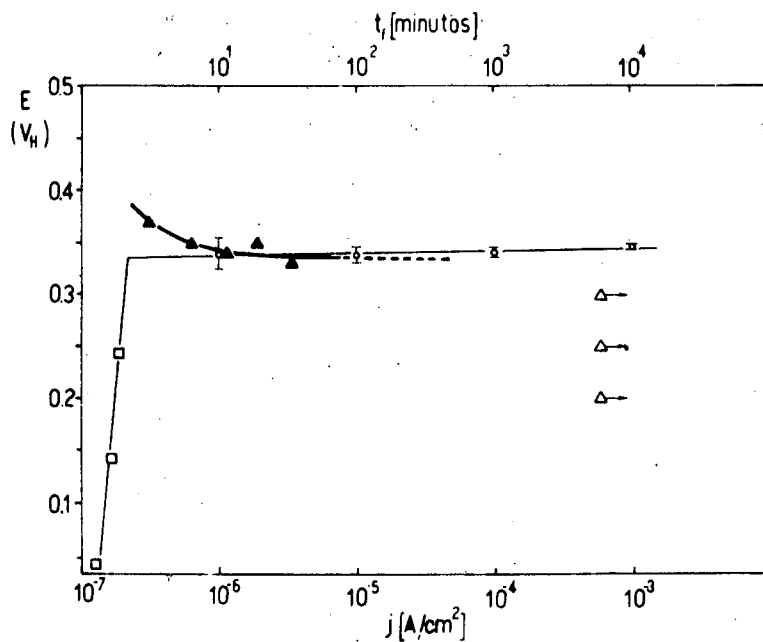


Fig. 10. Curvas de tiempo de fractura vs. potencial y curvas de polarización anódica del Zry-4 en ClNa 1N.

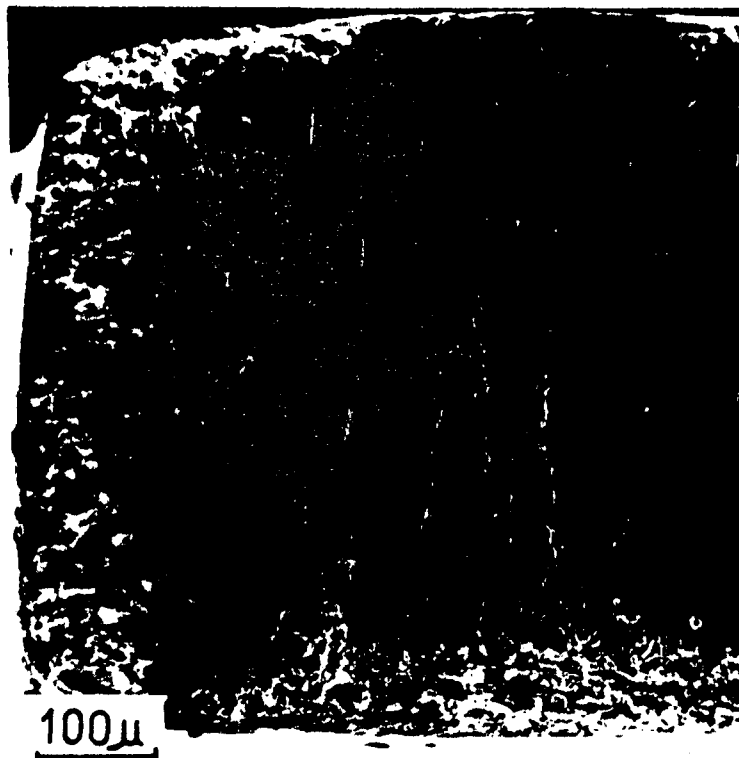


Fig. 11. Topografía de la superficie de fractura de probetas de Zry-4 sometidas a tracción bajo carga constante en ClNa 1N ($E = 0,05 V_H$, $t_f = 19,1$ min)

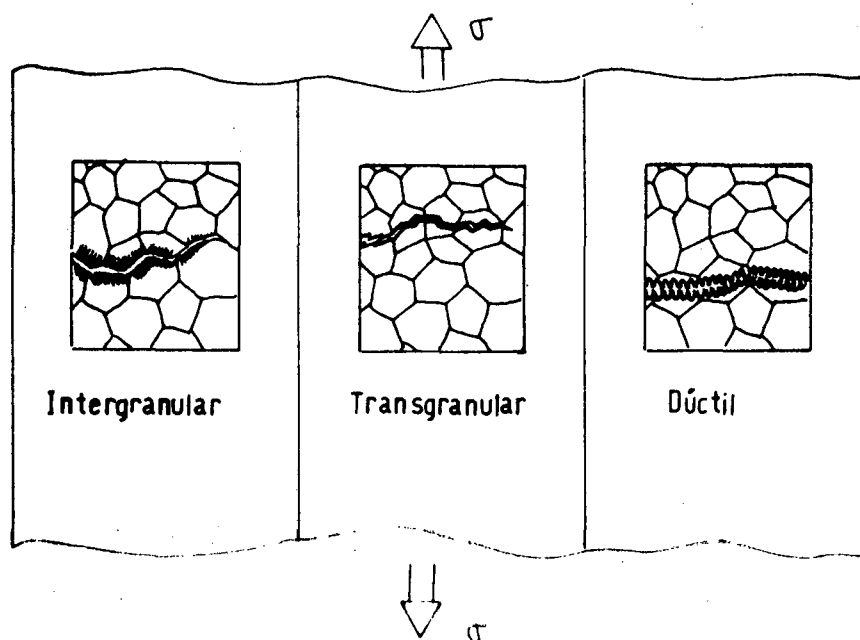


Fig. 12. Esquema de las diferentes etapas de la propagación de la fisura en Zry-4/ClNa.



Fig. 13. Fractografía de la zona intergranular ($E = 0,35 V_H$, $t_f = 19,1$ min)

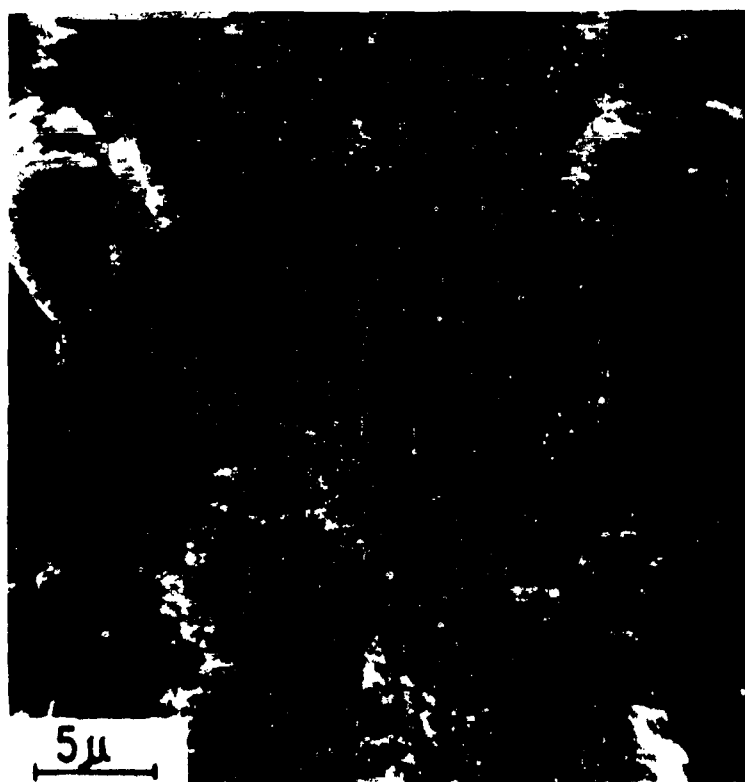


Fig. 14. Fractografía zona intergranular

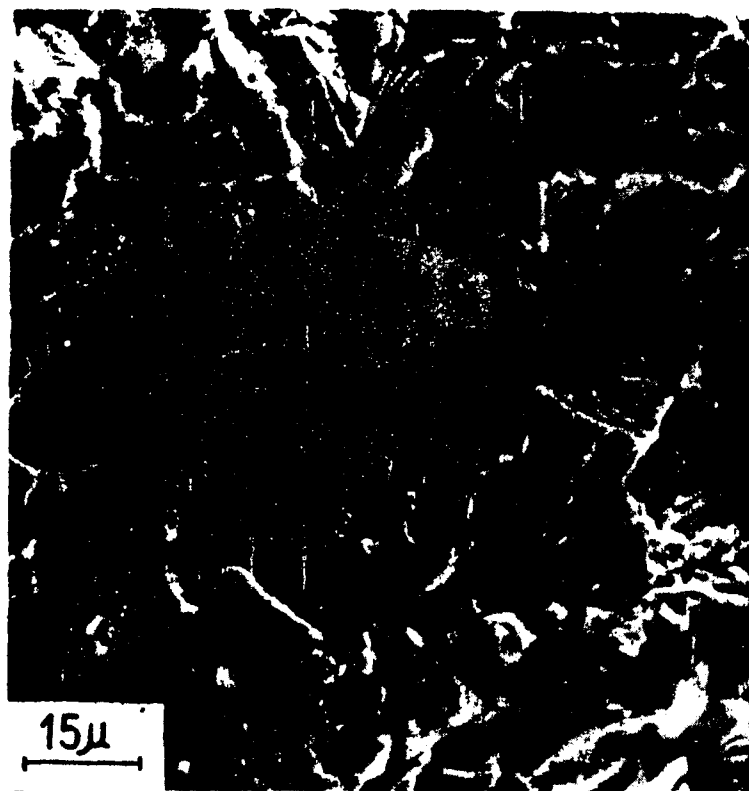


Fig. 15. Fractografía de la zona de transición intergranular-transgranular
($E = 0,33 V_H$, $t_f = 34$ min)



Fig. 16. Fractografía de la propagación intergranular, próxima al comienzo de la propagación transgranular

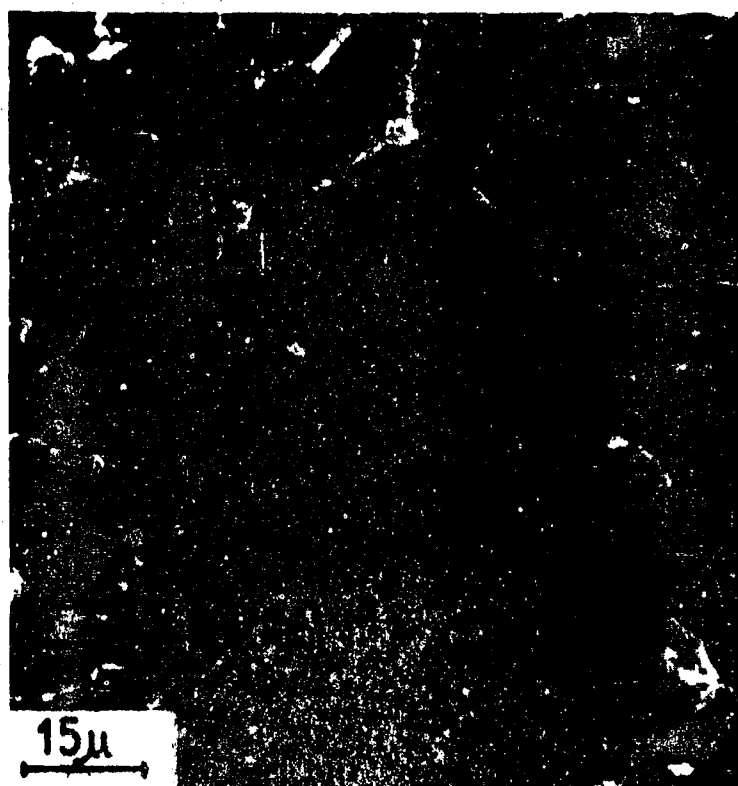


Fig. 17. Fractografía de la zona transgranular ($E = 0.33 V_H$, $t_f = 34$ min)



Fig. 18. Fractografía de la zona transgranular

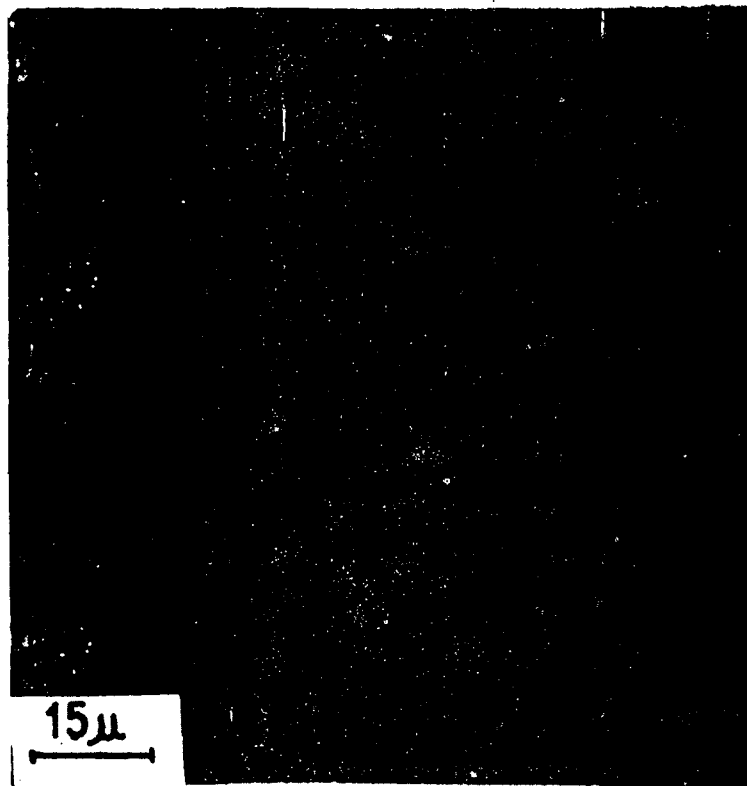


Fig. 19. Fractografía de la zona de transición transgranular - fractura dúctil
($E = 0.35 V_H$, $t_f = 6.4$ min)

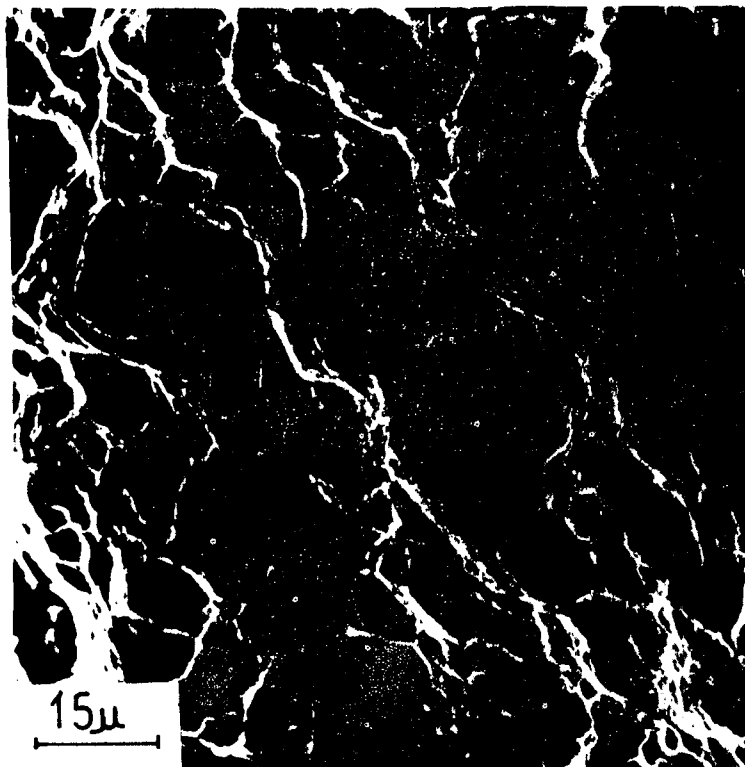


Fig. 20. Fractografía de la fractura dúctil ($E = 0.35 V_H$, $t_f = 19.1$ min)

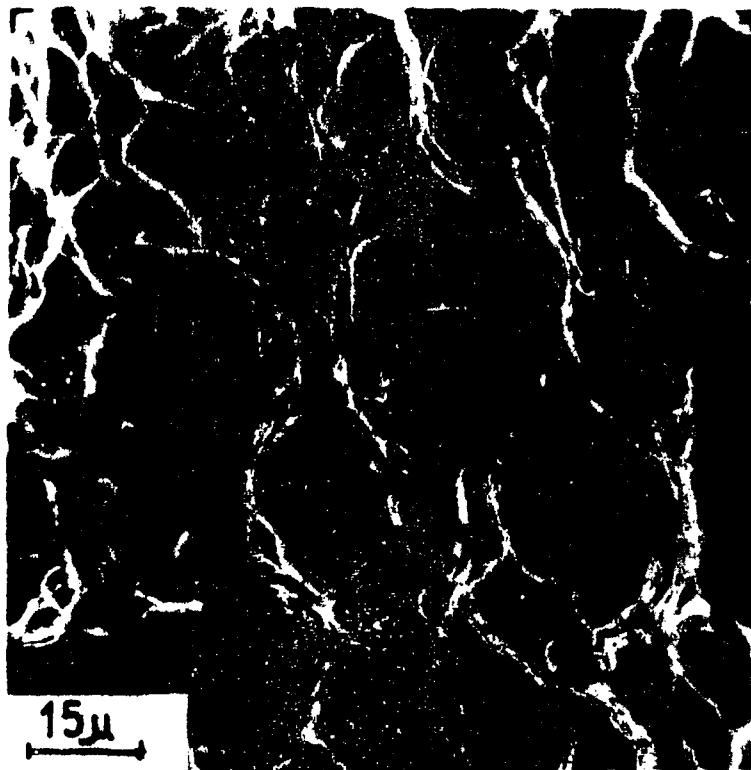


Fig. 21. Fractografía de la fractura dúctil del Zry-4 en aire

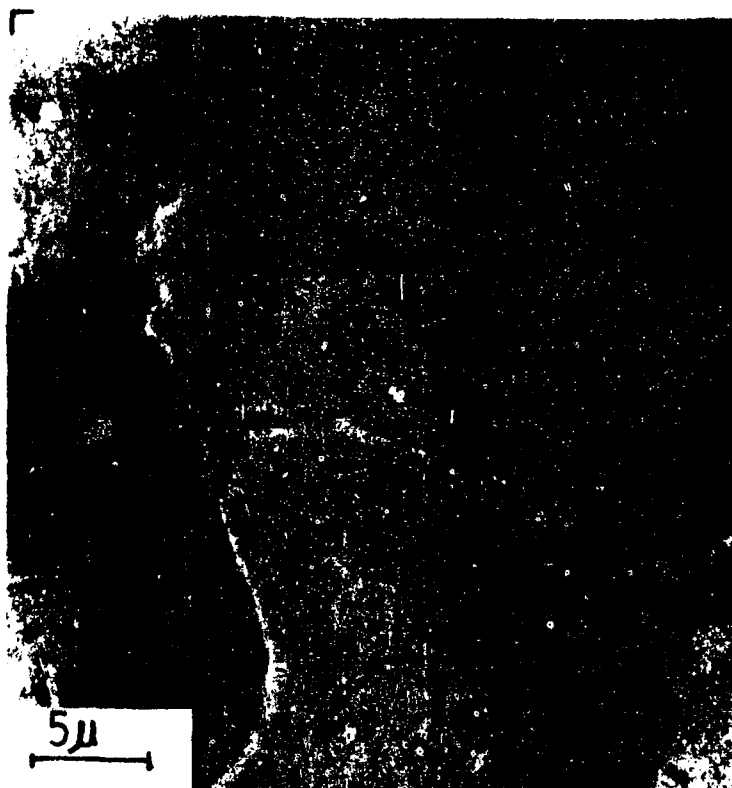
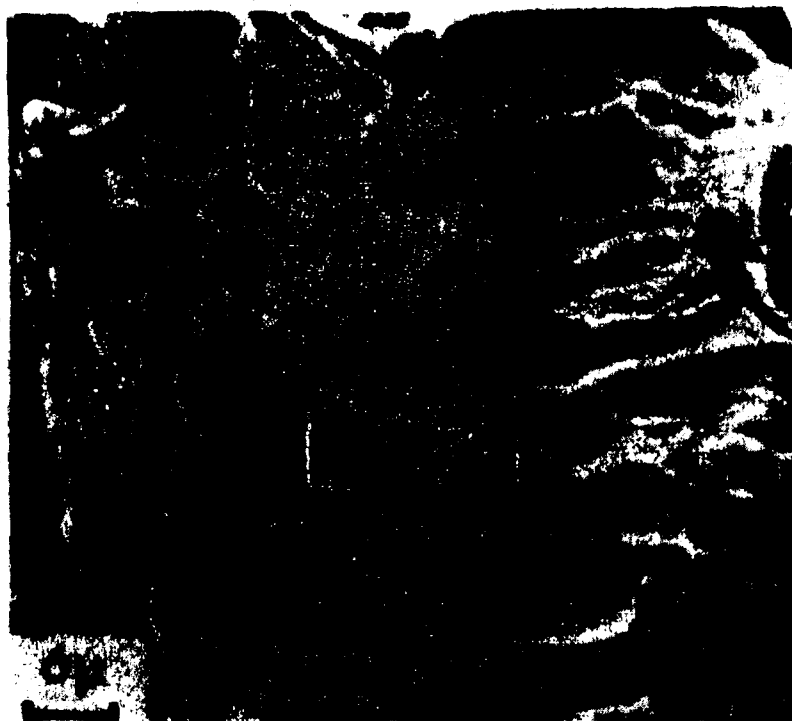


Fig. 22. Iniciación intergranular de la fisura en ensayos bajo carga constante ($E = 0,35 V_H$, $t_f = 19,1$ min)



Fractografía de Ti hidrurado y fracturado en aire (Ref.9).

PASSIVITY AND ITS BREAKDOWN ON IRON AND IRON BASE ALLOYS

鉄および鉄基合金の 不働態皮膜とその破壊

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STRAINING METAL ELECTRODE AS A TECHNIQUE FOR EVALUATION OF STRESS CORROSION CRACKING SUSCEPTIBILITY (AISI 304 IN NaCl + H₂SO₄ SOLUTIONS)

J. R. Galvele* and I. Maier**

The stress corrosion cracking (SCC) susceptibility of austenitic stainless steels in acid chloride solutions, at room temperature, has been the subject of extensive studies. Mazza and Greene¹ determined the solution composition ranges for SCC in H₂SO₄ + NaCl solutions. Bianchi, Mazza, and Torchio² measured the ranges of solution concentration and of potentials for SCC of AISI 304 in HCl solutions. Harston and Scully³ studied the process by scanning electron microscopy (SEM), showing that crack propagation occurred across {111} planes.

One obscure point in this process was the mechanism of crack propagation. According to present knowledge transgranular SCC initiation and propagation is related to a film rupture process at the slip steps.^{4,5} The SCC of austenitic stainless steels in acid chloride solutions, at room temperature, seemed to be an exception to this rule, since it occurred at potentials at which active dissolution should be expected. Nevertheless the assumption that in this case there was no film formation was based only on the electrode potential values at which cracking occurred. No other electrochemical measurements have been reported. In a recent publication, Galvele *et al.* showed that there was clear evidence of a film formation process during SCC of AISI 304 in HCl solutions.⁶ In the same paper the straining experiment results were used to determine the range of SCC susceptibility of the steel (Figure 1).

The aim of the present work was to find out if the proposed method was of general validity or if it was only the result of that particular system.

Straining experiments, at 10 %/min, were performed with AISI 304 stainless steel wire in deaerated 5N H₂SO₄, 5N H₂SO₄ + 0.5N NaCl, and 1N H₂SO₄ + 0.1N NaCl solutions. Following the method previously described⁶ the current density (cd) on the bare metal was calculated from the straining experiment results. By extrapolation of the anodic and cathodic polarization curves, the net anodic current density on the bare metal was estimated (i_b^+). Assuming a mean equivalent weight for AISI 304 of 26.0 and a density of 7.9 g/cm³, the crack penetration rate was calculated.

In 1N HCl solution (Figure 1)⁶ and in 5N H₂SO₄ + 0.5N NaCl solution (Figure 3) the penetration rate was potential dependent, its value increasing as the potential increased. Since general corrosion rate of the stainless steel in these solutions could be high, the penetration rate alone was not found to be a sufficient criterion for SCC

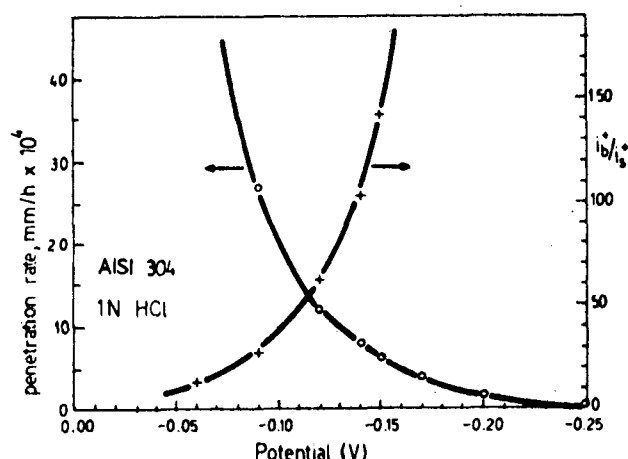


FIGURE 1

susceptibility evaluation. For this reason the use of a ratio of bare metal to filmed metal current densities was introduced (i_b^+/i_s^+).⁶ A high current density ratio value will indicate a high probability of sharp crack formation. The dissolution rate of the bare metal exposed at the slip steps will be much higher than that of the adjacent filmed metal. On the other hand, a low current density ratio will indicate that all the surface is corroding at a similar rate, irrelevant of the slip step formation. Under such conditions general corrosion will be found, and no cracking should be expected.

In Figure 1, at potentials higher than -0.050 (nhe) the penetration rate will be very high, but since the current density ratio is small, general corrosion is found instead of cracking. A similar effect, with a less clear transition, should be expected, at the same potential in Figure 3.

Figure 2 shows that a measurable penetration rate should be found for AISI 304 stainless steel in 5N H₂SO₄ solution. Nevertheless, since the current density ratio is very small, no cracking but general dissolution should be expected. This is in coincidence with the fact that no SCC was reported so far in this medium.

As for AISI 304 in 1N H₂SO₄ + 0.1N NaCl solution, the calculated penetration rate is slightly smaller than that for 5N H₂SO₄ solution. Nevertheless the current density ratio, in this case, increases as the potential decreases, reaching values of 80 and higher. Cracking should be expected in this solution. By comparison between Figures 3 and 4 it is concluded that the susceptibility to SCC is higher in 5N H₂SO₄ + 0.5N NaCl solution than in 1N H₂SO₄ + 0.1N NaCl solution. This observation is in agreement with the SCC experiments reported by Staehle.⁷

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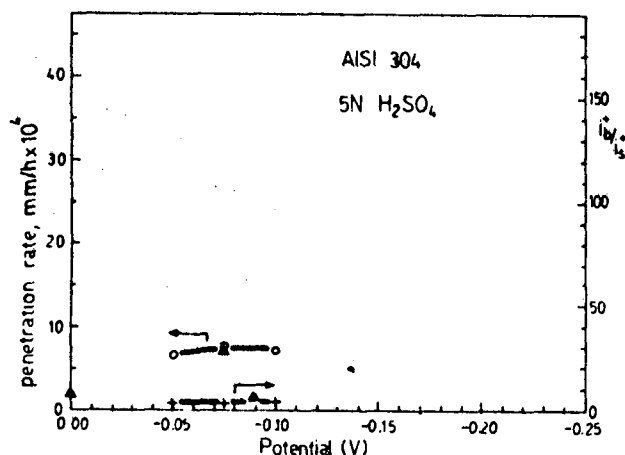


FIGURE 2

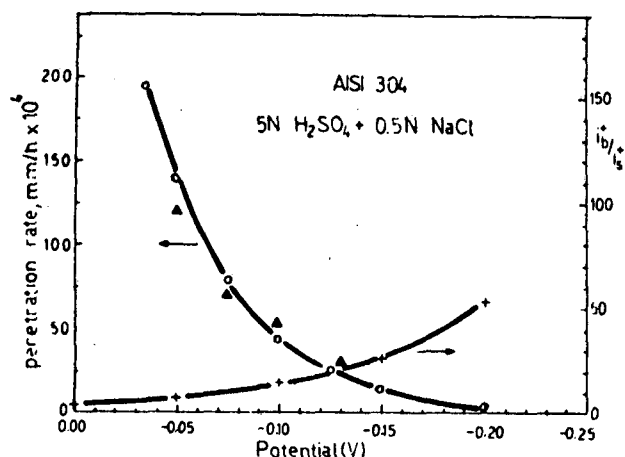


FIGURE 3

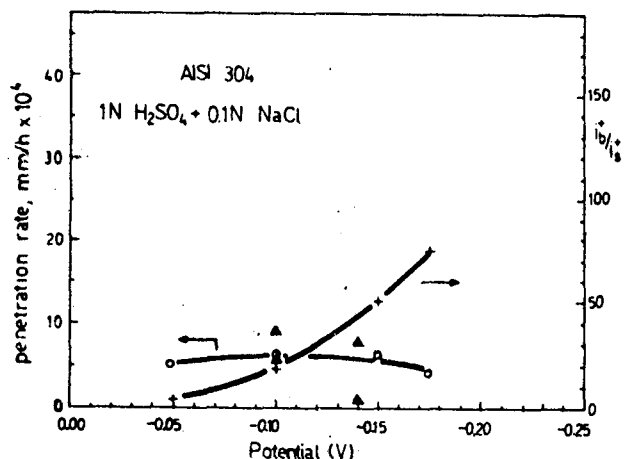


FIGURE 4

To check if the penetration rates predicted by straining experiments were relevant, long term exposure tests were performed. U-bend specimens were exposed to the solutions at constant potential. The exposure time ranged from 2 h, for the highest penetration rates, up to 15 days for the lowest. The penetration rates found ($\blacktriangle$) were in very good concordance with those predicted from the straining experiments. Besides no cracking was found at those potentials where the current density ratio was equal to, or

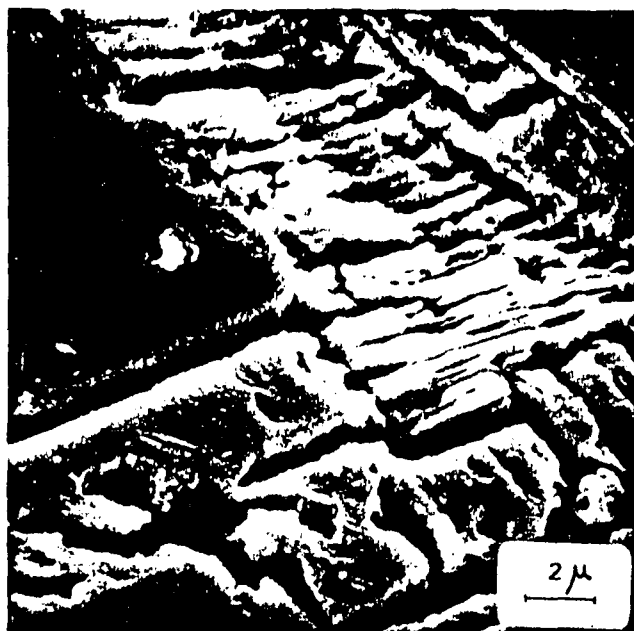


FIGURE 5



FIGURE 6

smaller than, 5.

A further check was made by observation of the corroded specimens with the SEM. In 5N $\text{H}_2\text{SO}_4 + 0.5\text{N}$ NaCl solution, after 2 h exposure at -0.075 V (nhe), sharp fissures were observed, with little corrosion on the adjacent surface, Figure 5. In 5N H_2SO_4 solution, on the other hand, after 4 h exposure at -0.110 V (nhe) incipient grooves were observed, surrounded by heavily corroded metal, Figure 6. Both results are in good agreement with the predicted current density ratios.

It is concluded that for SCC of stainless steels in acid chloride solutions the straining metal experiments are a means for quick evaluation of: (1) potential ranges for SCC susceptibility; (2) crack penetration rates; (3) crack mor-

Film Rupture Mechanism for Stress Corrosion Cracking of AISI 304 in HCl Solutions[★]

J. R. GALVELE, S. B. de WEXLER, and
I. GARDIAZABAL*

Abstract

The anodic behavior of AISI 304 stainless steel in 1M hydrochloric acid solution at 25 C has been studied at different electrode potentials under static conditions and during straining at 40%/minute. From the potential-time curves, current-time curves, and net anodic current densities, it is concluded that a film formation process takes place under stress corrosion cracking (SCC) conditions. It is proposed that SCC in this system occurs because of a film rupture process, with cracks starting at the bare metal exposed on the slip steps. From straining experiments alone, the range of electrode potentials for SCC was estimated. Above -0.100 V, no cracking could be found because of the little difference in current density between the bare metal and the filmed metal. Below -0.200 V, no SCC was detected because of the very low rate of crack propagation (less than 10^{-4} mm/hour).

The stress corrosion cracking (SCC) susceptibility of austenitic stainless steels in acid chloride solutions at room temperature has been the subject of extensive studies. Mazza and Greene¹ determined the solution composition ranges for SCC in H₂SO₄ plus NaCl solutions. Bianchi, Mazza, and Torchio² measured the ranges of solution concentration and of potentials for SCC of AISI 304 in HCl solutions. Harston and Scully³ studied the process by scanning electron microscopy (SEM), showing that crack propagation occurred across {111} planes.

One obscure point in this process is the mechanism of crack propagation. According to present knowledge, transgranular SCC initiation and propagation is related to a film rupture process at the slip steps.^{4,5} The SCC of austenitic stainless steels at room temperature seems to be an exception to this rule, since it occurs at potentials at which active dissolution should be expected.^{1,3} Nevertheless, the assumption that in this case there is no film formation is based only on the electrode potential values at which cracking occurs. No other electrochemical measurements have been reported. The aim of the present work was to find out if the

electrochemical behavior of AISI 304 steel, under SCC conditions, is that of a film free metal. The results showed that there is a film formation process, and that the range of potentials at which Bianchi et al.² found SCC is that at which a film rupture mechanism would be operative.

Experimental

The composition of the material used (AISI type 304) was: Cr 18.7; Ni 10.0; C 0.07. Three types of specimens were used. U-bent specimens measuring 15.0 x 1.0 cm and 0.1 cm thick were used for the SCC tests. For the polarization curves, specimens measuring 3.5 x 1.0 cm and 0.1 cm thick, with an electrical lead of the same material inert gas-tungsten arc-welded, were used, with the lead, the edges, and one of the faces covered with cured epoxy resin. The chemical determination of the dissolution rate was made with specimens measuring 5.0 x 1.3 cm and 0.1 cm thick with the electrical lead, and the top edge covered with cured epoxy resin. Prior to testing, the specimens were annealed for 30 minutes at 1070 C under an Argon atmosphere and water quenched. After heat treatment, they were pickled in 15% HNO₃ + 2% HF solution at 60 C for 5 minutes. Immediately before the experiments, the specimens were wet-ground with grade 600 SiC paper and washed with water, to minimize the interference of air formed films with the measure-

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lytes.

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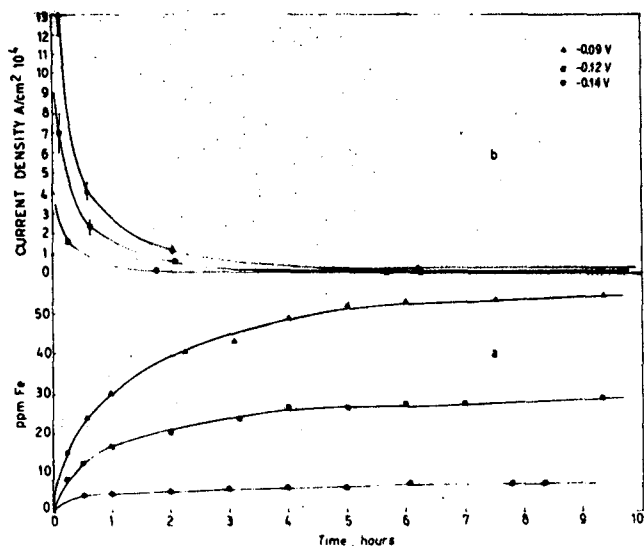


FIGURE 4 — Iron dissolution rate for AISI 304 in 1M HCl solution at constant potential, at 25 C. (a) = Dissolved iron as a function of time and (b) = partial anodic current density for iron dissolution at constant potential, calculated from (a).

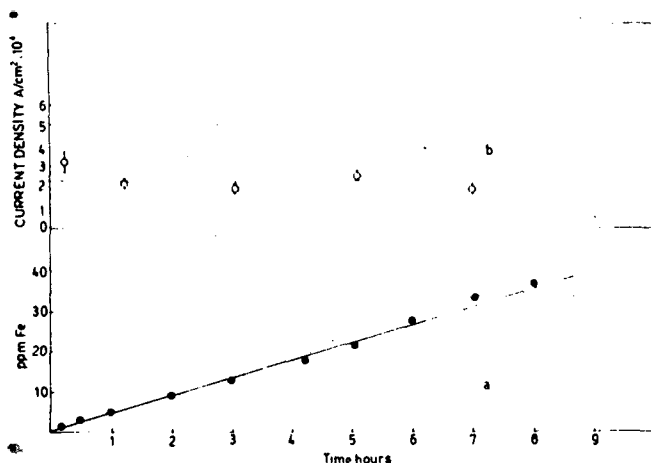


FIGURE 5 — Iron dissolution rate for high purity iron (Fe 99.997%) in deaerated 0.5 M H₂SO₄ solution at 25 C. Potential -0.300 V. (a) = Dissolved iron as a function of time and (b) = iron dissolution current density calculated from (a).

measurements were performed at three different potentials, and the net current density for iron dissolution was calculated (Figure 4b). In spite of what might be expected for an active metal dissolution, the current density did not remain constant with time, but dropped off. For the sake of comparison, the experiments were repeated with a well-known active electrode. High purity iron (99.997%) was used in deaerated 0.5 M H₂SO₄ at -0.310 V.⁹ Figure 5 shows the results obtained. The active iron gave a constant rate of dissolution, i.e., a constant current density, at constant potential. In the case of potentiostatic dissolution of AISI 304 steel, the current density did not remain constant with time, but changed according to a hyperbolic law (Figure 6), a type of behavior found in film formation processes.^{10,11}

From Figure 4b and the total measured current density, the approximate net cathodic current density was estimated. This current also dropped with time, showing that the process taking place on the metal surface interfered with the cathodic reaction.

Straining Metal Experiments

Potentiostatic current-time curves were drawn for AISI 304

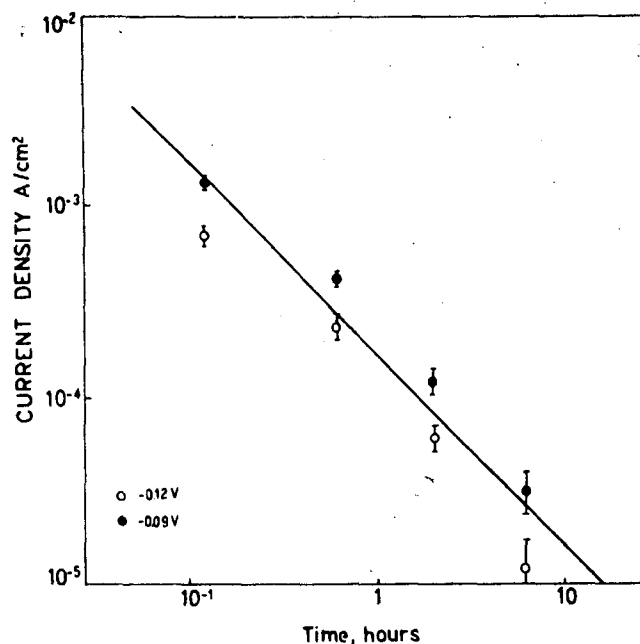


FIGURE 6 — Current-time curves for partial anodic current density of iron dissolution from AISI 304 in deaerated 1M HCl solution at 25 C.

wires strained in a deaerated 1M HCl solution at a strain rate of 40%/minute. Figure 7 shows the results obtained. As in the current-time curves, three different zones were detected. For potentials higher than -0.120 V, the straining of the wires produced an increase in the anodic current density. At potentials lower than -0.190 V, the straining of the wires was accompanied by an increase in the total cathodic current density. In both cases, the effect of straining on the current density was small. Between these two values, there was a range of potentials at which straining made the total current density change considerably, going from cathodic to anodic values. After fracture, the wires returned to the initial cathodic current density.

The range of potentials at which the anodic-cathodic changes occur (Figure 3 and 7) is of particular interest. It is precisely in such a range of potentials that Bianchi, et al.² reported SCC susceptibility of the AISI 304 in 1M HCl solution. The curves in Figure 7 are also additive combinations of partial anodic and cathodic processes. It would be of great interest to determine the net anodic and cathodic currents. Observations described above suggest the presence of a film on the AISI 304 in the HCl solution. If we assume that the metal is carrying a film, but make no assumption on the nature of such film, the results in Figure 7 could be explained in the following way. At potentials higher than -0.190 V, the film free metal, exposed by straining of the wire, shows a higher anodic current density than the filmed metal. The higher the potential becomes, the higher the anodic current density becomes. At potentials below -0.190 V, the potential is below the corrosion potential of the film free metal, and straining of the wire accelerates the cathodic reaction.

Net Anodic Current Density on the Filmed Metal

The current density on the filmed metal can be taken as the value measured before straining. Figure 8 shows those values for static metal. The static metal shows a corrosion potential of -0.130 V. At potentials higher than -0.130 V, the net anodic current density of alloy dissolution predominates over the net cathodic current density. Below -0.130 V the net cathodic current density of hydrogen evolution predominates over the anodic reaction. Below -0.180 V the contribution of the net anodic reaction becomes negligible and a Tafel line of slope of $b = -0.120$ V is found. This slope value occurs frequently for hydrogen evolution on metals,¹² and confirms the idea that the anodic contribution is negligible. By

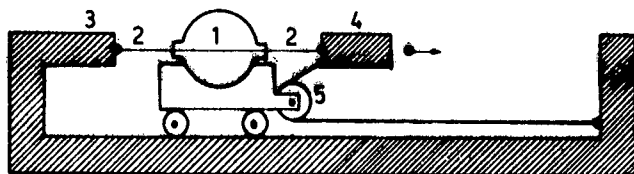


FIGURE 1 — Schematic view of wire straining arrangement. 1 = cell; 2 = specimen; 3 = fixed chuck; 4 = mobile chuck, and 5 = cell driving pulley.

ments.

The straining experiments were performed on AISI type 304 wire, 0.08 cm in diameter, with the following composition: Cr 18.1; Ni 9.69; C 0.07. The wires were used in the as-received condition, i.e., softened after drawing and slightly cold worked by subsequent coiling and uncoiling. Immediately before the straining experiment the wires were wet-ground with 600 grade SiC paper and washed with water. The cell used for the straining experiments was described in a previous paper.⁶ The potential was kept constant with a Tacussel PRT 20-2X potentiostat. The straining of the wires was performed with a motor-driven Hounsfield Tensometer, at constant rate of cross head displacement, using an initial strain rate of 40%/minute. The cell was coupled to the moving chuck of the Tensometer through a pulley so as to keep the corroding metal inside the cell during straining (Figure 1). Before applying the strain, the wires were exposed to the deaerated 1M HCl solution until the open circuit potential reached a value of -0.130 V (about a 2 hour exposure). Then the desired potential was applied, the current density of the stationary metal measured, and the Tensometer switched on.

All the measurements were made at 25 C. The solutions were prepared with double distilled water and analytical grade reagents, and were degassed with purified nitrogen.⁷ The potentials were measured through a Luggin capillary with a calomel reference electrode, and are reported on the hydrogen scale.

A Pyrex cell of 300 ml capacity, with double walls for thermal control, and with a tap at the bottom for the extraction of solution samples, was used for the chemical determination of the dissolution rate of the alloy. From time to time, 10 ml samples of the solution were taken and analyzed for the iron content by atomic absorption spectrometry.

Results and Discussion

Potential-time Curves

A preliminary set of experiments was performed, repeating those reported by Bianchi, Mazza, and Torchio.² U-bent specimens for AISI 304 were exposed to aerated 1M HCl solution for about 300 hours. The SCC reported by them was confirmed.

Simultaneously with the exposure of the U-bent specimens, the open circuit potential of the specimens was measured. The potential changed with time, going from -0.180 V up to -0.140 V. The corroded surface of the specimens showed interference colors, suggesting the presence of a film on the metal surface.

In a second series of experiments, the corrosion potential of unstressed specimens was measured in a deaerated 1M HCl solution (Figure 2). In the deaerated solution, the corrosion potential of the stainless steel also changed with time, going from a minimum value of -0.200 V up to -0.140 V after a 5 hour exposure. Measurements on AISI 316 were also included in Figure 2. Potential rises, like those shown in Figure 2, were usually ascribed to film formation processes.⁸ Similar processes would take place in both steels and would be much faster on the AISI 316.

Potentiostatic Current-Time Curves

The change in current density with time, at constant potential, was determined for AISI 304 steel in a deaerated 1M HCl solution. The measurements were extended up to a 10 hour exposure. Figure 3 shows the results obtained at various potentials. Three different

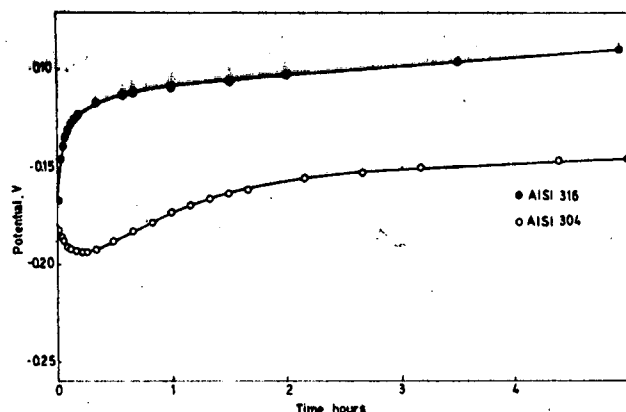


FIGURE 2 — Open circuit potential-time curves for AISI 304 and AISI 316 in deaerated 1M HCl solution at 25 C.

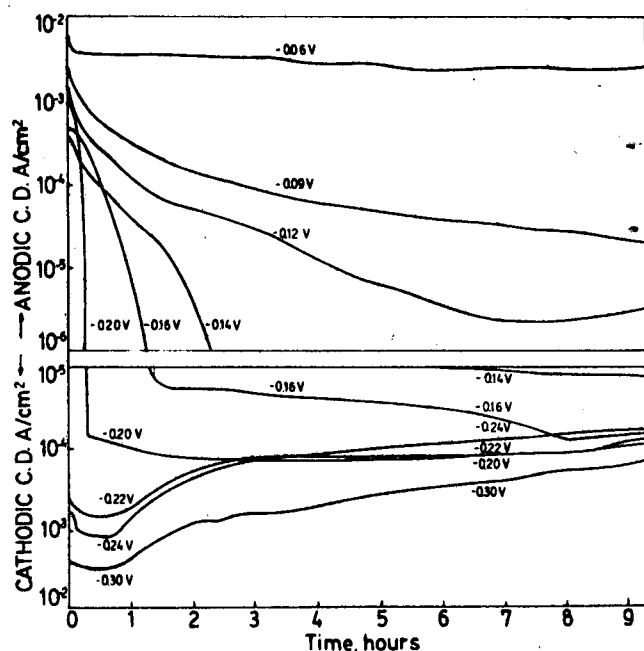


FIGURE 3 — Current-time curves at constant potential for AISI 304 in deaerated 1M HCl solution at 25 C.

families of curves were observed. For potentials equal to or higher than -0.120 V, decreasing anodic current densities were found. The current density decrease rate was potential dependent, and the lower the potential the more noticeable it became. A second family of curves was found for potentials equal to or lower than -0.220 V. Here again the current density showed a decreasing trend, but remained cathodic all the time. Between -0.120 and -0.220 V, on the other hand, the current density, initially anodic, decreased with time, becoming cathodic. The time necessary to get a steady state current density was potential dependent, and varied from 1 to 8 hours.

Net Anodic Current Density

The current densities in Figure 3 are the results of the additive combination of two partial processes: one net anodic current due to alloy dissolution, plus one net cathodic current due to hydrogen evolution. The changes observed between -0.120 and -0.220 V indicate that the values of the net currents changed with time. Chemical methods were used to determine the net anodic current density. Because of the very low current densities involved, the only changes measurable with the atomic absorption technique were those of iron concentration. Figure 4a shows the change in iron concentration with time in the deaerated 1M HCl solution. The

TABLE 1 – Current Density on the Bare Metal, Calculated from Straining Experiments (Equation 2)

Potential V(SHE)	Current Density on the Bare Metal (i_b) (A/cm ²)	
	15% Elongation	30% Elongation
-0.060	5.6×10^{-3}	5.1×10^{-3}
-0.120	9.4×10^{-4}	9.8×10^{-4}
-0.140	1.4×10^{-3}	1.3×10^{-3}
-0.160	2.2×10^{-4}	2.0×10^{-4}
-0.170	2.7×10^{-4}	1.4×10^{-4}
-0.180	1.6×10^{-4}	1.3×10^{-4}
-0.190	1.3×10^{-4}	0.7×10^{-4}
-0.200	-2.2×10^{-4}	-1.7×10^{-4}
-0.220	-2.5×10^{-4}	-2.9×10^{-4}
-0.260	-3.3×10^{-4}	-2.0×10^{-4}

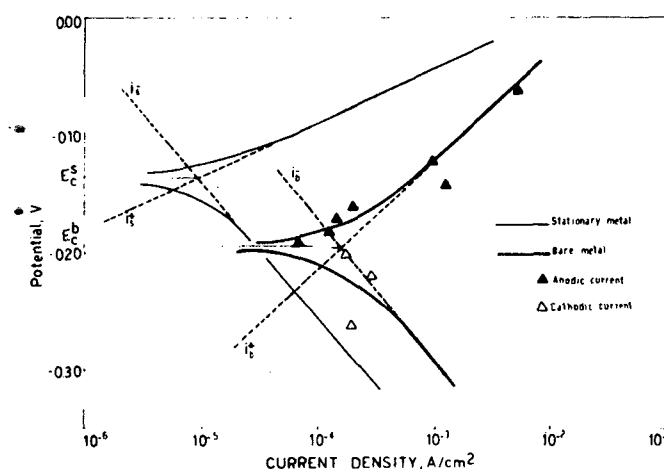


FIGURE 9 – Bare metal calculated polarization curve for straining AISI 304 in deaerated 1M HCl solution at 25 C. i_b^+ = bare metal net anodic current density; i_b^- = bare metal net cathodic current density; i_a^+ = stationary metal net anodic current density; i_a^- = stationary metal net cathodic current density; E_c^s = stationary metal corrosion potential, and E_c^b = bare metal corrosion potential.

rate of reaction increased as the potential was lowered. As the potential increased, on the other hand, the difference between the bare metal and the filmed metal tended to vanish. Eventually at a high potential, there would be no difference between both rates of dissolution.

The exposure of bare metal to the solution will initiate attack along slip lines leading to the formation of fissures. The higher the difference is between the current density on the bare metal and the current density on the filmed metal, the sharper will be the fissures. The ratio of the current density on the bare metal to that on the filmed metal (i_b^+/i_a^+) can be taken as the measure of crack sharpness. As shown in Figure 10, for potentials higher than -0.100 V, with a ratio of currents lower than 10, no real cracks should be expected since the dissolution rate of the sides of the cracks will be comparable to that of the advancing edges of the cracks. This observation is in coincidence with Bianchi *et al.*,² who found that over -0.100 V the AISI 304 steel was not susceptible to SCC in 1M HCl solutions. Dissenting from what these authors say, it was found that SCC susceptibility disappears not because of anodic protection, but because of the blunting effect of a low current density ratio. On the other hand, according to the current density ratio, SCC should occur at any potential below -0.100 V.

Another limiting factor for SCC is the rate of crack propagation. From the net anodic current density calculated for the bare

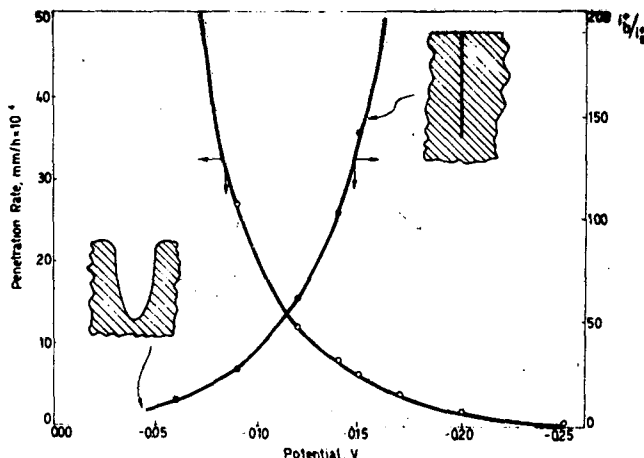


FIGURE 10 – Calculated crack penetration rate, and bare metal to filmed metal current density ratio (i_b^+/i_a^+), as a function of potential for stressed AISI 304 in 1M HCl solution at 25 C. Insert: Expected fissure morphology.

metal, it is possible to estimate the rate of crack propagation. Assuming a mean equivalent weight for AISI 304 of 26.0 and a density of 7.9 g/cm³, at -0.170 V a crack propagating at a dissolution rate of 3.0×10^{-4} A/cm² (Figure 9) will advance at a speed of 3.7×10^{-4} mm/hour. Figure 10 shows crack propagation rates calculated from the straining experiments. The rate of crack propagation dropped substantially when the potential decreased. This again is in agreement with Bianchi *et al.*, since they reported that no SCC occurs below -0.200 V. According to our straining experiments, the rate of crack propagation at such a potential should drop below the measurable values. Theoretically SCC will stop only at potentials where the alloy becomes thermodynamically stable.

Figure 10 shows schematically the expected fissure morphology for different potentials. These expectations are based on the straining experiments alone, but they were confirmed by U-bend specimens. Figures 11 and 12 show U-bend specimens exposed to 1M HCl solution at constant potential. The specimen in Figure 11 was exposed at -0.050 V for 30 hours. According to Figure 10, the ratio of bare metal current to filmed metal current at that potential is on the order of eight, so no fissures should be expected. The specimen in Figure 12 was exposed at -0.150 V for 206 hours. The ratio of currents, at this potential, is about 140 and cracking should be found. The results in Figures 11 and 12 support the assumptions made during the analysis of the straining experiment results.

Nature of the Surface Film

The Tafel slope for the net anodic current on the bare metal (Figure 9) is in good agreement with the value reported by Schwabe and Voigt¹⁶ for active dissolution of iron *inhibited* by chloride ions. The difference between the polarization curve for the bare metal and that for the static metal suggests the presence of a slow down process in the dissolution of the metal. Several of the observations made in the present work indicate that a solid film of corrosion products should be the cause of this slow down. This idea is favored first by the appearance of interference colors on the metal surface during potential-time measurements. Secondly, Figure 6 supports the idea of a film formation process. Finally, when determining potentiokinetic polarization curves on AISI 304 stainless steel in 1M HCl solutions, it was observed that at potentials higher than -0.100 V a visible black film is formed on the specimens. This film is undermined by the dissolution process and eventually becomes detached from the surface at potentials higher than +0.010 V. Thinner invisible films could be reasonably expected below -0.100 V. One possible reason for stating that there was no film formation on stainless steel could be that all the oxide films reported so far for Fe-Cr-Ni alloys would be thermodynamically unstable in a 1M HCl solution. But this is not the case, for example, with iron in acid

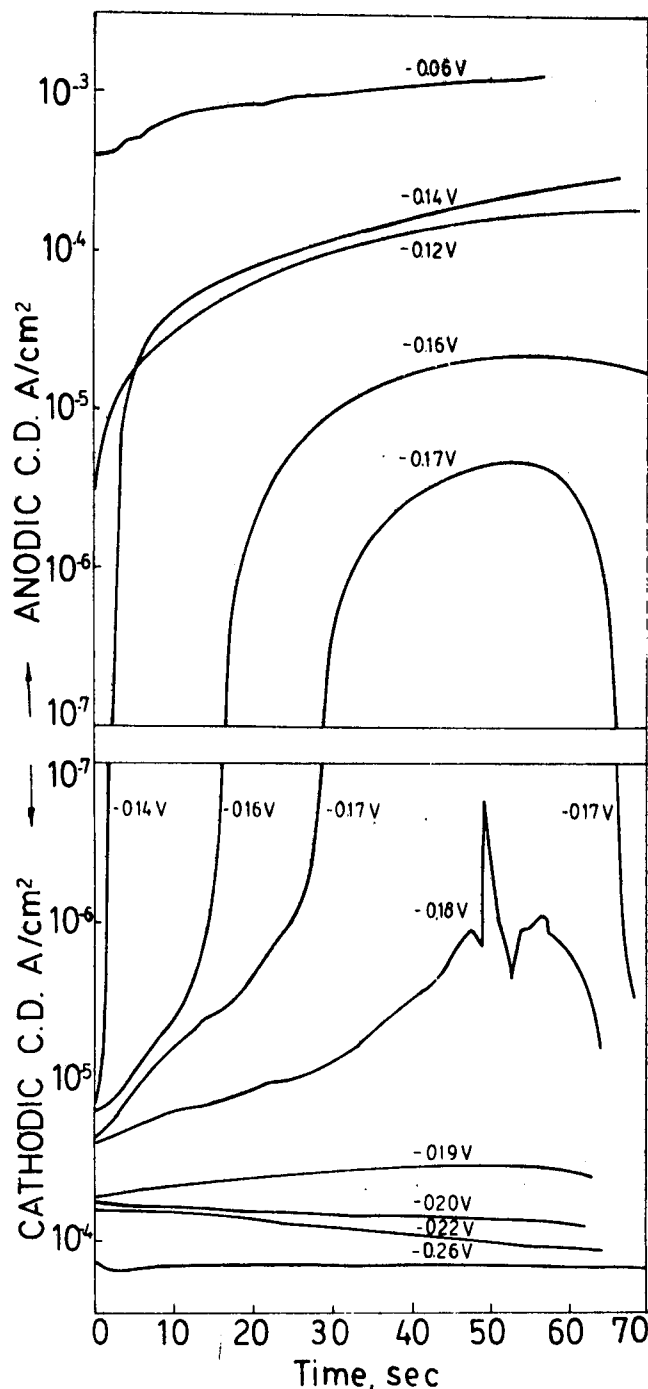


FIGURE 7 — Current-time curves, at constant potential, for straining AISI 304 in deaerated 1M HCl solution at 25 C. Strain rate: 40%/minute.

extrapolation of the cathodic branch of the curve in Figure 8, it was possible to separate the net anodic component of the polarization curve of the static metal from the cathodic component. In this way, it was found that the net anodic reaction followed a logarithmic law, with a slope of $b = +0.045$ V. The chemically measured net anodic current density values (described above) was included in Figure 8. The net current density for iron dissolution is in very good agreement with the net current density graphically determined for the alloy dissolution. The agreement between both methods confirms the validity of the graphical method used in Figure 8.

Net Anodic Current Density on the Bare Metal

The current density of the straining metal can be analyzed following a method similar to that used by Hoar and Galvele¹³ for

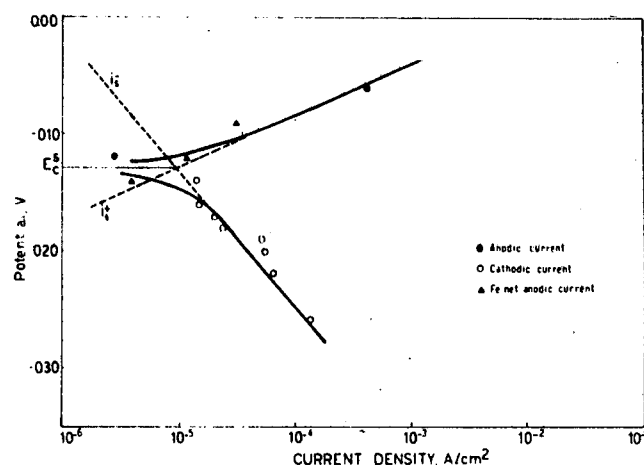


FIGURE 8 — Polarization curve for static AISI 304 in 1M HCl solution at 25 C. i_s^+ = stationary metal net anodic current density; i_s^- = stationary metal net cathodic current density, and E_c^5 = stationary metal corrosion potential.

SCC of mild steel in nitrate solutions, and later by Hoar and Jones¹⁴ for SCC of mild steel in caustic solutions. If it is assumed that the surface film is brittle compared with the ductile metal beneath it, and that the current density on the filmed metal remains at its original value, the current density over the bare metal may be calculated. The amount of bare surface produced on straining the wires is given by:¹⁵

$$\% \text{ Bare surface} = 100 \left[1 - \left(\frac{L_0}{L} \right)^{1/2} \right] \quad (1)$$

where L_0 is the initial length of the specimen, and L is the length at any time during straining. For small linear strains, $\% \text{ Bare surface} \approx \frac{1}{2} \% \text{ Strain}$. For example, after 30% elongation at -0.160 V the current density was $1.7 \times 10^{-5} \text{ A/cm}^2$ (anodic), and the initial current density was $-1.5 \times 10^{-5} \text{ A/cm}^2$ (cathodic). If the change in current density is attributed to the reaction taking place on the bare surface ($\approx 15\%$ of the total area), then we have:

$$(i_s \times A_s) + (i_b \times A_b) = i_y \quad (2)$$

i_s being the current density on the static metal; A_s the fraction of area covered by a film; i_b the current density on the bare metal; A_b the fraction of area of bare metal, and i_y the current density on the straining metal. For the example mentioned above we have:

$$\left[(-1.5 \times 10^{-5}) \times 0.85 \right] + (i_b \times 0.15) = 1.7 \times 10^{-5} \quad (3)$$

and

$$i_b = 2.0 \times 10^{-4} \text{ A/cm}^2 \quad (4)$$

Table 1 shows the i_b values calculated for 15% and 30% elongation. The current density on the bare metal remained fairly steady during straining, indicating a slow refilming process.

The graphical method for net anodic and cathodic currents was also applied to the bare metal. Figure 9 shows the results for 30% elongation. For the sake of comparison, the results for the filmed metal were included. Because of the small number of cathodic data, it was assumed that the anodic reaction followed a logarithmic law, and a linear extrapolation was made. The Tafel slope of the anodic reaction was $b = 0.095$ V, which is comparable to the values from 0.080 to 0.114 V reported by Schwabe and Voigt¹⁶ for active dissolution of iron in presence of chloride ions. The cathodic reaction will probably be shifted as shown in Figure 9, but there are not enough data to confirm it.

Figure 9 shows that the anodic reaction on the bare metal was much higher than that on the filmed metal. The difference in the

PASSIVITY BREAKDOWN OF HIGH PURITY IRON AND AISI 4340 STEEL IN 0.5M NaCl SOLUTION*

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Abstract—The anodic and cathodic electrochemical behaviour of high purity iron and of AISI 4340 high strength steel in unbuffered 0.5M NaCl solution has been studied. The results were correlated with the SCC failure mechanism of the steel. The pitting potentials of both high purity iron and AISI 4340 steel are coincident. Heat treatment affected the pitting potential of the steel very little. Failure of AISI 4340 steel under both anodic and cathodic polarization was found. SCC under anodic polarization was closely related to the pitting potential. Conditions at the metal-solution interface for pit maintenance are given.

1. INTRODUCTION

THE scope of this work was to study the passivity breakdown of iron and to correlate the polarization curves of AISI 4340 high strength steel with its SCC susceptibility in neutral 0.5M NaCl solution.

Electrochemical polarization curves as a method of elucidating the mechanism of failure in high strength steels have been reported.¹⁻⁵ Bhatt and Phelps¹ studied the SCC behaviour of USS 12 Mo-V martensitic stainless steel in 3%NaCl neutral solution. It was found that anodic polarization reduced the time to failure. With low cathodic current densities, the time to failure was greatly extended, but at relatively high cathodic current densities the time to failure became progressively shorter. The authors postulated that with anodic polarization the cracking mechanism was corrosion along an active path through the steel, whereas the cracking mechanism with cathodic polarization was hydrogen embrittlement.

In this work potentiostatic techniques were used to differentiate both processes. The results showed that failure under both anodic and cathodic polarization in AISI 4340 high strength steel is due to the same mechanism of crack propagation, presumably hydrogen embrittlement. It was found also that the pitting potential of iron is related to the maintenance of localized acidity on the metal-solution interface.

2. EXPERIMENTAL

Polarization test specimens of $0.6 \times 0.2 \times 4$ cm were cut out from the original bar steel. After pickling in picric acid solution (1% picric acid in a mixture of 100 cm³ ethyl alcohol and 5 cm³ conc. hydrochloric acid) at 20°C for 10 min, the samples were homogenized at 1200°C for 2 h and then slowly cooled in the oven. After that the specimens were austenitized for 15 min at 830°C and quenched into mineral oil. Some of the specimens were tested with this heat treatment. The others were annealed at 150, 250, 350, 450, 550 and 650°C. The 99.997% iron wire was annealed 30 min at 950°C previously degreasing in carbon tetrachloride. Some of the polarization tests were made with the iron without any annealing. All the heat treatments were done in argon atmosphere.

A copper wire lead was soldered to one end of the samples; they were polished with fine alumina.

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FIGURE 11 — Uneven general corrosion for stressed AISI 304 in 1M aerated HCl solution at -0.050 V and 25 C, 30 hours exposure. Cross-section. 400X



FIGURE 12 — SCC for AISI 304 stainless steel in 1M aerated HCl solution at -0.150 V and 25 C, 206 hours exposure. Cross-section. 400X

chloride solutions. Oftedal¹⁷ reported that iron in HCl + NaCl solutions at $0 < \text{pH} < 1.2$ shows an active behavior, with no film formation, while at $\text{pH} > 1.5$ evidence was found of a film formation process. According to Pourbaix's diagrams,¹⁸ no iron oxide should be stable below $\text{pH} = 4$, and in Oftedal experiments the oxide film should be in a metastable equilibrium. By extrapolation, since the chromium oxide is stable at pH values much lower than the iron oxide, a chromium rich oxide film should be expected to be metastable during anodic dissolution in the 1M HCl solution. One possible reason for the formation of an oxide film could be the localized change in pH produced by the cathodic reaction of hydrogen evolution. Another possibility could be the formation of a chloride rich corrosion product film, but clearly more information is necessary on this subject.

Conclusions

From the anodic behavior of AISI 304 in deaerated 1M HCl solution, it is concluded that this steel does not behave as an active metal. A potential and time dependent corrosion slow down process is observed. From the net anodic current-time curves, it is concluded that a film formation process is taking place. Straining experiments confirm this supposition and form the basis for predicting the occurrence of SCC.

Cracks initiate on the slip steps and propagate as the result of exposure of the bare metal to the solution. The anodic dissolution that takes place on the bare metal accounts for the crack propagation rate. When the potential is increased over the corrosion potential, the difference between the dissolution rate of the bare metal and that of the filmed metal is reduced. As a result, the corrosion along the slip lines does not differentiate from the general dissolution of the static metal, and no SCC is found. Decreasing the potential below the corrosion potential, the difference between the bare metal and the filmed metal dissolution rate increases, but the rate of crack propagation diminishes, and eventually SCC stops. The range of potentials for SCC estimated from straining experiments is in coincidence with that found experimentally by Bianchi *et al.*²

The kinetics of bare metal dissolution agrees with the results published for chloride inhibited iron dissolution. The subsequent slow down process is attributed to film formation, probably a high chromium oxide, hydroxide, or hydroxichloride film.

Acknowledgment

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TABLE 1. COMPOSITION OF AISI 4340 STEEL (wt. %)

C	Mn	Si	Ni	Cr	Mo
0.40	0.84	0.22	1.78	0.92	0.35

The unpolished face and edges of the samples were covered with cured epoxy resin. The 99.997% iron wire samples were pickled for 2 min in 30% v/v HNO₃ at room temperature immediately before the electrochemical test.

All the polarization curves were made in 0.5M NaCl solution at $25 \pm 0.5^\circ\text{C}$ in a Pyrex cell, with a platinum counter electrode. The electrode potentials were measured through a Luggin capillary with a saturated calomel reference electrode. All the potentials are reported in the normal hydrogen electrode scale.

Smooth specimens used for stress corrosion cracking tests had the same heat treatment described before. The annealing temperatures in this case were 150, 350 and 550°C. The chemical composition, heat treatment and mechanical properties of AISI 4340 high strength steel tested in this work are shown in Tables 1 and 2. The stress corrosion tests were made in aerated 0.5M NaCl solution at room temperature in a constant load machine with a cell made in acrylic and silicone rubber to avoid leaks at the cell joints. These tests were made at a static load equivalent to 50–60% of the steel yield point. The time to failure was recorded for specimens under potentiostatic control. The maximum waiting time to check failure or no failure was 100 h. Solutions were prepared with analytical grade reagents and distilled water, and were de-aerated with purified nitrogen.

The electrode potential was controlled by a Tacussel PRT 20–2X potentiostat. Quasi-stationary potentiostatic curves were obtained by changing the potential in steps of 20 mV and waiting for the current to reach a stationary value (from 15 to 140 min). Each curve was repeated 2 or 3 times with good reproducibility. Current-time curves at constant potential were obtained by switching the potential from the open circuit potential to the chosen value, and recording the current for up to 5 h. A new specimen was used for each potential. Before measurement, the specimens were cathodically polarized for 20 min at a constant current density (50 $\mu\text{A}/\text{cm}^2$) in order to reduce the initial surface iron oxide. The sample was allowed to attain a stationary open circuit potential before starting the polarization curve.

TABLE 2. MECHANICAL PROPERTIES OF AISI 4340 STEEL USED

Annealing temperature °C	0.2% yield point Kg/cm ²	hardness RwC
150	162	55
350	141	47
550	109	40

3. RESULTS

3.1. Electrochemical behaviour of Fe 99.997%

Figure 1 shows a polarization curve for annealed iron 99.997% in de-aerated 0.5M NaCl solution. In this curve we observed three zones: the first one ranging between -0.45 and -0.37 V is an active zone. At more positive potentials there was a decrease in the current due to a narrow passivity zone, while at potentials more noble than -0.32 V there was a big increase in the current associated to a pitting phenomenon. Nagayama and Cohen⁶ also reported the existence of active and passive zones for pure iron, in sodium borate plus boric acid neutral solution.

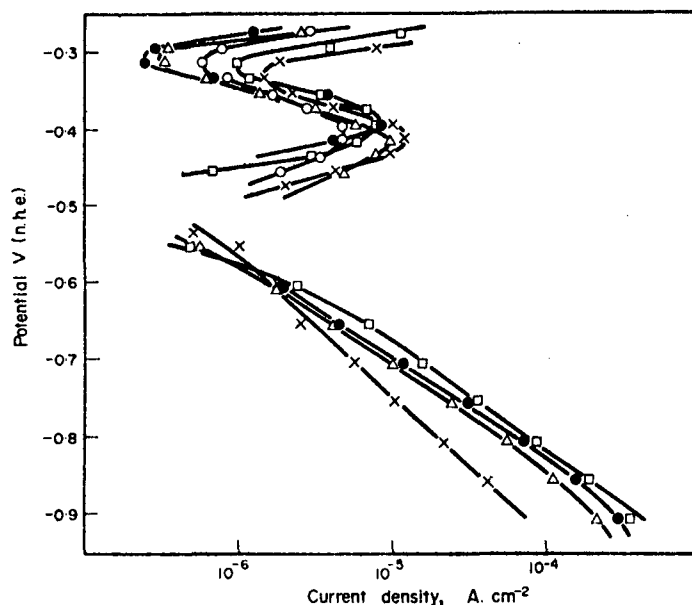


FIG. 1. Anodic and cathodic polarization curves in de-aerated 0.5M NaCl solution at 25°C: $\times$ high purity iron; $\square$ AISI 4340 steel annealed at 150°C; $\circ$ AISI 4340 steel annealed at 250°C; Δ AISI 4340 steel annealed at 450°C; $\bullet$ AISI 4340 steel annealed at 650°C.

To confirm the existence of the above described zones, current-time curves at constant potential were measured for high purity iron in de-aerated 0.5M NaCl solution at 25°C. It was observed that for electrode potentials more negative than -0.35 V the current density decreased continuously indicating the growth of a passive film (Fig. 2). No electrochemical attack was detected on the metal surface. At electrode potentials equal to or higher than -0.32 V the current increased continuously and round-shaped polished bottom pits developed on the metal surface (Fig. 3). From these results it was concluded that the pitting potential of high purity iron in de-aerated 0.5M NaCl neutral solutions at 25°C was -0.35 V and that there was a passivation process occurring in the supposed active zone.

The pitting potential of iron in 0.5M NaCl solutions at pH 3 and 11 was galvanostatically determined at 25°C. Sodium hydroxide or hydrochloric acid was used to adjust the pH of the solutions. Pitting potential values of -0.34 V at pH 3 and -0.32 V at pH 11 were measured. The corrosion potential of iron at pH 3 was coincident with its pitting potential value in neutral NaCl solution. Similar results were found in 0.05M and 2M NaCl solutions at pH 3. At higher pH values (7 and 11) the corrosion potential was lower than at pH 3.

3.2. Electrochemical behaviour of AISI 4340 high strength steel

Figure 1 also shows typical polarization curves of AISI 4340 steel in de-aerated 0.5M NaCl solution at 25°C. It was found that the anodic behaviour of Fe 99.997% and AISI 4340 steel in de-aerated 0.5M NaCl solution were similar. There was no



25 μ m



FIG. 3. Pits developed on high purity iron in de-aerated 0.5M NaCl solution at 25°C.

FIG. 7. Nucleation of fissures in AISI 4340 steel annealed at 350°C in aerated 0.5M NaCl solution at 25°C.

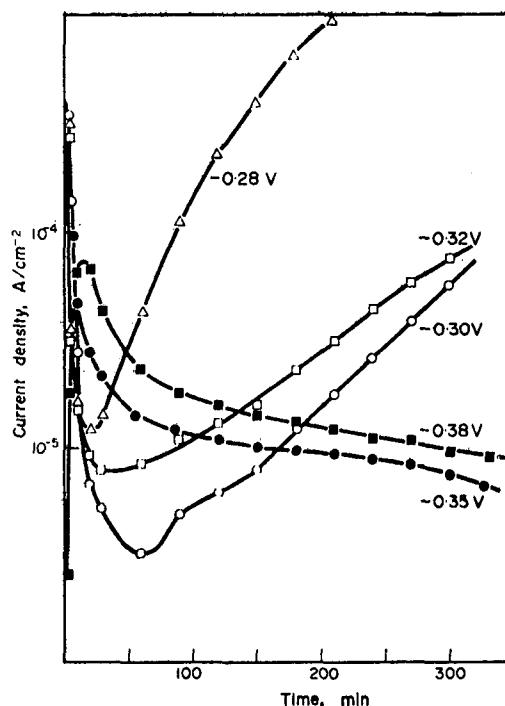


FIG. 2. Constant potential current density-time curves for high purity iron in de-aerated 0.5M NaCl at 25°C.

difference due to changes in the microstructure or material composition. Different microstructures did not affect the hydrogen cathodic reaction either.

Current-time curves for AISI 4340 steel annealed at 250 and 650°C in de-aerated 0.5M NaCl solution at 25°C were measured. Pitting potential for 250°C annealing is -0.32 V while for 650°C annealing is -0.35 V. The pits nucleated preferentially on MnS inclusions or near to them. Optical observation of the samples tested in the passive range showed interference colours which indicated the presence of a transparent surface film.

Stress corrosion tests were made with AISI 4340 steel in order to correlate the time to failure with electrode potential. Results for three different annealing temperatures are shown in Figs. 4-6. In these figures the polarization curves of the AISI 4340 steel were included in order to correlate both results.

Figure 4 shows the time to failure vs electrode potential behaviour for 150°C annealing temperature. Both at low potentials (cathodic zone) and at potentials higher than pitting potential the time to failure is very short. At intermediate potentials, corresponding to the pseudo-active and passive zone, the time to failure is two orders of magnitude longer. The same type of behaviour was observed for the 350°C annealing temperature (Fig. 5). In this case, no failures were observed at intermediate potentials and there was a shift of the cathodic failure curve to more negative potentials. Both anodic and cathodic failures were intergranular along the austenitic boundaries. The fissures were nucleated in pits (Fig. 7).

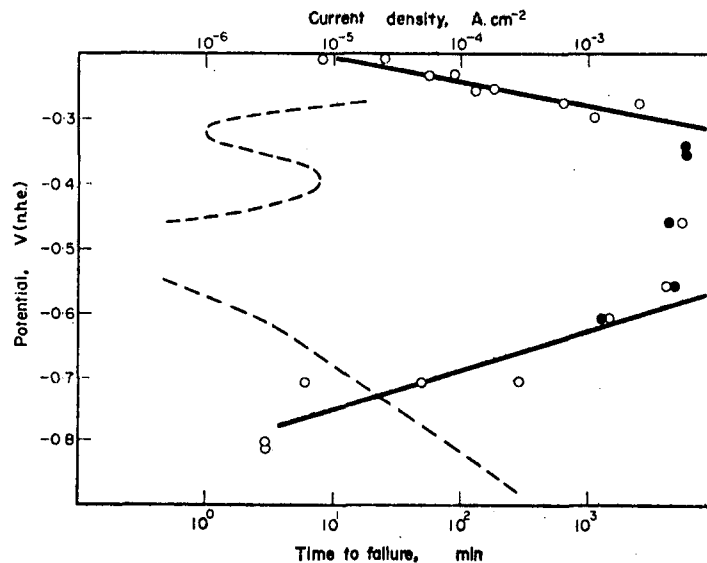


FIG. 4. Time to failure data vs potential for AISI 4340 steel annealed at 150°C in aerated 0.5M NaCl solution at 25°C. ○ Failure; ● No failure; --- Anodic and cathodic polarization curves for the same system.

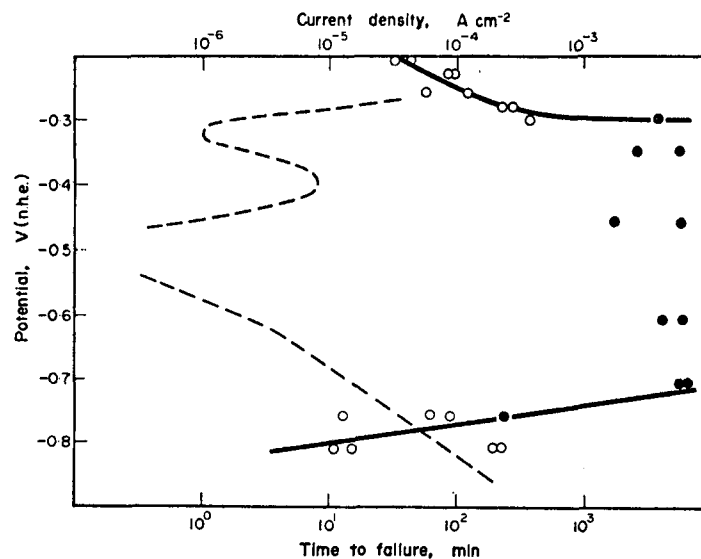


FIG. 5. Time to failure data vs potential for AISI 4340 steel annealed at 350°C in aerated 0.5M NaCl solution.

Figure 6 shows a different behaviour for 550°C annealing temperature. There is no cathodic failure curve, while the anodic failure curve is shifted to more positive potentials and higher times to failure. No SCC was observed with this annealing temperature. The failure at potentials higher than -0.3 V was due to a reduction in

the sample section (mechanical failure) produced by a general corrosion attack. As in the polarization curve experiments, the sample surface remained clean at passive, pseudo-active and cathodic potentials, while a black oxide film developed at the pitting potential.

3.3 Oxide film composition

Some of the pitting corrosion theories are based on adsorption and solid state migration of aggressive ions through the passive film.⁷⁻¹⁰ McBec and Kruger,¹⁰ for example, determined the ellipsometric properties of iron at passive and pitting potentials and found a change in the film properties at the pitting potential. They suggested a mechanism of chloride ions penetration through the oxide film.

Electron diffraction was used in the present work in order to investigate the composition of the oxide film in the passive and pitting ranges. High purity iron samples previously annealed and pickled in 30% HNO₃ were anodically polarized in 0.5M NaCl solution at pH 7. Before applying the anodic potential, the oxide film on the metal surface was cathodically reduced at -0.86 V. After that, one of the samples was polarized at -0.30 V (pitting zone) for 3 h, and another sample was polarized at -0.38 V (passive zone) for 4 days. No difference in the oxide film composition was found (Table 3). In both cases the oxide film seemed to be lepidocrocite ($\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$).

4. DISCUSSION

4.1 Pitting potential of iron

The presence of lepidocrocite ($\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) oxide films on iron has been reported by Mellors *et al.*,¹¹ for iron in NaNO₂ plus NaCl solutions. In the present work it was found to occur also in de-aerated NaCl solutions. The presence of such a film,

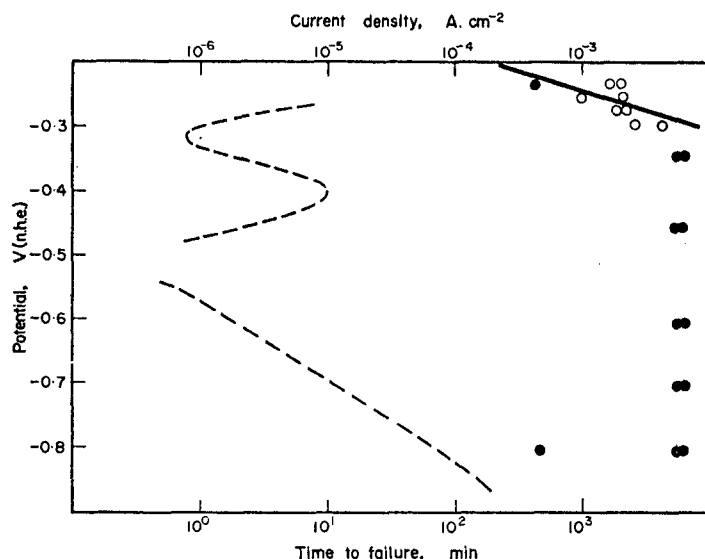


FIG. 6. Time to failure data vs potential for AISI 4340 steel annealed at 550°C in aerated 0.5M NaCl solution at 25°C.

TABLE 3. ELECTRON DIFFRACTION DATA FOR IRON OXIDE DEVELOPED AT PASSIVE AND PITTING POTENTIALS

IRON OXIDE							
PASSIVE POTENTIAL		PITTING POTENTIAL		$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (*)		Fe_2O_3 (*)	
R (Å)	d (Å)	R (Å)	d (Å)	d (Å)	I/I ₁ -	d (Å)	I/I ₁ -
-	-	-	-	0,28	100	-	-
$1,38 \cdot 10^8$	3,26	$1,30 \cdot 10^8$	3,26	3,26	90	2,05	34
-	-	-	-	2,79	10R	2,78	19
$1,78 \cdot 10^8$	2,49	$1,78 \cdot 10^8$	2,49	2,47	80	2,52	100
$2,00 \cdot 10^8$	2,21	$2,00 \cdot 10^8$	2,21	2,36	20	-	-
-	-	-	-	2,09	20	2,08	24
-	-	-	-	1,937	70	-	-
-	-	$2,40 \cdot 10^8$	1,85	1,848	20	-	-
-	-	-	-	1,732	40	1,70	12
-	-	$2,80 \cdot 10^8$	1,58	1,566	20	1,61	33
-	-	-	-	1,535	20	-	-
-	-	-	-	1,524	40	-	-
-	-	-	-	1,496	10R	1,48	53
-	-	-	-	1,449	10	-	-
$3,08 \cdot 10^8$	1,44	$3,09 \cdot 10^8$	1,43	1,433	20	1,27	11

*Inorganic Index to the Powder Diffraction File, 1969, ASTM publication PD 1 S-19 i.

even below the pitting potential, would indicate that the formation of this film is not related with the passivity breakdown process. It has been reported that iron oxychloride and lepidocrocite are isomorphic.¹² The diffraction patterns of both products are quite different,¹³ however, and no evidence was found of the presence of iron oxychloride in the corrosion products. Nevertheless, a primary step of iron oxychloride nucleation followed by a lepidocrocite passive film growth cannot be ruled out. This would explain why lepidocrocite is formed instead of the more frequent magnetite film found for iron in neutral solutions.⁸

The fact that the pitting potential of iron is equal to the corrosion potential of the metal in a more acid solution is in agreement with a recently published mechanism¹⁴ according to which pit initiation is related to the appearance of local acidity in the metal-solution interface. It has been shown¹⁴ that, contrary to the evidence of Vetter and Strehblow,¹⁵ the critical acidification necessary for pit initiation can be reached even in the very early stages of pit growth. A fissure in the oxide film might give a

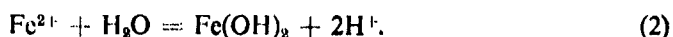
diffusion path long enough to get the necessary acidification at the metal-solution interface. A solution of pH 7, as used in the present work, should be in a borderline between passivation and active dissolution.

Several authors have shown that the solution inside a pit is more acidic than the solution outside.¹⁶⁻¹⁸ For iron it was reported^{16,18} a pH value of 3-4 inside the pit, crack or crevice. The mechanism of pitting proposed by Galvele *et al.*^{14,19,20} assumes that this acidification is a *necessary* condition for pit growth, and that the pitting potential is the minimum potential at which such acidification could be maintained.

In the case of iron, the following reactions will take place inside the pits:



followed by:

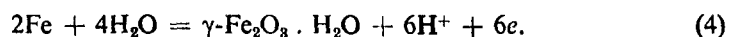


Another reaction taking place inside the pits is:



The last reaction is confirmed by the observation of hydrogen evolution from active pits.

Outside the pits, and at an appropriate potential, the following reaction should be expected:



Since the pH inside the pit is lower than the pH of the bulk solution, a further process should be considered, and that is the diffusion of protons from the pit to the bulk solution:



At the stationary state, the rate of proton production, reaction (2) will be equal to the rate of proton consumption, reactions (3) plus (5). This stationary state should be possible only at potentials higher than the corrosion potential of iron in an acidic pit-like solution. At the corrosion potential of iron in the acidic pit-like solution the rate of reaction (1) will be equal to the rate of reaction (3), and no net production of protons will occur. Meanwhile, reaction (5) will dissipate any localized acidity present in the pit. At a lower potential, reaction (3) will be faster than reaction (1) and a net consumption of protons will take place. A process of metal dissolution with a locally acidified solution, such as occurs in pitting, is possible only when the electrode potential of the metal is higher than the corrosion potential of the same metal in a pit-like solution. This was confirmed in the present work, where it was found that the pitting potential of iron in an unbuffered NaCl solution is equal to the corrosion potential of the same metal in a pH 3 0.5M NaCl solution.

4.2 SCC of AISI 4340

Figures 4 and 5 show two regions of SCC susceptibility, as reported by Bhatt and Phelps.^{1,2} The lower potential region appears at potentials where hydrogen evolution is observed. As for the high potential region, SCC starts at the pitting potential. Upon increasing the potential, an oxide film is formed on the metal, and this acts as an inert barrier. It is only when this oxide film breaks down that SCC reappears. At first sight, the hydrogen could not be the cause of SCC at such high potentials in a pH 7 solution. The equilibrium potential of hydrogen in neutral solutions is -0.413 V, while the pitting potential of iron is -0.350 V. Nevertheless, Shively *et al.*²¹ found hydrogen permeation under anodic polarization. Smith *et al.*¹⁸ measured the electrochemical conditions at the tip of an advancing stress corrosion crack in AISI 4340, and found that, due to the reduction in pH, hydrogen evolution was possible. Wilde,²² studying other high strength martensitic steels, concluded that hydrogen embrittlement was the mechanism acting both at low and at high potentials.

Shively *et al.* used in their experiments pre-cracked specimens, but the same conclusions apply to the smooth specimens used in the present work. Since the pH inside the pit is between 3 and 4, hydrogen evolution can take place at potentials much higher than in a neutral solution. The equilibrium potential for hydrogen electrode at pH 4 is -0.236 V, and at pH 3 is -0.177 V, so hydrogen evolution is thermodynamically possible at the pitting potential (-0.350 V). The correlation between the pitting potential and SCC susceptibility gives a way by which SCC could be inhibited. It is known that certain additives to the corrosive environment act as inhibitors to the pitting process. Uhlig *et al.*^{23,24} studied inhibitors for pitting corrosion of aluminium and stainless steel. In both cases the inhibitors increased the pitting potential. Being salts of weak acids, the inhibitors interfere with the appearance of a critical acidification on the metal-solution interface.¹⁴ For iron, buffer solutions for a pH about 8 or higher should inhibit the high potential SCC of AISI 4340. A borate solution of a concentration higher than the chloride concentration of the solution (0.5M) should give good results.

5. CONCLUSIONS

1. It was found that high purity iron and AISI 4340 show a passivity breakdown potential in de-aerated NaCl solutions.
2. The pitting potential of iron is the minimum potential at which localized acidity could be maintained at the metal-solution interface, and is given by the corrosion potential of iron in the acidic pit-like solution.
3. The pitting potential of AISI 4340 is equal to the pitting potential of high purity iron. The heat treatment of the steel does not affect the pitting potential.
4. Electrochemical failure of AISI 4340 in NaCl solutions occurs within two ranges of potential, the higher range being determined by the pitting potential of the steel.
5. The high potential SCC susceptibility of AISI 4340 should be inhibited if pitting inhibitors were present in the media.

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ANODIC BEHAVIOUR OF MILD STEEL DURING YIELDING IN NITRATE SOLUTIONS*

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Abstract—The anodic behaviour of mild steel during yielding, at constant potential in various hot nitrate solutions, has been studied. The influence of solution composition, pH, strain rate and electrode potential, has been examined. Yielding of oxide-covered steel is accompanied by a large increase in anodic current density. This increase is almost independent of strain rate and is a linear function of percentage strain; the anodic c.d. on the yielding metal bared by rupture of the oxide layer can be as high as $2\text{A}/\text{cm}^2$. At low strain rates stress corrosion "cracking" can be observed. The rate of "crack" propagation was estimated microscopically as up to $\sim 0.25\text{cm}/\text{h}$, which is equivalent to an anodic dissolution of the advancing edge of the "crack" of up to $\sim 2\text{A}/\text{cm}^2$. The stress corrosion "crack" is therefore considered to be a fissure of which the yielding advancing edge is bared metal that can dissolve anodically at up to $2\text{A}/\text{cm}^2$ while the static sides become oxide-covered so that the anode c.d. there is many times smaller.

Résumé—Une étude a été faite du comportement anodique de l'acier doux pendant le fluage, à un potentiel constant dans différentes solutions nitrées chaudes. On a examiné l'influence de la composition de la solution, du pH, de la vitesse de déformation et du potentiel des électrodes. Le fluage de l'acier à revêtement d'oxyde est accompagné d'une augmentation importante de la densité du courant anodique. Cette augmentation est presque indépendante de la vitesse de déformation et est une fonction linéaire du pourcentage de déformation; la densité de courant anodique au lieu de rupture sur le métal déformé dénudé de la couche d'oxyde peut s'élever jusqu'à $2\text{A}/\text{cm}^2$. A des vitesses de déformation faibles on peut observer un effet de "déchirure" par suite de l'effort corrosif. La vitesse de propagation de la "déchirure" a été évaluée au microscope comme allant jusqu'à $\sim 0,25\text{cm}/\text{h}$, qui équivaut à une dissolution anodique du bord en progression de la "déchirure" allant jusqu'à $\sim 2\text{A}/\text{cm}^2$. La "déchirure" par suite de l'effort corrosif est donc considéré comme étant une fissure dont le bord en progression se déformant est du métal dénudé qui peut se dissoudre anodiquement jusqu'à $\sim 2\text{A}/\text{cm}^2$ tandis que les bords statiques se revêtent d'oxyde de sorte que la densité du courant anodique à cet endroit-là est de nombreuses fois plus faible.

Zusammenfassung—Das Anodenverhalten von Flusseisen während Strecken bei konstanter Spannung in verschiedenen heissen Lösungsnitraten ist untersucht worden. Der Einfluss der Lösungszusammensetzung, pH, Dehnungsgeschwindigkeit und der Elektrodenpotential wurde untersucht. Das Strecken von Oxyd-überzogenem Stahl erfolgt mit gleichzeitiger, starker Vergrößerung der Anodenstromdichte. Diese Vergrößerung ist beinahe unabhängig von der Dehnungsgeschwindigkeit und ist eine lineare Funktion der prozentualen Dehnung. Die Anodenstromdichte auf dem dehrenden blanken Metallriss der Oxydschicht kann bis zu $2\text{A}/\text{cm}^2$ gross sein. Bei niedrigen Dehnungsgeschwindigkeiten kann Spannungskorrosions "Rissbildung" beobachtet werden. Die Geschwindigkeit der "Riss" Fortpflanzung wurde mikroskopisch auf bis zu $0,25\text{cm}/\text{Std.}$ geschätzt, was einer anodischen Auflösung des fortschreitenden Randes vom "Riss" bis auf etwa $2\text{A}/\text{cm}^2$ gleichkommt. Der Spannungskorrosions-"Riss" wird daher als ein Sprung angesehen, dessen fortschreitende Streckkante blankes Metall ist, welches sich anodisch unter bis zu $2\text{A}/\text{cm}^2$ auflösen kann, während die statischen Seiten sich mit Oxyd bedecken, sodass dort die Anodenstromdichte vielfach kleiner ist.

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INTRODUCTION

THE ANODIC behaviour of 18Cr–8Ni type stainless steels while yielding in 42wt-% aqueous magnesium chloride at 154°C was studied by Hoar and West,^{1,2} who discovered marked yield-assisted anodic dissolution, which was confirmed by Hoar and Scully.³ The experiments were performed at ~ -0.15 to $-0.05V(\text{nhe})$, which is the range of potential in which stress corrosion cracking of the *stressed* 18–8 steel occurs under the same chemical conditions.^{4,5} Since the cracks propagate at $\sim 1\text{ mm/h}$ and since yielding material was shown to dissolve at $\sim 0.6\text{ A/cm}^2$, equivalent to 0.75 mm/h penetration, the earlier hypothesis of Hoar and Hines^{4,5} that cracks propagate by anodic dissolution of their yielding advancing edges, their static sides being scarcely affected, received strong support.

The stress corrosion cracking of mild steel in hot nitrate solutions has been examined in several publications.^{6–15} Logan⁸ proposed that crack propagation is caused by mechanical fracture of the oxide film at the yielding advancing edge, so that rapid anodic dissolution can occur. This was criticized by Parkins^{7,16} because it did not take into account the specificity of the media that give stress corrosion cracking. Furthermore, a mechanism of crack propagation by involving anodic dissolution alone would require a high c.d. at the advancing edge. Logan^{8,17} pointed out that there should be a high driving force for anodic dissolution when the oxide film is broken, but did not show that the required high anodic c.d. could be sustained. No data have been published for the anodic behaviour of mild steel during yielding in nitrate solutions.

We now report measurements of high anodic c.d.s. on mild steel exposed to hot nitrate solutions, simultaneously undergoing traction at high strain rates and anodic dissolution at constant potential. We compare these with microscopic measurements of crack propagation of the same material under the same conditions but at low strain rates, and show that the c.d. available at the *rapidly* yielding “*crack*” *advancing edge* is sufficient to account for the rate of “*crack*” propagation.

A difficulty arises in the measurement of anodic c.d. on mild steel in hot nitrate solutions. In experiments in chloride solution, it is simple to study anodic reactions at or just below the “natural” corrosion potential of isolated metal in such solutions exposed to the atmosphere, by removing all dissolved oxygen, the major cathodic reactant; thus Hoar and West^{1,2} and Hoar and Scully³ were able to measure the anodic c.d. at and below the “natural” corrosion potential of 18Cr–8Ni steel in hot magnesium chloride solution by rigorous de-aeration and the use of a separate cathode. But in hot nitrate solutions, the nitrate ion itself is a cathodic reactant; consequently at the corrosion potential of isolated metal in de-aerated solution, there is a local anodic c.d. equal to the cathodic c.d. of nitrate reduction, and below the corrosion potential the measurable c.d. is *cathodic*. Consequently it was necessary in the present work to examine the anodic reaction at potentials sufficiently positive to the corrosion potential so that the cathodic reaction was small compared to the anodic. Fortunately, although the present results refer to potentials more positive than those found in “natural” nitrate cracking, they include actual measurements of the greatly accelerated crack propagation found under these anodic conditions.

EXPERIMENTAL TECHNIQUE

Materials

Experiments were made with 1mm diameter mild steel wire kindly supplied by the British Welding Research Association.* The chemical composition was C, 0.10%; Mn, 0.53%; Si, 1.16%; S, 0.013%; P, 0.013%. The wire, cut into pieces about 40cm long, was degreased, vacuum annealed for 8h at 1100°C, and slowly cooled in the furnace. The final material had a mean grain size of about 0.035mm diameter.

Just before the experiments, the area of the wire to be exposed to the electrolyte solution was cleaned with 4/0 emery paper, etched with dilute nitric acid, washed with distilled water and with industrial methylated spirit, and dried with hot air.

All the solutions were prepared with "AnalaR" grade chemicals, with the exception of calcium nitrate and calcium hydroxide, which were G.P.R. grade. The concentration

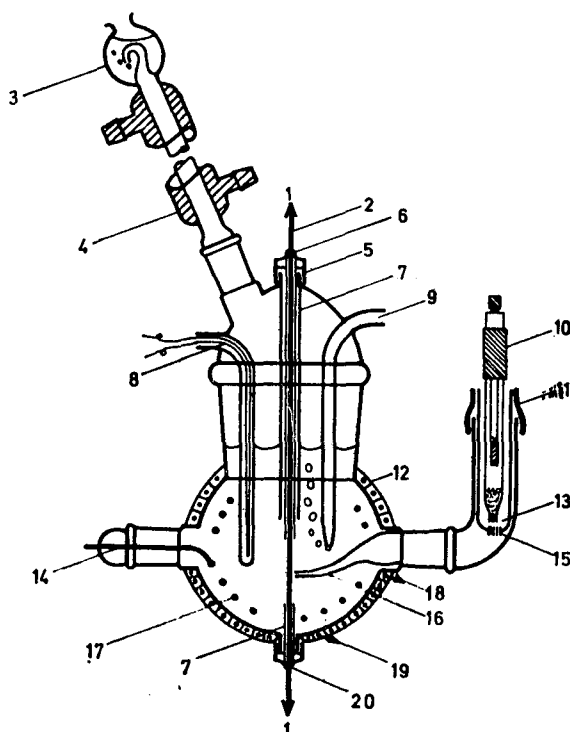


FIG. 1. Cell used for constant experiments at constant strain rate.

- | | |
|--|--------------------------------|
| 1, to Tensometer chuck; | 11, p.v.c. tape seal; |
| 2, specimen; | 12, asbestos insulation; |
| 3, bubbler for egress of nitrogen; | 13, saturated KCl salt bridge; |
| 4, water condenser; | 14, cathode connection; |
| 5, polyethylene seal; | 15, porous plug; |
| 6, Picien seal; | 16, Luggin capillary; |
| 7, polyethylene sheath; | 17, platinum cathode; |
| 8, thermocouple leads; | 18, 19, heater supply; |
| 9, nitrogen; | 20, Araldite seal. |
| 10, saturated calomel reference electrode; | |

*Now the Welding Institute.

of the nitrate solutions used in all experiments was 4N. The solutions were de-aerated with "White Spot" quality nitrogen further purified by bubbling the gas through a solution of reduced chromium sulphate, by the method of Gilroy and Mayne.¹⁸

Cell

The cell was a modification of that described by Hoar and West;² details are shown in Fig. 1. The top and bottom ends were of polyethylene, and were secured to the cell by a wire fastener. The bottom end was fixed to the specimen with Araldite resin and this end of the specimen was fixed to the moving chuck of a Hounsfield Tensometer. The wire at the top was sealed with Picien wax; this sealing permitted the de-aeration of the cell and did not interfere with the movement of the wire during traction. Cemented to both plastic ends and extending into the cell were two polyethylene capillaries that covered the wire, leaving a definite area of specimen exposed to the solution.

The potential of the specimen was measured via a Haber-Luggin capillary vs. a saturated calomel half-cell at room temperature. The counter-electrode was a helix of platinum wire.

Temperature in the cell was measured with a chromel-alumel thermocouple and was regulated by changing the power supplied to the heating coil, or varying the speed of the bubbling nitrogen. Temperature was controlled to $102^{\circ} \pm 0.5^{\circ}\text{C}$.

Apparatus

Potential measurements were made with a Dynacap electrometer millivoltmeter. Current was measured and recorded with a Kipp & Zonen micrograph-BD 2 recorder. The range of the recorder was extended with a range-unit, which allowed recordings from $0.1\mu\text{A}$ to 500mA (full-scale) in eleven ranges. The error in any of the ranges was 1% of the measured current. As well as the recording pen, a second pen was used to mark on the chart the time of initiation of yielding of the specimens, and of their fracture. Potential was controlled with a Tacussel ASA 4BT potentiostat. Traction was applied to the wires with a modified motor-driven Hounsfield Tensometer.

Procedure

For traction experiments, the wire was fitted in the cell, the cell fixed to the Tensometer, and a stream of purified nitrogen passed into the cell, which was meanwhile slowly heated. After about $\frac{1}{2}\text{h}$, the condenser was partly removed and the boiling nitrate solution was poured into the cell. The condenser was then replaced, the small bubbler was filled with the solution, the salt bridge filled with saturated KCl, and the reference electrode connected to the circuit. After waiting for 5min, to allow the solution to reach the working temperature, the potentiostat was connected and the desired potential was applied to the specimen. After a further 40min, the motor of the Tensometer was switched on, and the wire was pulled. This lapse of 40min was kept constant in all the traction experiments; it allowed a reasonable time for de-aeration of the solution, and for the anodic current on the specimen to fall to an almost stationary value, with the formation of a magnetite film on the surface.

At the end of a run, the cell was dismantled, the specimen was washed with water

and alcohol, and dried with hot air. The portion of specimen that had been in contact with the solution was cut and stored in a desiccator, or mounted for observation.

The reported potentials have been converted to the normal hydrogen scale (nhe) by adding 0.242V to the value vs. the saturated calomel electrode, which was at room temperature; no attempt was made to eliminate or measure liquid-junction or thermal emfs.

The reported strain rates are calculated from the total extension rate and the length of heated wire within the cell, which suffers very nearly the whole of the measured extension: the approximations involved will be considered elsewhere.¹⁹

RESULTS AND INTERPRETATION

Corrosion potential of static mild steel

Preliminary experiments were made to examine the influence of time of exposure and of oxygen content on the "corrosion" potential of isolated and static mild steel in several hot nitrate solutions. Figure 2 shows a typical potential-time curve, and Table 1 collects the results of "rest" potentials after 2h, when they had become approximately constant. During these tests, the specimens became covered with films of oxide, probably magnetite, either thick enough to appear black, or thin enough to show interference colours, except at high pH. If the film is porous to solution, the

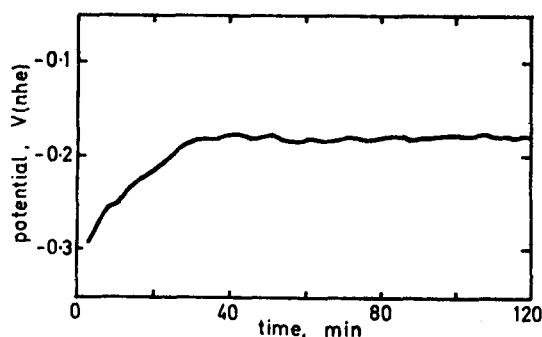


FIG. 2. Typical potential-time curve.
Mild steel in 4N NaNO_3 , pH 3.4 (at 25°C), 102°C.

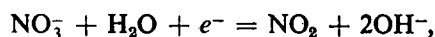
TABLE 1. CORROSION POTENTIAL OF STATIC MILD STEEL AFTER 2h EXPOSURE IN HOT NITRATE SOLUTIONS

Solution	Initial pH	Potential (under N_2) [V(nhe)]	Potential (under O_2) [V(nhe)]	Behaviour under stress
4N NaNO_3 + HNO_3	3.4	- 0.18	- 0.10	s.c.c.
4N NaNO_3	5.2	- 0.25		s.c.c.
4N NaNO_3 + NaOH	10.3	- 0.27		Does not crack
4N $\text{Ca}(\text{NO}_3)_2$	3.7	- 0.12		s.c.c.
4N $\text{Ca}(\text{NO}_3)_2$ + $\text{Ca}(\text{OH})_2$	11.3	- 0.25	- 0.21	Does not crack
4N NH_4NO_3 + NH_4OH	7.4	- 0.12		s.c.c.

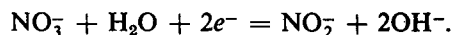
corrosion process can be represented schematically by Fig. 3(a), in which the over-all anodic reaction is



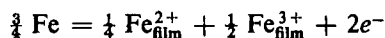
At the cathode, probable reactions are



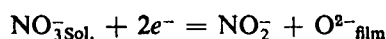
or over-all,



Consequently, the electrolyte solution will tend to become more acid at any points that are especially anodic, and more alkaline at any points that are especially cathodic, although since the film formed is, *when static*, fairly uniform and not very porous, the anode and cathode reactions are very much intermingled and the over-all change in solution pH may not be marked, the main entities produced by corrosion being at all times magnetite and nitrite ion. Indeed, if a *perfect* magnetite film is formed, always in close contact with the metal, the process is as represented schematically in Fig. 3(b), with the anodic reaction



at the metal/film interface, and the cathodic reaction



at the film/solution interface. It is likely that this solid-state process takes place along with the solution process noted in Fig. 3(a).

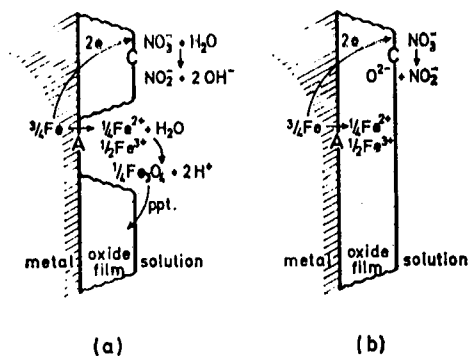


FIG. 3. Formation of magnetite by reaction of iron with nitrate solutions: (a) by precipitation process, (b) by solid-state process.

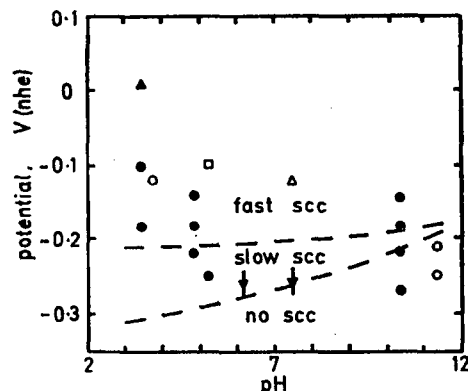


FIG. 4. Behaviour of stressed mild steel in hot nitrate solutions of various initial pH and different potentials.

- , NaNO_3
- , $\text{Ca}(\text{NO}_3)_2$
- △, NH_4NO_3
- ▼, NH_4NO_3 (Parkins)¹⁰
- ▲, LiNO_3 (Parkins)¹⁰
- , NaNO_3 (Parkins)¹⁰

Figure 4 is a plot of the results of Table 1 as rest potential vs. initial pH at room temperature. Some results of Parkins and Usher¹⁰ are included. We note that the rest potential becomes more positive with decrease of initial pH and in the series of nitrates $\text{Na}^+ - \text{Ca}^{2+} - \text{NH}_4^+$. The rate of crack propagation in nitrate cracking of mild steel is known to increase with decrease of initial pH of the solution and with change of cation in the same series. More positive rest potential indicates a higher c.d. for the anodic process if this remains qualitatively unchanged, or a stimulation of the cathodic process. The results are therefore in harmony with the hypothesis that crack propagation proceeds by anodic dissolution. Stimulation of the cathodic process of NO_3^- reduction by decrease of pH is well known, and the influence of Ca^{2+} and NH_4^+ is probably to limit the rise of pH at the cathode zones.

Interrupted traction experiments

A preliminary series of interrupted traction experiments was made mainly in 4N calcium nitrate solutions of pH 3.7, at a potential of $-0.10\text{V}(\text{nhe})$. Several strain rates were used and the traction was interrupted once or twice before the wire fractured. In each case the variations of the current were recorded. Some experiments were made maintaining the load after interrupting the traction, and in others the load was removed during the interruption. No difference was observed between the results of the two procedures.

Figure 5 shows a typical result. When the potentiostat was switched on, there was a high current flow, which decreased with time; after some 30min the current reached a quasi-stationary, small value. The process is typically one of potentiostatic growth of an oxide layer; at the end of the experiments a black layer was visible on the surface of the specimens. When the passivation condition reached by the specimen was disturbed by traction of the metal, the current increased rapidly. When the traction was stopped, the current decreased again, with the film re-forming just as before

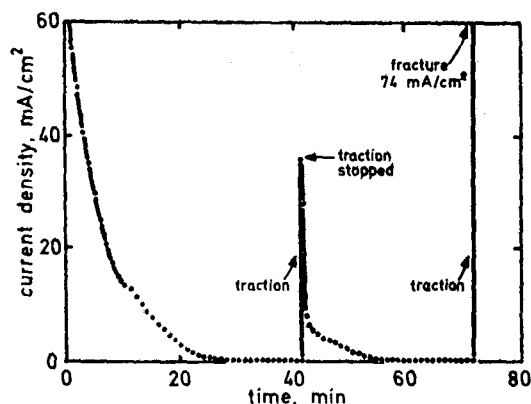


FIG. 5. Potentiostatic formation of magnetite film on mild steel anode in hot calcium nitrate solution, and influence of traction.
 4N $\text{Ca}(\text{NO}_3)_2$, pH 3.7 (at 25°C), 102°C, $e_H = 0.10\text{V}$.
 Strain rate 28%/min.

yielding. These results indicate that at the beginning there is oxide-film formation, and that, during traction, the current increases because of the fracture of the film.

The current increase during traction cannot be attributed to the mechanical opening of cracks in the metal, as suggested by Long and Uhlig¹⁴ for a similar case; metallographic examination of wires pulled at high strain rates and showing high anodic c.d.s. revealed no detectable cracks—the high c.d.s. are found *before* the cracks have had time to grow to visible depths. "Cracks" appeared only when slow strain rates were applied, so that relatively long periods were available for their propagation. They are not the cause of the current increase, but are propagated by the current, concentrated at their rapidly yielding advancing edges.

Constant strain-rate experiments

Figure 6 shows typical current-time curves for mild steel strained in 4N calcium nitrate solutions pH 3.7, at 102°C. The potential was kept constant at $-0.10\text{V}(\text{nhe})$ (about 20mV higher than the rest potential of mild steel in the same solution, Table 1), and four different strain rates were applied. When traction was started the current increased with time, the rate of increase remaining almost constant until the wire broke. The rate of current increase was higher for higher strain rates, and the current density at fracture was almost the same for each strain rate. All the experiments were repeated several times; in each case the current density after passivation before traction was about $0.17\text{mA}/\text{cm}^2$, and it reached nearly $100\text{mA}/\text{cm}^2$ at the time of fracture.

The current-density/strain diagram in Fig. 7 is based upon the data in Fig. 6. The data in the c.d./time diagram approach one common line in the c.d./strain diagram. Thus for the strain rates here used, the c.d. is proportional to the amount of strain that the specimens have undergone. This indicates that once a fissure is formed in the brittle oxide film, and fresh metal is exposed to the solution, the current flowing through the fissure remains constant until the wire breaks; the process of film healing is slow or negligible while the metal is yielding.

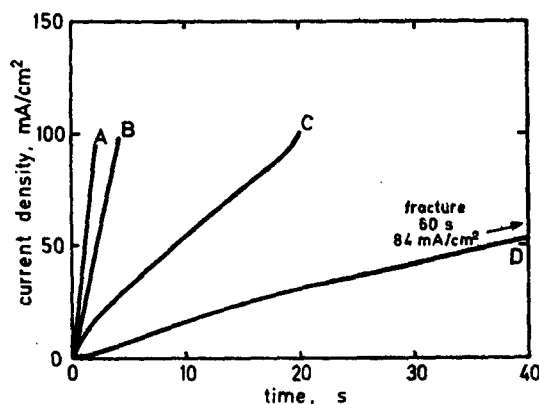


FIG. 6. Potentiostatic current-density/time curves for oxide-covered mild steel yielding at different strain rates in hot calcium nitrate solution.
 4N $\text{Ca}(\text{NO}_3)_2$, pH 3.7 (at 25°C), 102°C, $e_H = -0.10\text{V}$.
 Strain rate: A, 307%/min; B, 154%/min; C, 31%/min; D, 8%/min.

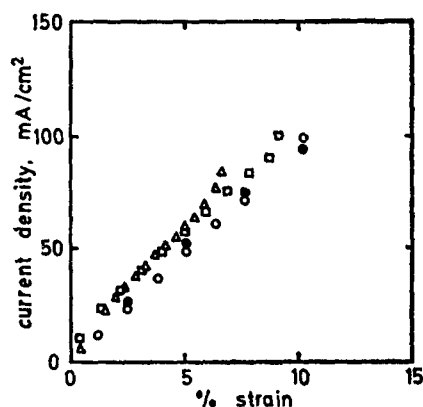


FIG. 7. Variation of current density with % strain (data from Fig. 6.)
 4N $\text{Ca}(\text{NO}_3)_2$, pH 3.7 (at 25°C), 102°C, $e_H = -0.10\text{V}$.
 Strain rate: ●, 307%/min; ○, 154%/min; □, 31%/min; △, 8%/min.

Similar experiments were performed in sodium nitrate solutions. Figure 8(a-f) shows c.d./time curves for such solutions at two pH values and for several potentials. Figure 9(a-f) shows the corresponding c.d./strain diagrams; again, the data for different strain rates approximate one common line in the c.d./strain diagrams, except in Fig. 9(d, e), which will be considered later.

The potentials used for the data in Figs. 7, 9(a) and 9(d) are slightly more positive than the rest potentials of the same mild steel in the same solutions, Table 1. It is well known that increasing the electrode potential in the range -0.30 to $-0.15\text{V}(\text{nhe})$ of mild steel in nitrate solutions^{8,9} shortens the time to fracture. Correspondingly, Fig. 9(a) and (b) shows that an increase in potential from -0.22 to $-0.18\text{V}(\text{nhe})$ produces an increase of about four times in the c.d. at equal percentage strain.

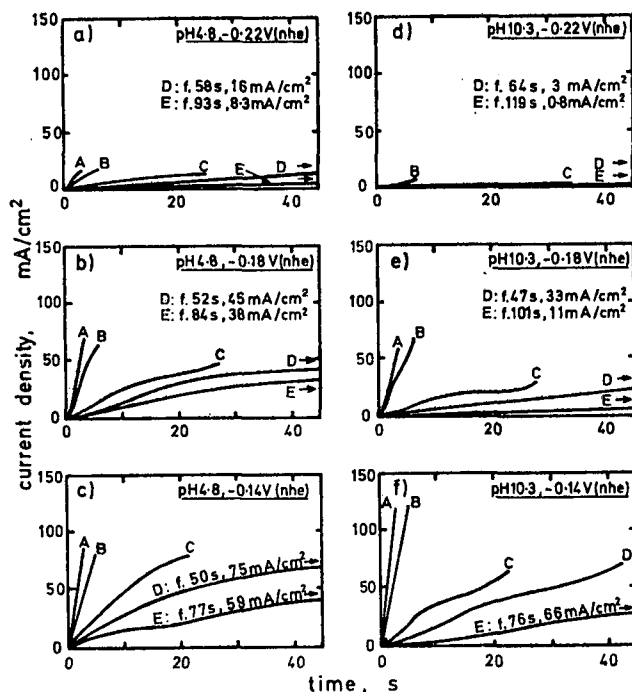


FIG. 8. Potentiostatic c.d./time curves for oxide-covered mild steel yielding at different strain rates in hot sodium nitrate solution.

4N NaNO₃, 102°C.

Strain rate: a, 307%/min; b, 154%/min; c, 31%/min; d, 15%/min; e, 8%/min.

For the same amount of deformation, the c.ds. were higher in calcium nitrate than in sodium nitrate solutions, and higher at pH 4.8 than at pH 10.3. These results are in harmony with the classification of stress corrosion cracking aggressiveness of nitrate solutions suggested by Parkins and Usher,¹⁰ if cracking is indeed produced by anodic dissolution.

Figure 9(d) shows that for mild steel in sodium nitrate solutions at pH 10.3 only at the highest strain rates does the yielding affect the current density. It is probable that at pH 10.3, local acidity does not develop at the anodes, and consequently oxide-film healing can occur relatively rapidly even on fresh metal exposed by the fissuring of the oxide film produced by traction. Only at higher potentials will the rate of anodic dissolution increase and thus favour the formation of localized acidity. There will then be competition between the healing process and the dissolution attack, and results such as those given in Fig. 9(e) are not unexpected. Still further increase in potential may well make dissolution predominant over the healing, so that behaviour as shown in Fig. 9(f) occurs. This last figure, compared with Fig. 9(c), indicates that the stress corrosion cracking of mild steel in sodium nitrate solution at pH 10.3 should be as rapid as that at pH 4.8, provided that the potential is raised to -0.14V(nhe).

From the c.d./strain diagrams an approximate calculation of the c.d. on bare metal, or in the cracks when they occur, can be made. It is assumed that the c.d.

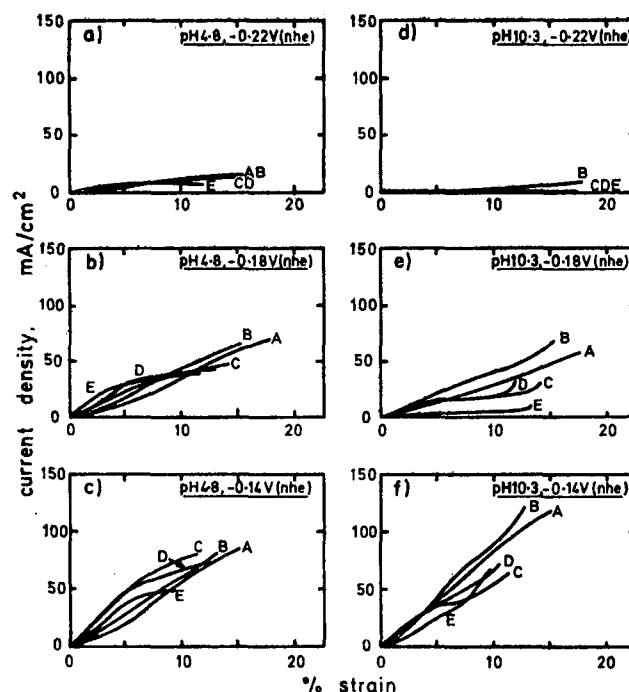


FIG. 9. Variation of c.d. with % strain at different strain rates, pH and potential.
4N NaNO₃, 102°C.
Strain rate: a, 307%/min; b, 154%/min; c, 31%/min; d, 15%/min; e, 8%/min.

flowing through the unbroken film or through its pores is not affected by the traction, so that it remains at the low value measured just before traction. Since this initial c.d. is more than two orders of magnitude smaller than the total apparent c.d. measured during traction, it can be ignored. Figure 6 shows that in calcium nitrate solutions after 10 per cent strain, when $\sim 5\%$ of the total area is new exposed metal,* the c.d. is 100mA/cm^2 . Thus the c.d. on the fresh metal is of the order of 2000mA/cm^2 . Results of the same calculation for other experiments are collected in Table 2.

Metallographic examination of the yielded specimens showed that the (inter-granular) length of the cracks was proportional to the time of traction of the wire. At high strain rates it was difficult to distinguish crack penetration from surface irregularities of the yielded specimen. For slower strain rates, allowing longer exposures, the penetrations could easily be measured; typical micrographs are shown in Fig. 10. Values of the c.d. required to propagate cracks by anodic dissolution were calculated from the penetration rates found in specimens strained at 8%/min, and are given in Table 2. It may be seen that the measured anodic c.ds. are quite sufficient to account for the measured penetration rates.

*When a wire of length l_0 extends to length l , it shrinks circumferentially, so that the net increase in its area is easily shown to be $1 - (l_0/l)^2$.²⁰ Thus for small linear strains, $\%(\text{increase in area}) \approx (\frac{2}{3}\% \text{ strain})$.

TABLE 2. CURRENT DENSITY AT NEW EXPOSED METAL IN FISSURES IN THE OXIDE FILM PRODUCED BY TRACTION, COMPARED WITH CURRENT DENSITY REQUIRED TO ADVANCE "CRACKS" IN THE METAL AT MICROSCOPICALLY MEASURED RATE

Solution	Potential [V(nhe)]	Initial pH	C.D. measured (A/cm ²)	Time to fracture (s)	Average depth of "cracks" at fracture (μm)	C.D. required (A/cm ²)
4N Ca(NO ₃) ₂	- 0.10	3.7	2.01	35	25	2.08
4N NaNO ₃	- 0.14	4.8	1.48	77	32.5	1.21
4N NaNO ₃	- 0.18	4.8	0.80	84	20	0.69
4N NaNO ₃	- 0.22	4.8	0.26	93	5	0.16
4N NaNO ₃ + NaOH	- 0.14	10.3	1.32	76	19	0.73

DISCUSSION

The present results show that when mild steel anodes are deformed in tension in hot calcium and sodium nitrate solutions, at controlled potentials of up to 100mV above the "natural" corrosion potential, a considerable increase in the anodic c.d. is observed, which is approximately proportional to the amount of strain and independent of the strain rate. The results are different from those obtained by Hoar and Scully⁸ for stainless steel in hot chloride solutions, where the measured anodic c.d. shows a very rapid rise on yielding and then remains almost constant, because the whole area of the metal surface at once becomes very active during yielding. In the present case the yield-assisted anodic dissolution results from the fracture of the oxide film over a relatively small area, around 5 per cent of the total.

The correlation between the c.d. at the breaks of the oxide film and the rate of crack propagation strongly indicates that the cracks propagate entirely by electrochemical dissolution, without the contribution of any process of mechanical rupture of the metal. The yield-assisted current increase and the rate of crack propagation are similarly affected by variables such as type of solution, electrode potential and pH; this gives further support to the hypothesis of crack propagation by the anodic dissolution of yielding metal at the crack advancing edge.

In controlled-potential experiments in 5N *ammonium* nitrate solutions, Sklarska-Smialowska¹² found rapid stress corrosion cracking between -0.28 and -0.10V(nhe), but she observed no oxide formation in potential-sweep polarization experiments below "about -0.1V". However, the rate of the potential sweep towards the positive direction was 20mV in 10s; it is probable that had the potential been maintained at, say, -0.15V(nhe) for some time, a fall in anodic c.d. accompanied by visible oxide formation would have been observed. As our Fig. 4 shows, even at -0.10V(nhe) the fall of c.d. and the growth of the oxide layer continues for well over 1000s in 4N calcium nitrate solution. It is of course possible that stress corrosion cracking of mild steel held at -0.28 to -0.10V(nhe) in ammonium nitrate solutions occurs without the formation of oxide, but we think it likely that oxide formation begins at potentials around -0.25V(nhe) (although of course more slowly than at -0.10V(nhe)). In our experiments in 4N sodium nitrate at pH 10.3, no film could be observed at -0.22V(nhe) and there was no yield-assisted anodic dissolution, Fig. 8(d), or stress

corrosion cracking; but at -0.18 and especially at $-0.14\text{V}(\text{nhe})$, the black film was formed and yield-assisted anodic dissolution, Fig 8(e, f), and stress corrosion cracking, occurred. The transition in this solution appears to be at about $-0.18\text{V}(\text{nhe})$.

We think that the present experiments, and the earlier results of other workers, support a mechanism for the stress corrosion cracking of mild steel in hot nitrate solutions, either under "isolated" conditions or at anode potentials up to some 100mV above the corrosion potential, that can be summarized as follows. It is, of course, based on the early ideas of Logan,^{8,17} but constitutes an extension of them.

1. Oxide film grows by anodic action on the metal surface; on isolated metal, the concomitant cathodic process is nitrate reduction, accompanied by oxygen reduction if the solution is aerated. Under sufficient load, brittle fractures appear in the oxide because of local microscopic strain of the ductile metal beneath it.

2. At such a fracture, repair begins by rapid anodic conversion of the exposed metal to fresh oxide. If the fracture is (as is likely) coincident with a grain boundary in the metal, the anodic conversion is especially rapid—Parkins and Usher¹⁰ showed that grain-boundary trenching is a preferential mode of anodic corrosion.

3. At a grain-boundary trench, the stress intensification is sufficient to cause further and more rapid yielding of the exposed metal, so that the new oxide formed is not well adherent and does not stifle further anodic attack.

4. The "crack"—better termed a "fissure"—now propagates by rapid anodic dissolution of its yielding advancing edge, while its static sides become protected by being converted into adherent oxide. Since the fissure thus remains "sharp", it continues to propagate unless either (a) the stress is diminished, (b) the anodic process is prevented by a lowering of the potential, i.e. by cathodic protection.

It is still not possible to be certain whether the greatly enhanced anodic reaction of yielding metal is caused solely by removal of oxide film and inability to reform it rapidly enough or with sufficient adhesion, or whether it is also assisted by a mechanochemical stimulation of the actual anodic process; however, in special experiments we could find no mechanochemical effect in oxide-free mild steel strained in hot nitrate solutions. Moreover, at more positive anode potentials, $+0.2-0.8\text{V}(\text{nhe})$, Sklarska-Smialowska¹³ found a region of evident partial anodic passivity, with oxide/film formation, accompanied again by rapid stress corrosion cracking; whereas at still higher potentials there was almost complete passivation by a *very thin* compact oxide film and little or no stress corrosion cracking, evidently because under such conditions a broken film can reform very rapidly even on yielding metal.

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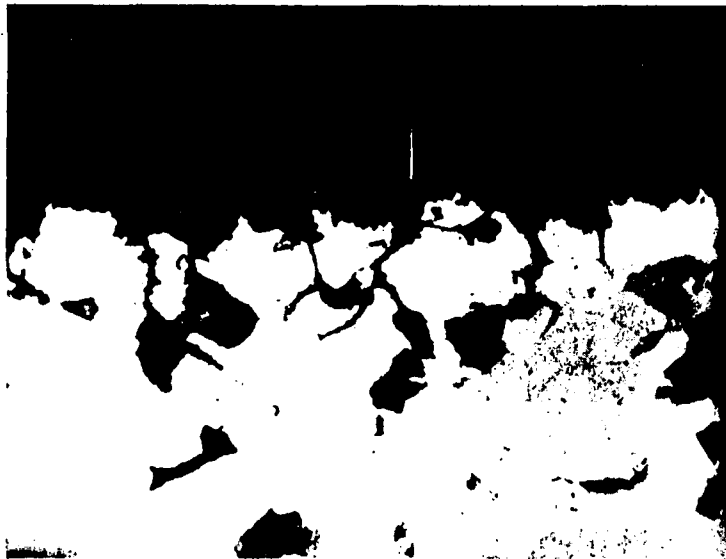


FIG. 10. Stress corrosion cracks (partly transgranular) in mild steel.
4N $\text{Ca}(\text{NO}_3)_2$, pH 3.7 (at 25°C), 102°C, $e_{\text{H}} = 0.10\text{V}$. ($\times 400$)

Transport Processes and the Mechanism of Pitting of Metals

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ABSTRACT

A pit model was developed on the assumption that the metal ions hydrolyze inside the pits and that the corrosion products are transported by diffusion. Concentrations of Me^{2+} , $\text{Me}(\text{OH})^+$, and H^+ ions, as a function of pit depth and current density, for Zn, Fe, Ni, Co, Al, and Cr were calculated. The main reason for passivity breakdown at the initial stages of pit growth, was found to be the localized acidification due to metal ions hydrolysis. Assuming a critical pH value for pit initiation, the following experimental facts could be explained: (i) the effect of the external pH on the pitting potential of Fe and stainless steel; (ii) the effect of sodium borate concentration on the pitting potential of Zn; (iii) the effect of weak acid salts on the pitting potential of Al; (iv) the oscillations of the electrode potential of stainless steel and nickel in solutions of $\text{Cl}^- + \text{SO}_4^{2-}$ ions; (v) the existence of a pitting inhibition potential; and (vi) the existence of a pitting protection potential. Through analysis of the transport processes inside a pit it was also concluded that the pitting potential of a metal should change with the Cl^- ion concentration according to the equation

$$E_p = E_p^\circ - B \cdot \log [\text{Cl}^-]$$

$B = 0.059\text{V}$ being the slope of the curve at room temperature.

It is a generally accepted fact that pitting starts at a certain critical potential, known as pitting potential (1). Yet the nature of such a potential still remains uncertain. Several explanations have been given, such as zero charge potential, potential-induced ion migration, electrically produced mechanical breakdown, competitive adsorption, salt-formation equilibrium potential, etc. (1). Nevertheless, none of these mechanisms could account for the way in which variables such as pH, ionic concentration, and inhibitor concentration affect the pitting potential. In recent publications, Wexler and Galvele (2) and Alvarez and Galvele (3) reported that the pitting potential was the minimum potential at which localized acidity could be maintained inside a pit. The present paper, based on simple transport equations shows that such acidification can be obtained even at the very early stages of pitting, and that, as was recently reported (4), transport calculations inside the pit explain why variables such as an aggressive anion concentration, nonaggressive anion concentration, external pH, presence of weak acid salts, and alloying elements modify the pitting potential of a metal.

It is concluded that most of the observations made so far on the pitting potential can be explained simply by transport phenomena, and that processes like competitive adsorption, salt formation, film contamination,

etc., even though present during the pitting process, do not play a major role in fixing the pitting potential.

Several authors have shown that the solution inside a pit, as well as that inside a crack or crevice, has a composition quite different from that in the bulk solution (5-10). As early as 1937 Hoar (11) proposed a mechanism of "autocatalytic" pit propagation, which considered that the main cause of pitting was the drop of pH inside the pit. Other authors (12, 13) postulated that the condition for pitting initiation was an increase of chloride ion concentration on the metal-solution interface. In a similar way Kaesche (14) considered the formation of saturated AlCl_3 inside a pit the necessary condition for the pitting of aluminum.

After studying the pitting of iron in various environments, Vetter and Strehblow (15, 16) questioned all mechanisms based on local composition changes. These authors assumed that the causes of pitting should be present in all the stages of pit growth, even in the smallest detectable pits. Pits as small as one micron in diameter, growing with current densities of the order of $1-9 \text{ A/cm}^2$ were detected in iron. According to their calculations, the origin of pitting could not be attributed to changes in pH, in potential, or in ionic concentration, since such changes would be meaningless in the initial stages of pitting. However, the pitting model developed by Vetter and Strehblow cannot be taken as a realistic model; according to their model the pH inside the pit increases during pit growth, while in practice the pH was found to decrease (5-10).

Pickering and Frankenthal (17) developed a much simpler pit model, and they analyzed the changes in

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Key words: pitting of metals, pitting potential, transport processes, pitting inhibitors.

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composition to be expected in the pit. Nevertheless, the model by Pickering and Frankenthal could not be applied in its original form to all pitting cases because, again, it would lead to pH increases inside the pit as the pit grew.

Pit Model

In the present paper a pit model similar to that developed by Pickering and Frankenthal is used (Fig. 1). Their model was developed for a metal that would dissolve in an acid solution and consequently always resulted in a decrease in the pH inside the pit. To overcome this difficulty, the model used herein assumes that the pH of the bulk solution can take any value from acid to alkaline values.

The model by Pickering and Frankenthal takes into consideration the transport of ions both by diffusion and by electrical migration. In this way, complex formulae are obtained when the study of the hydrolysis of the metal ions, or modifications of the external pH are attempted. Since, as shown by Vetter and Strehlow (18), pitting initiation takes place with small changes in the electrolyte composition, it is reasonable to assume that the bulk solution acts as a supporting electrolyte for the metal ions and the hydrolysis products produced during pitting initiation. In this way the transport equations are considerably simplified, since only transport by diffusion remains important. The following are the main modifications introduced in the model used in the present paper:

(i) Instead of a single charge transfer reaction, a more general expression is used for the anodic reaction taking place inside the pit



The dissolution reaction is assumed to take place at the bottom of the pit, (Fig. 1) as in the model by Pickering and Frankenthal. No reaction takes place at the walls of the pit. In this way a unidirectional pit model is obtained, with a considerable simplification in the mathematical treatment.

(ii) Reaction [1] is assumed to occur in a sodium salt of an aggressive but noncomplexing anion. The pH of the bulk solution could have any value, and is given as a boundary condition.

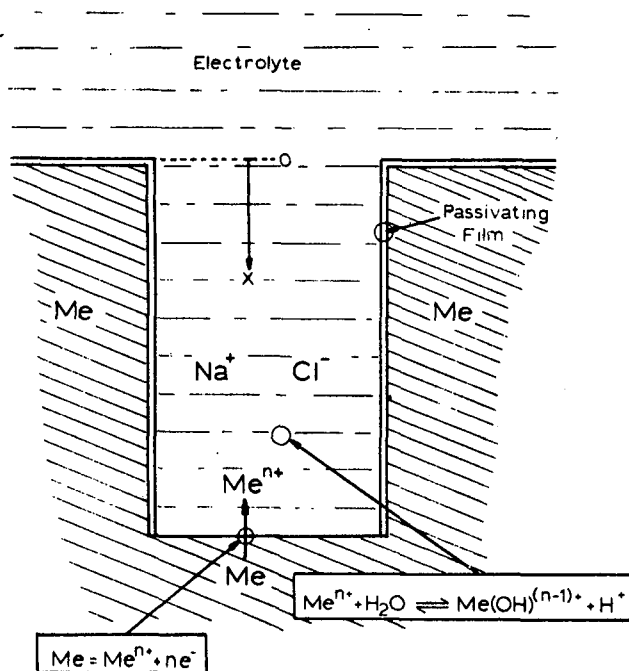


Fig. 1. Unidirectional pit model

(iii) It is assumed that reaction [1] is followed by a hydrolysis equilibrium of the type

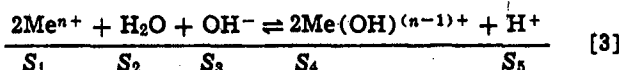


and that this equilibrium is very quickly reached (18).

Reaction [2] is a simplified description of the processes taking place inside a pit. Polynuclear complexes could be formed, or further degrees of hydrolysis could occur. Nevertheless, reaction [2] will give the minimum degree of acidification expected inside a pit. On the other hand, either no polynuclear complexes are reported for the metals used in the present work, or their formation rate is very slow (18, 19).

(iv) The last, and most important, modification introduced to the Pickering and Frankenthal model is the assumption that the aggressive anion salt acts as a supporting electrolyte for the ionic species formed in reactions [1] and [2].²

Since it is assumed that the bulk solution could have any pH value, reaction [2] has to be rewritten to account for the contribution of the OH⁻ ions at pH values higher than 7



From Eq. [3] we find that inside the pit there are five species (S_1 - S_5), the concentrations of which should be calculated. The detailed mathematical treatment for a system like this can be found in Vetter's work (20). The five unknown concentrations are calculated by resolution of the five following equations: the flow of the species containing Me atoms will be given by

$$D_1 \frac{dC_1}{dx} + D_4 \frac{dC_4}{dx} = \frac{i}{n \cdot F} \quad [4]$$

the flow of the species containing O atoms will be given by

$$D_2 \frac{dC_2}{dx} + D_3 \frac{dC_3}{dx} + D_4 \frac{dC_4}{dx} = 0 \quad [5]$$

and the flow of the species containing H atoms will be given by

$$2D_2 \frac{dC_2}{dx} + D_3 \frac{dC_3}{dx} + D_4 \frac{dC_4}{dx} + D_5 \frac{dC_5}{dx} = 0 \quad [6]$$

Finally, the two following equilibrium relations must be considered

$$*K_1 = \frac{C_4 \cdot C_5}{C_1} \quad [7]$$

which is the law of mass action applied to reaction [2] and

$$K_w = C_3 \cdot C_5 \quad [8]$$

which is the ionic product of water. In the above equations, D_j is the diffusion coefficient in cm²/sec, C_j is the concentration in mole/cm³ of the species j , n is the charge of the metal ion as given in Eq. [1], F is the Faraday constant, $*K_1$ is the equilibrium constant of reaction [2], i in A/cm² is the current density of reaction [1], and x is the pit depth in cm where $x = 0$ at the opening of the pit.

The assumed boundary conditions for $x = 0$ are $C_1 = 0$; $C_3 = K_w \cdot 10^{-\text{pH}}$ mole/liter; $C_4 = 0$; and $C_5 = 10^{-\text{pH}}$ mole/liter. As a first approximation all the diffusion coefficients, except those for H⁺ and OH⁻ ions, are taken as equal to 10⁻⁵ cm²/sec; therefore $D_1 = D_2 = D_4 = 10^{-5}$ cm²/sec, $D_3 = 5.3 \times 10^{-5}$ cm²/sec, and $D_5 = 9.3 \times 10^{-5}$ cm²/sec. The equilibrium constants used were taken from the review by Sillen and

² This assumption is exact only when the supporting electrolyte is in great excess over the electroactive species. However, it has been shown (Ref. (20), p. 175) that even a minor addition of supporting electrolyte of the order of magnitude of the concentration of the electroactive species reduces to a large degree the influence of the electric field.

Table I. Hydrolysis constants and solubility constants (19)

Metal	Hydrolysis constant ($\ast K_1$)	Solubility constant (K_{s0})
Cr ³⁺	10 ⁻⁴ (M · 1 ⁻¹)	10 ⁻³⁰ (M ⁴ · 1 ⁻⁴)
Fe ³⁺	10 ⁻⁷ (M · 1 ⁻¹)	10 ^{-16.1} (M ³ · 1 ⁻³)
Co ³⁺	10 ⁻¹⁰ (M · 1 ⁻¹)	10 ⁻¹⁵ (M ³ · 1 ⁻³)
Ni ³⁺	10 ⁻¹⁰ (M · 1 ⁻¹)	10 ⁻¹⁵ (M ³ · 1 ⁻³)
Zn ²⁺	10 ^{-9.15} (M · 1 ⁻¹)	10 ^{-16.6} (M ² · 1 ⁻²)
Al ³⁺	10 ^{-5.02} (M · 1 ⁻¹)	10 ⁻³³ (M ⁴ · 1 ⁻⁴)

Martell (19), and the values chosen for the calculations are reported in Table I.

By multiplying Eq. [5] by 2 and subtracting from Eq. [6], the terms for S_2 are eliminated

$$-D_3 \frac{dC_3}{dx} - D_4 \frac{dC_4}{dx} + D_5 \frac{dC_5}{dx} = 0 \quad [9]$$

Equation [8] is solved for C_3 , and this expression is substituted for C_3 in Eq. [9]. Equation [7] is solved for C_1 , and the resultant expression is substituted for C_1 in Eq. [4]. By integration, the following two equations are obtained

$$\frac{n \cdot F \cdot D_1}{\ast K_1} C_4 \cdot C_5 + n \cdot F \cdot D_4 \cdot C_4 = x \cdot i + k \quad [10]$$

$$D_5 \cdot C_5 - D_3 \cdot K_w \frac{1}{C_5} - D_4 \cdot C_4 = k' \quad [11]$$

Using the above-mentioned boundary conditions, constants k and k' are calculated. Equation [11] is solved for C_4 , and the resulting expression is substituted for C_4 in Eq. [10]. By giving values to C_5 , the values of the parameter $x \cdot i$ are calculated. With the same values of C_5 , the values of C_4 are calculated in Eq. [11]. Then C_1 is calculated in Eq. [7] and C_3 in Eq. [8]. No calculations are made for C_2 .

Ionic Concentration Diagrams

The above-mentioned calculations were made for the ionic concentration diagrams of the following systems: Zn/Zn²⁺ (Fig. 2); Fe/Fe²⁺ (Fig. 3); Ni/Ni²⁺ (Fig. 4); Al/Al³⁺ (Fig. 5); and Cr/Cr³⁺ (Fig. 6). The diagram in Fig. 4 applies also to Co/Co²⁺, since the same $\ast K_1$ value was used for Ni and for Co (see Table I).

The pH values for the bulk solution were chosen so that the oxide film might be under thermodynamically stable conditions according to Pourbaix diagrams (21). The pH values used were pH 7 for aluminum and chromium, pH 9 for zinc, and pH 10 for iron, nickel, and cobalt.

The straight line C_{Me}^- in the diagrams indicates the total of the concentrations of all the species containing Me atoms. The line is broken for a concentration of 10 mole/liter to indicate that saturation of the Me salt should be reached. Actually, the present treatment is valid only for diluted solutions, and deviations from the calculated diagrams should be expected for such high concentrations.

The ionic concentration diagrams give the concentrations of Me^{n+} , $Me(OH)^{(n-1)+}$, and H^+ ions as functions of $x \cdot i$. If the current density inside the pit is known, the diagram will show the ionic concentrations along the pit. On the other hand, at a certain given pit depth the diagram will show the current density required to get a certain change in the ionic concentration. For example, let us consider the case of iron in 1.0M NaCl solution at pH 10 (Fig. 3). Let us assume that the iron sample has two pits different in size, one of them 10⁻⁶ cm deep and the other 10⁻⁴ cm deep. If the current density inside the pits is 1 A/cm², the $x \cdot i$ values will be 10⁻⁶ and 10⁻⁴ A/cm, respectively. From Fig. 3 it is concluded that the composition at the bottom of the shallower pit will be 10⁻⁵M Fe²⁺, 5.0 × 10⁻⁴M Fe(OH)⁺, and pH 8.5. On the other hand, the

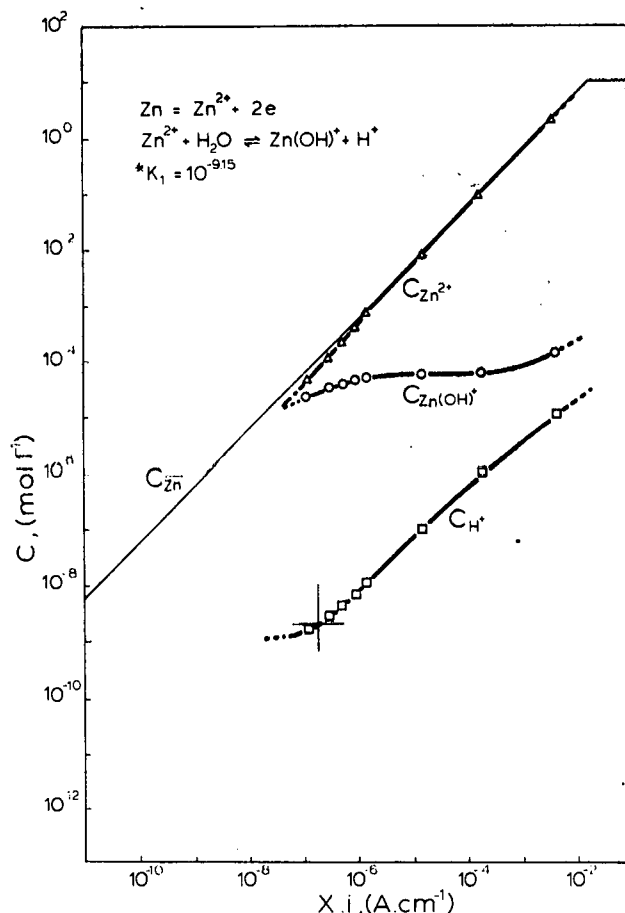


Fig. 2. Concentrations of Zn²⁺, Zn(OH)⁺, and H⁺ as a function of the product of the depth x and the current density i is a uni-directional pit.

composition at the bottom of the deeper pit is going to be: 5.0 × 10⁻²M Fe²⁺, 5.6 × 10⁻⁴M Fe(OH)⁺, and pH 5.1. The diagram predicts that the larger changes in composition and in pH will be found at the bottom of the deeper pit.

We can also compare two different specimens, with pits of equal size, but with different current densities inside the pits. For example, if the pits are 10⁻³ cm deep in both specimens, but the current density inside the pits is 10⁻¹ A/cm² in one of the samples and 10⁻⁴ A/cm² in the other, the composition at the bottom of the pits is going to be 5.0 × 10⁻²M Fe²⁺, 5.6 × 10⁻⁴M Fe(OH)⁺, and pH 5.1 in the first specimen ($x \cdot i = 10^{-4}$ A/cm), and 5.0 × 10⁻⁸M Fe²⁺, 5.0 × 10⁻⁸M Fe(OH)⁺, and pH 9.95 in the second ($x \cdot i = 10^{-7}$ A/cm). While important changes in composition should occur with current densities of 1 A/cm², virtually no changes should be expected for a current density of 10⁻⁴ A/cm².

No assumptions are made as to the way in which the current density could be obtained. In practice, it will mean that the electrode potential is properly changed. In most cases of acid solutions, such as those inside a pit, a logarithmic relation between current density and electrode potential should be expected.

Figures 2-6 show that, in spite of what Vetter and Strehlow have indicated, the H⁺ ion concentration inside the pit undergoes important changes when the pit size or the current density inside the pit is changed. It is also shown that, as found in practice, the pH inside the pit is lower than that of the bulk solution. From the data in Fig. 3, the pH along a crevice or a crack in iron can be estimated. It was found (Fig. 7) that the pH predicted by the present model is somewhere between 3 and 4, for an external pH of 10. This

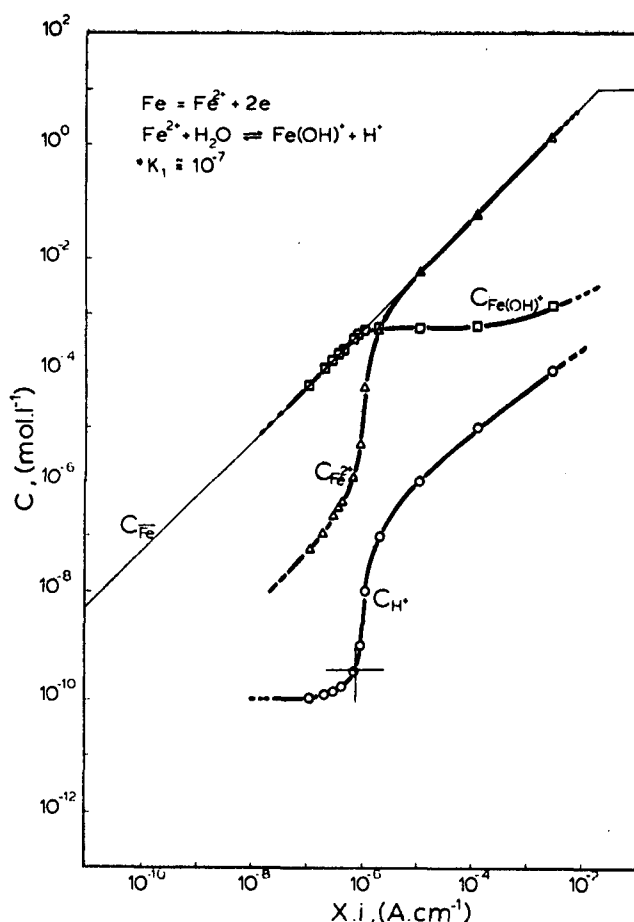


Fig. 3. Concentrations of Fe^{2+} , Fe(OH)^+ , and H^+ as a function of the product of the depth x and the current density i in a uni-directional pit.

prediction is in good agreement with the experimental observations reported by Smith, Peterson, and Brown (6).

Critical H^+ Ion Concentration

To be able to use the present ionic concentration diagrams in the study of pitting it is necessary to find the minimum degree of acidification necessary for sustained pit activity.

As a first approximation, the criterion used by Pourbaix for the potential vs. pH diagrams (21) was applied in the present paper. Pourbaix separates the passivity zones from the corrosion zones as follows. The solubility product of the passivating oxide film being known, the pH value at which such oxide film will be in equilibrium with a solution containing traces of metal ions is calculated. The concentration of the metal ions is arbitrarily taken as equal to 10^{-6} mole/liter. Such pH values are calculated herein by using the K_{s0} values reported in Table I. The calculated pH values are indicated in Fig. 2-6 by means of a cross (+) on the H^+ ion concentration line. The pH values calculated are pH 9.5 for iron, cobalt, and nickel; pH 8.7 for zinc; pH 6.0 for chromium; and pH 5.0 for aluminum. All these values are in reasonably good agreement with those reported by Pourbaix (21), with the exception of chromium which, according to Pourbaix, should be somewhere between 3.5 and 4.8.

Due to the scattering of the K_{s0} reported values (19), and to the arbitrarily choosing 10^{-6} mole/liter as the metal ion concentration, the calculated critical pH values have an error of at least plus or minus one unit pH. This criterion of choosing the critical pH values is clearly a rough approximation and experimental information is necessary. In the case of zinc,

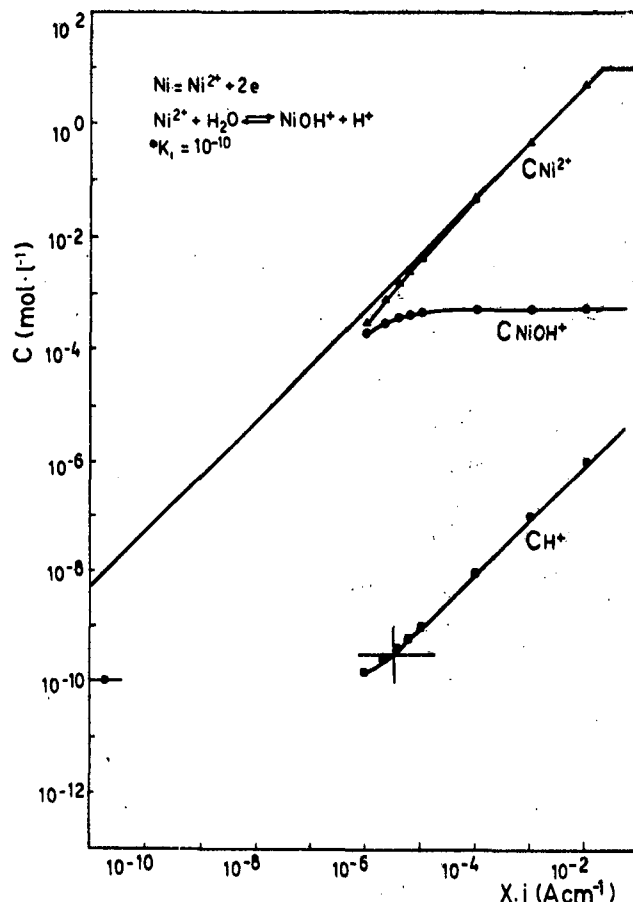


Fig. 4. Concentrations of Ni^{2+} , Ni(OH)^+ , and H^+ as a function of the product of the depth x and the current density i in a uni-directional pit.

the pH value calculated, 8.7, is in good correspondence with the experimental results reported by Davies and Lotlikar (22). These authors found that zinc, in galvanostatic measurements, was passivated in solutions of pH 9.2, 10.0, and 11.0, and did not get passive in solutions at pH 8.2.

For iron the estimated pH value was 9.5. Vetter and Strehlow (23) reported passivity to pitting transitions for iron at pH values as low as 8.0. On the other hand, Alvarez and Galvele (24) found that the pitting potential of iron is pH independent for pH values lower than 10, and pH dependent at values higher than 10. It was then concluded that the critical pH for iron should be around 10.

No experimental information is available for other metals or alloys. Nevertheless, the concept of a critical pH for depassivation was applied to stainless steels by Defranoux and Tricot (25). These authors found that the presence of chloride ions produced an increase in the critical pH for depassivation of stainless steels.

Current Density inside the Pits

To be able to use the ionic concentration diagrams it is also necessary to know the current density inside the pits. For aluminum in NaCl solutions, Kaesche (14) reported that the minimum current density inside the pits was recorded at the pitting potential and had a value of 0.3 A/cm². For aluminum in 4M NaCl solution, the current density inside the pits increased with the electrode potential, following what seemed to be a logarithmic law with a slope of $b = 0.150\text{V}$. At a potential 0.100V over the pitting potential the current density inside the pits was close to 1.1 A/cm².

Szklarska-Smialowska and Janik-Czachor (26) measured the current densities within pits for Fe-16Cr alloy in 0.7N NaCl + 0.7N Na₂SO₄ solution. They

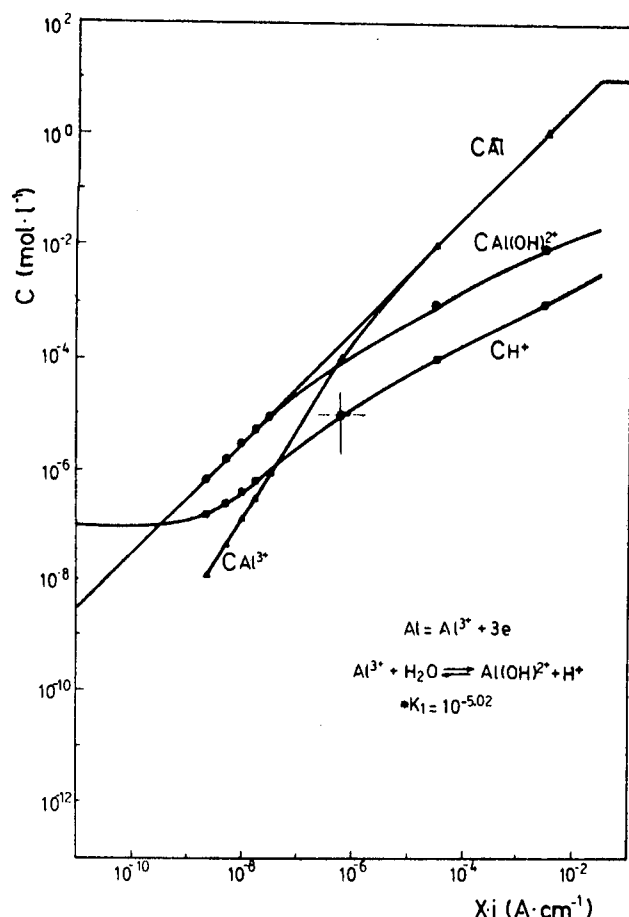


Fig. 5. Concentrations of Al^{3+} , Al(OH)^{2+} , and H^+ as a function of the product of the depth x and the current density i in a unidirectional pit.

found that the current density inside the pits was a function of potential, and according to the interpretation made by Sato *et al.* (27) it would follow a logarithmic law with a slope of $b = 0.220\text{V}$. For the Fe-16Cr alloy Szklarska-Smialowska and Janik-Czachor reported a pit initiation potential of about 0.50V (SCE) and a pit passivation potential of -0.05V (SCE). From Sato's paper it is inferred that the current density at the pit initiation potential was about 8.0 A/cm^2 , while at the pit passivation potential it dropped to 0.1 A/cm^2 .

Sato *et al.* (27) reported that in austenitic stainless steels, for potentials higher than 0.60V (SCE) the current density inside the pits became potential independent, reaching a value of 8 A/cm^2 .

Schwenk (28), working with 18/10 chromium-nickel austenitic stainless steels, reported a current density inside the pits, at the pitting potential, of the order of 0.5 A/cm^2 . He also found that the reaction inside the pit followed a Tafel law, with a slope of $b = 0.087\text{V}$.

For pure iron, Vetter and Strehblow (15) reported pit initiation current densities ranging from 0.9 up to 2.0 A/cm^2 . For nickel pits of 1μ diameter, Vetter (29) reported current densities as high as $50\text{--}70\text{ A/cm}^2$.

From the above-mentioned results, it can be safely assumed that the current density inside a pit, at the initiation stage, is of the order of 1 A/cm^2 .

Pit Initiation Conditions

Figures 2-6 show that for most of the metals studied the critical pH is reached with $x \cdot i$ values lower than 10^{-6} A/cm . Since at pit initiation conditions the current density inside the pit is at least 1 A/cm^2 , it is concluded that the necessary acidification can be obtained

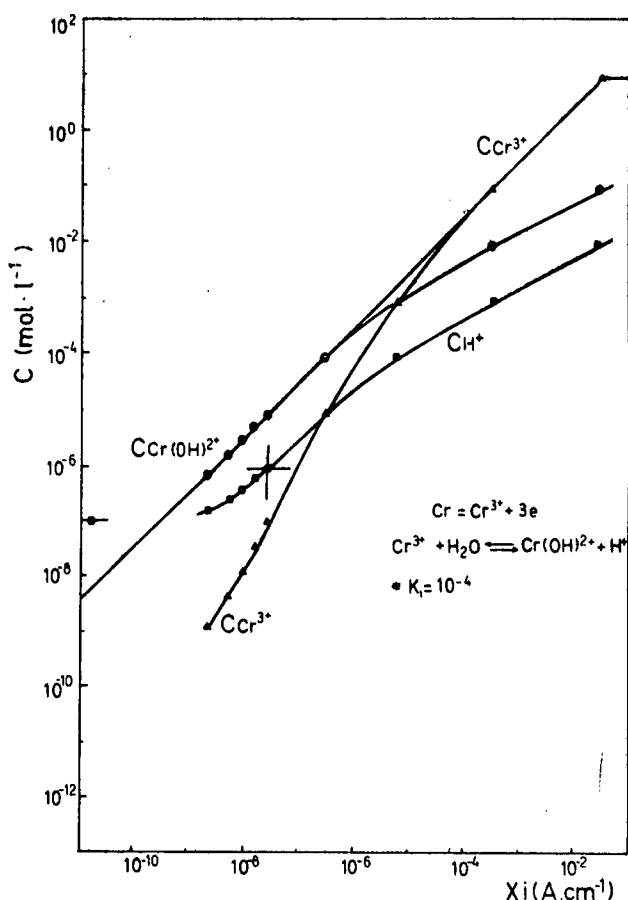


Fig. 6. Concentrations of Cr^{3+} , Cr(OH)^{2+} , and H^+ as a function of the product of the depth x and the current density i in a unidirectional pit.

in pits as small as 10^{-6} cm . This means that a crack in the passivating oxide film would give a diffusion path long enough to reach the critical pH. If such cracks are present, it would only be necessary to apply a potential high enough to reach the above-mentioned current density.

As for the existence of such cracks in the passive oxide film, there is abundant literature in favor of it. Current oscillations below the pitting potential were reported for aluminum (30), for zinc (31), and for stainless steels (32) showing the presence of a film rupture-reformation process. Vetter and Strehblow (16) reported that a change in the electrode potential, just before the injection of chloride ions, produced a noticeable increase in the pit density in iron. This was interpreted as a production of defects in the oxide film as a result of the potential shift. Sato (33) calculated the tensions induced in the oxide film by electrostriction, and concluded that they were high enough to produce mechanical breakdown of the oxide film. Fromhold (34) also found that the transport of ions through the passive film would produce stresses large enough to cause mechanical breakdown of the oxide film.

It can be concluded that film breakdown is constantly occurring on a passive metal. Nevertheless, the exposure of bare metal does not necessarily lead to localized corrosion. Straining metal experiments (2, 3, 30) have shown that the exposure to bare metal does not lead to pitting, unless the electrode potential is equal to, or higher than, the pitting potential.

Once the crack in the passive film is produced, if the electrode potential is high enough, a net anodic-current density will circulate through the fissure. From the diagrams in Fig. 2-6 it should be possible to predict at which current density the critical acidification can be reached, or if the metal will repassivate.

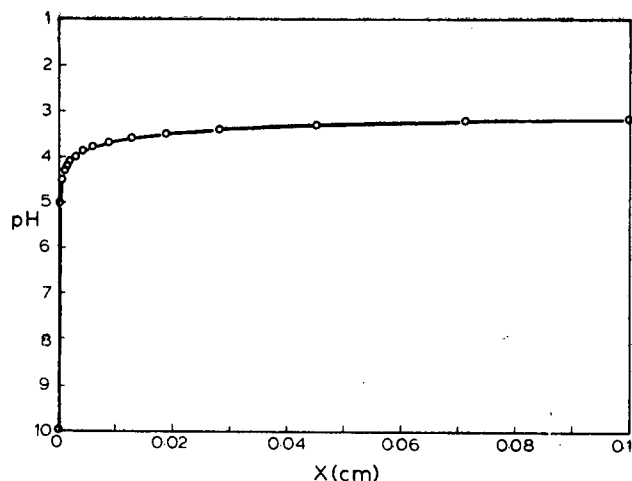


Fig. 7. Calculated pH profile for iron along a pit or crevice. External pH = 10, current density = 1 A/cm², $*K_1 = 10^{-7}$ mole/liter.

Figures 2-6 show that the critical acidification varies from metal to metal. For aluminum, for example, it is much higher than for iron or nickel. Nevertheless, in all cases the critical acidification is reached for very low $x \cdot i$ values.

So far it has been assumed that the current density inside the pit is of the order of 1 A/cm². For some metals, as is probably the case with chromium, it might happen that such high current densities could not be reached. Then the metal would not be susceptible to pitting. Nevertheless, the critical $x \cdot i$ value can be reached even with small current densities, provided that a sufficiently long diffusion path is present. That would be the case in a crevice. In this way, a metal could be resistant to pitting, but susceptible to crevice corrosion. From the electrochemical point of view both processes would be equal, the only difference being the length of the diffusion path.

Effect of the External pH on the Pitting Potential

A large increase in the pH of the bulk solution inhibits the pitting process. Leckie and Uhlig (35) reported that the pitting potential of stainless steel was independent of the pH in the range of 1-7, but for pH values higher than 7 the OH⁻ ion acted as pit inhibitor. In the same way, Venu *et al.* (36) and Rajagopalan *et al.* (37) reported that the presence of NaOH inhibited the passivity breakdown of steels in NaCl solutions.

By appropriate modification of the boundary conditions, it is possible to calculate the effect of the external pH on the concentration profiles in the ionic concentration diagrams. Calculations were performed for iron, assuming external pH values ranging from pH 7 to 12 (Fig. 8). The external pH was found to modify the shape of the H⁺ ion concentration curve inside the pit. The critical pH for iron is somewhere between 9 and 10. If the pH of the bulk solution is 10, the critical pH value would be reached with $x \cdot i$ values of about 10⁻⁶ A/cm. By increasing the external pH to 11, $x \cdot i$ values of 10⁻⁵ A/cm are required. For pH 12 the critical acidification is reached only with $x \cdot i$ values of 10⁻⁴ A/cm. The experimental conditions being equal, this means that the current density has to increase one order of magnitude whenever the pH of the bulk solution is increased one unit. If the relation between potential and current density inside the pit follows a logarithmic law, then it should be expected that the pitting potential will follow a law of the type

$$E_p = A + b \cdot \log C_{OH^-} \quad [12]$$

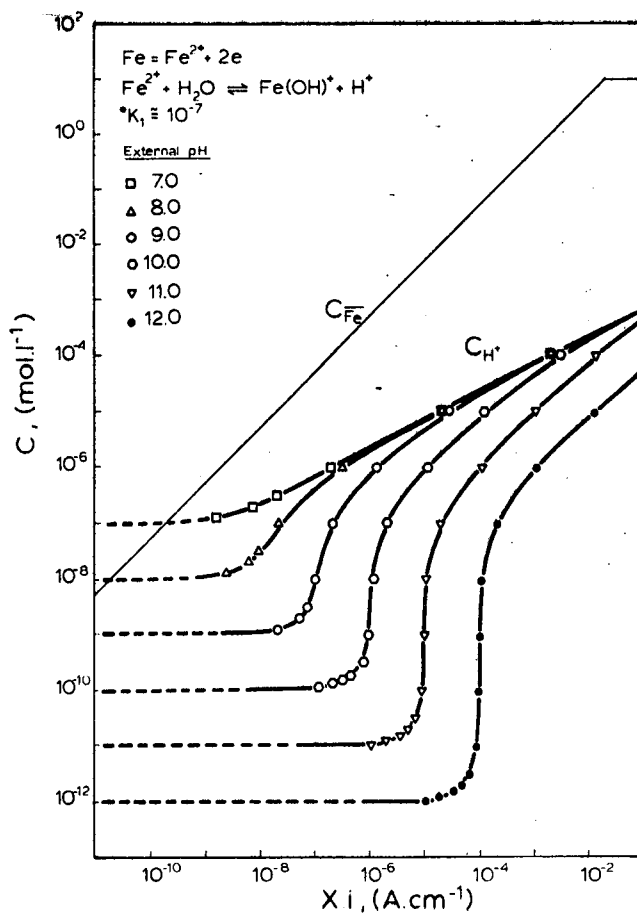


Fig. 8. Effect of the external pH on the concentration of H⁺ as a function of the product of the depth x and the current density i in a unidirectional iron pit.

Through galvanostatic experiments with high purity iron in NaCl solutions, Alvarez and Galvele (24) found that the pitting potential of iron was independent of the pH between pH 7 and 10, but showed a logarithmic relation, as in Eq. [12], from pH 10 to pH 12; the slope of the curve being $b = 0.020V$.

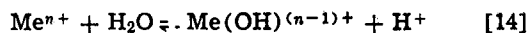
Presence of Anions of Weak Acid Salts

It is known that the presence of weak acid salts inhibits pitting by increasing the pitting potential. The pitting potential of aluminum is increased by the presence of soluble salts of acetate (38), benzoate (38), chromate (38,39) or tartrate (39). Pitting of zinc is inhibited by a borate buffer (40), and the pitting potential of iron in the presence of a borate buffer (23) is more than 100 mV higher than in its absence (41).

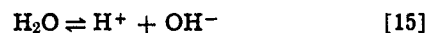
Anions of weak acids, because of their buffer properties, should modify the hydrogen ion concentration profiles in Fig. 2-6. Under these circumstances, the following equilibrium will take place inside the pit



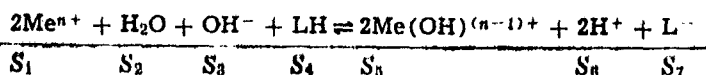
where LH is the weak acid, and L⁻ is the anion of the weak acid. The equilibrium constant of the reaction will be K_a . The other equilibrium reactions are



with the equilibrium constant $*K_1$, and



with the equilibrium constant K_w .
The over-all reaction will be



[16]

The boundary conditions are chosen as above, making allowance for the fact that the concentration of protons in the bulk solution will be related to the concentration of the weak acid (LH) and that of its anion (L^-) through Eq. [13].

Figure 9 shows the ionic concentration diagram for zinc in the presence of 10^{-2}M borax plus 1.0M NaCl solution. By comparison with Fig. 2, the presence of the borate salt is found to shift the hydrogen ion concentration line to higher $x \cdot i$ values. This means that, under otherwise equal conditions, in the presence of borax higher current densities are required to reach the critical acidification. Figure 10 shows the degree of shifting of the hydrogen ion concentration line for various borax concentrations. For borax concentrations lower than 10^{-4} , little effect should be expected from the weak acid salt. For higher borax concentrations an increase of one order of magnitude in the concentration of borax results in an increase of about one order of magnitude in the $x \cdot i$ values. If the relation between potential and current density inside the pit follows a logarithmic law, it follows that the pitting potential of zinc should be related to the borax concentration by an equation of the type

$$E_p = A' + b' \cdot \log C_b \quad [17]$$

C_b being the concentration of the buffer salt. The value of b' should be equal to the Tafel slope of the metal in a pitlike solution.

The results in Fig. 9 are in good agreement with the measurements of pitting potentials for zinc reported by Augustynski *et al.* (40). These authors found a

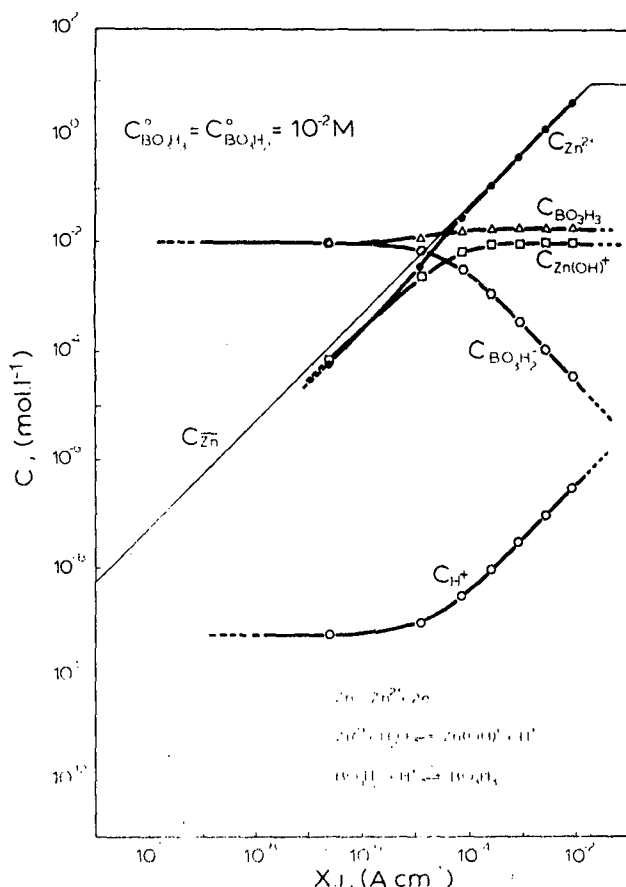


Fig. 9. Effect of 10^{-2}M borax on the concentrations of Zn^{2+} , $\text{Zn}(\text{OH})^+$, and H^+ as a function of the product of the depth x and the current density i in a unidirectional zinc pit.

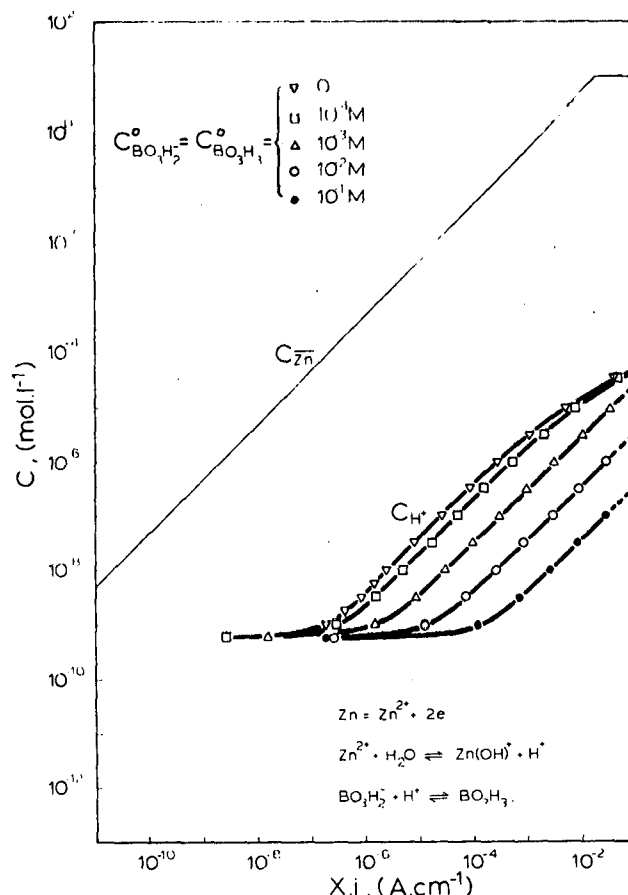


Fig. 10. Effect of the borax concentration on the H^+ concentration as a function of the product of the depth x and the current density i in a unidirectional zinc pit.

logarithmic relation between the pitting potential and the buffer concentration for zinc in NaCl and in NaClO_4 solutions. When the buffer concentration is higher than that of the aggressive anion, the pitting potentials measured by Augustynski *et al.* are higher than those predicted by Eq. [17]. The reason for this is that under such circumstances the aggressive anion is not acting as a supporting electrolyte, and the concentration buildup of the buffer anion inside the pit must be accounted for.

Diagrams similar to those in Fig. 10 were found for iron in the presence of borax. Vetter and Strehblow (23) reported a pitting potential of -0.17V (NHE) for iron in a 0.1M NaCl solution containing 0.029M KH_2BO_3 + 0.021M H_3BO_3 . In the absence of buffers, Semino and Galvele (41) measured pitting potentials from -0.32 to -0.34V (NHE). A diagram calculated for the solution used by Vetter and Strehblow shows that in their solution the $x \cdot i$ values were about two orders of magnitude higher than in that used by Semino and Galvele. The Tafel slope for iron inside the pit should be somewhere between 0.080 and 0.114V (42). Equation [17] predicts a difference of 0.160 – 0.230V in the pitting potential values, which fits very well with the difference of 0.150 – 0.170V found between the experimental results.

From Eq. [13] one would expect that salts from acids of different strength should have different effects on the ionic concentration diagrams. Figure 11 shows the effect of 0.1M weak acid salt on the proton concentration line inside the pit for aluminum. The calculations were made for four different acid strengths, going from

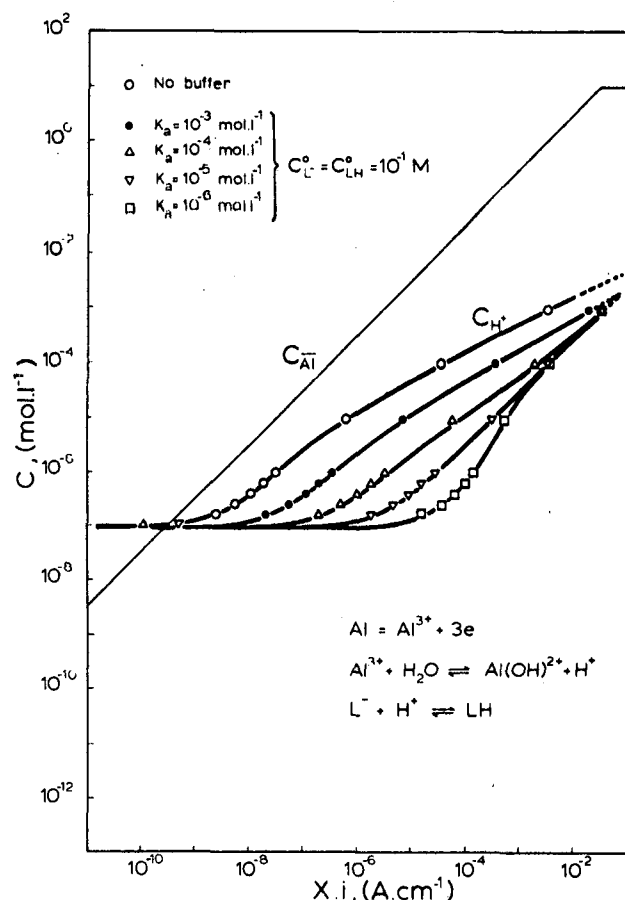


Fig. 11. Effect of the K_a of the buffer on the H^+ concentration as a function of the product of the depth x and the current density i in a unidirectional aluminum pit.

$K_a = 10^{-6}$ up to $K_a = 10^{-3}$ mole/liter. The lower the value of K_a , the higher the $x \cdot i$ values. From Fig. 11 it is concluded that the salt with the lowest K_a should be the most effective pitting inhibitor. Table II shows K_a values for various weak acids. From Table II and from Fig. 11 it can be concluded that from among chromate, acetate, and benzoate, chromate should be the most effective and benzoate the least, in correspondence with the experimental results reported by Böhni and Uhlig (38). Tartrates should be the least effective inhibitors, as reported by De Micheli and Galvele (39). According to Table II silicates and borates should have good inhibitor properties.

The present model does not take into consideration the possibility of formation of insoluble compounds between the metal ions and the weak acid anions. Such precipitates would occlude the pits, thus enhancing the inhibition capacity of the weak acid salt.

Aggressive Anion Concentration

If the concentration of the aggressive anion salt is changed over a wide range of values, the assumption that such salt is acting as a supporting electrolyte is not valid. In this case the electric field inside the pit cannot be ignored, and Eq. [4-6] are not valid. The following equations should be used [Ref. (20), p. 171]

Table II. Ionization constants of weak acids

Aqueous solution	$\text{p}K_a$ at 25°C	Reference
Acetic acid	4.76	43
Benzoic acid	4.20	43
Boric acid	9.23	43
Chromic acid	6.50	19
$\text{HCrO}_4^-/\text{CrO}_4^{2-}$		
Silicate K_1	11.81	19
Tartaric acid K_1	3.03	43

$$\frac{i \cdot \nu_j}{n \cdot F} = D_j \left[\frac{dC_j}{dx} + z_j \cdot C_j \cdot \frac{F}{R \cdot T} \cdot \frac{d\phi}{dx} \right] \quad [18]$$

for the reacting species, where ν_j is the stoichiometric factor of the species S_j , and $d\phi/dx$ is the electric field. For the nonreacting species the following equation is used

$$C_j = C_0 \cdot e^{-(z_j \cdot F/RT) \cdot \phi} \quad [19]$$

A further equation used is the condition of electro-neutrality

$$\sum z_j \cdot C_j = 0 \quad [20]$$

The resolution of the above equations for a system where hydrolysis equilibrium is included is quite complex. Nevertheless, the resolution for a simpler system gives very useful information.

Let us assume that the metal is dissolving according to reaction [1]. Neglecting for a while the hydrolysis reaction of the metal ions, we will assume that the only ionic species present are: Me^{n+} ; Na^+ ; and Cl^- . Under these conditions the following set of equations has to be solved

$$\frac{i}{n \cdot F} = D_{\text{Me}} \left[\frac{dC_{\text{Me}}}{dx} + n \cdot C_{\text{Me}} \cdot \frac{F}{R \cdot T} \cdot \frac{d\phi}{dx} \right] \quad [21]$$

for Me^{n+} ions

$$C_{\text{Na}} = C_0 \cdot e^{+\psi} \quad [22]$$

for Na^+ ions, where $\psi = F \cdot \phi / R \cdot T$

$$C_{\text{Cl}} = C_0 \cdot e^{-\psi} \quad [23]$$

for Cl^- ions, and the electroneutrality condition

$$n \cdot C_{\text{Me}} + C_{\text{Na}} - C_{\text{Cl}} = 0 \quad [24]$$

C_{Na} and C_{Cl} in Eq. [24] are substituted for Eq. [22] and [23]

$$n \cdot C_{\text{Me}} = C_0 \cdot e^{+\psi} - C_0 \cdot e^{-\psi} \quad [25]$$

Equation [25] is substituted for $n \cdot C_{\text{Me}}$ in Eq. [21]. By differentiating Eq. [25], dC_{Me}/dx is obtained, and it is substituted for in Eq. [21]. By integration of Eq. [22], and taking into account the following boundary conditions for $x = 0$ ($C_{\text{Me}} = 0$; $C_{\text{Na}} = C_0$; $C_{\text{Cl}} = C_0$; and $\phi = 0$), Eq. [26] is obtained

$$i \cdot x = C_0 \cdot D_{\text{Me}} \cdot F \cdot [(n+1) \cdot e^{+\psi} + (n-1) \cdot e^{-\psi} - 2 \cdot n] \quad [26]$$

For $n = 1$ the equation developed by Pickering and Frankenthal is obtained (17). By solving Eq. [26] for $n = 3$, $D_{\text{Me}} = 10^{-5} \text{ cm}^2/\text{sec}$, and $C_0 = 1.0 \text{ M}$, the diagram in Fig. 12 is obtained. Up to $x \cdot i$ values of 10^{-3} A/cm , the line for C_{Me} in Fig. 12 is the same as C_{Al} in Fig. 5. For $x \cdot i$ values higher than 10^{-3} A/cm a small deviation is found. This indicates that the assumption of a supporting electrolyte, made while drawing Fig. 5 was valid, since the correction for ϕ at low $x \cdot i$ values is negligible.

According to Fig. 12, a measurable electrical potential, ϕ , appears only for high $x \cdot i$ values. For 1.0 M NaCl solution at $x \cdot i = 10^{-2} \text{ A/cm}$, the electrical potential could get up to some 0.035 V . For lower C_0 values higher electrical potentials are found (Fig. 13). In a 10^{-3} M NaCl solution at $x \cdot i = 10^{-2} \text{ A/cm}$, the electrical potential increases up to 0.200 V .

If the value of $x \cdot i$ is known, Fig. 13 can be used to evaluate the electrical potential, ϕ , under the experimental conditions of pitting potential measurement. There is not any precise information available, and only a rough estimation can be made. From the information in the literature, as mentioned above, we can assume that the current density inside a pit is of the order of 1 A/cm^2 . As for the size of the pits, when measuring the pitting potential value they are usually visible under the optical microscope, so they must be at least 10^{-2} cm big. Then, an estimate for $x \cdot i$ value,

under stable pitting growth, would be $x \cdot i \geq 10^{-2}$ A/cm. For such $x \cdot i$ values Eq. [26] is reduced to

$$x \cdot i \approx (n+1) \cdot C_0 \cdot D_{Me} \cdot F \cdot e + \psi \quad [27]$$

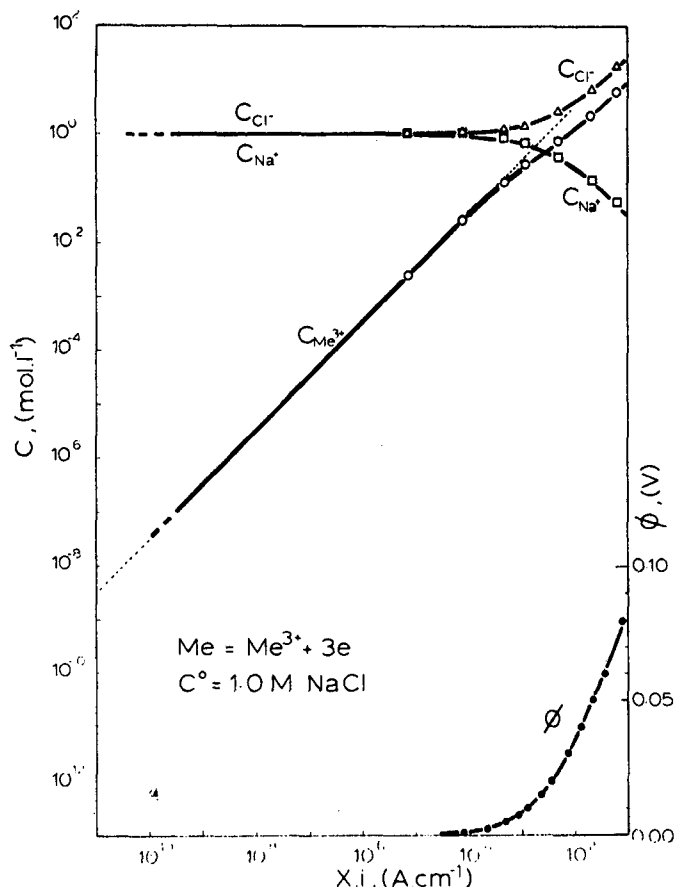


Fig. 12. Concentrations of Me^{3+} , Na^+ and Cl^- , and ϕ as a function of the product of the depth x and the current density i in a unidirectional pit.

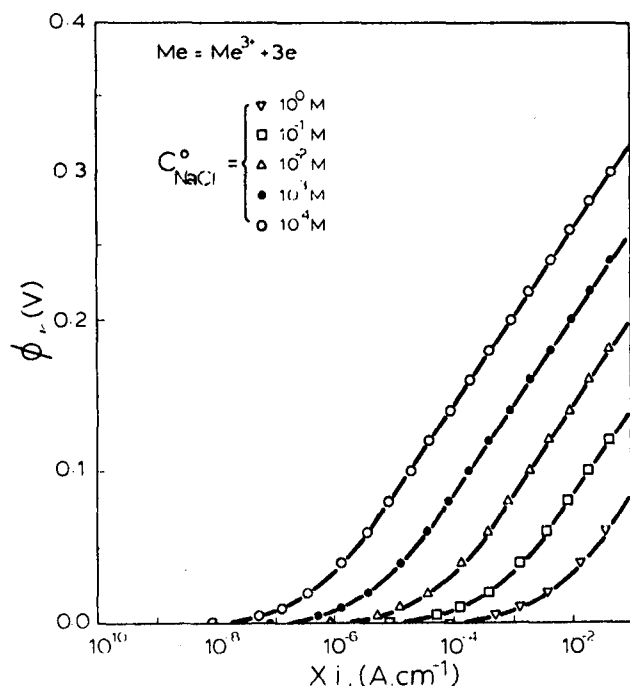


Fig. 13. Value of ϕ for various aggressive anion concentrations as a function of the product of the depth x and the current density i in a unidirectional pit.

If the pitting potentials are measured at approximately constant $x \cdot i$ values, then for two different NaCl concentrations we have

$$C_0^I \cdot e + \psi_I = C_0^{II} \cdot e + \psi_{II} \quad [28]$$

Replacing for the value of ψ , and taking logarithms

$$\ln C_0^I + \frac{F}{R \cdot T} \phi_I = \ln C_0^{II} + \frac{F}{R \cdot T} \phi_{II} \quad [29]$$

reordering and changing to decimal logarithms

$$\phi = \phi_0 - \left[\frac{R \cdot T}{F} \cdot \ln 10 \right] \cdot \log C_0 \quad [30]$$

Equation [30] would give the change of electrical potential inside the pit when the pitting potential is measured as a function of the NaCl concentration. This electrical potential should be subtracted from the measured pitting potential value to get the real pitting potential.

Equation [30] has a negative slope, with a value $b = 0.059V$ at $25^\circ C$. Table III shows experimentally measured slopes for pitting potentials vs. aggressive anion concentration. If, as assumed above, the $x \cdot i$ values are close to 10^{-2} A/cm, then the electrical potential inside the pits accounts for all the changes in the pitting potential found for iron (24), aluminum (44), aluminum-copper alloys (44), nickel (45), nickel-copper alloys (45), and zirconium (46), and perhaps for stainless steel (47). It also accounts for half the slope found for titanium (48). The agreement between Eq. [30] and the experimental results in Table III is very good in view of the fact that Eq. [30] is valid only for dilute solutions, and that the results in Table III have not been corrected for ohmic drops outside the pits.

Figure 12 also gives information about pit initiation conditions. According to some authors (12, 13) chloride ion buildup on the metal-solution interface would be the key factor for pit initiation. Figure 5 shows that the critical change in H^+ ion concentration is obtained with $x \cdot i$ values of the order of 10^{-6} A/cm. On the other hand, Fig. 12 shows that to get any significant change in the chloride ion concentration $x \cdot i$ values of the order of 10^{-4} - 10^{-3} A/cm are required. This means that for pit initiation, where x values are of the order of 10^{-6} cm, the critical proton concentration could be reached with current densities of 1 A/cm², while any measurable change in the chloride concentration would require current densities as high as 100-1000 A/cm². This consideration seems to exclude chloride ion buildup as a primary condition for pit initiation.

Mixed Electrolytes: NaCl + Na₂SO₄ Solutions

Sulfate ions are known to inhibit pitting of stainless steels in chloride solutions (35). Equations [18-20] can also be used to study a mixed electrolyte such as NaCl + Na₂SO₄ solutions. Equations [18] and [19] show that for anions of different charge, those with

Table III. Effect of the aggressive anion concentration on the pitting potential, experimental values for the slope of the curve $E_p = A - B \log C_X$

Metal or alloy	Slope B , (V)	Medium	Reference
Aluminum	-0.073	NaCl solution	44
Al-4% Cu	-0.046	NaCl solution	44
Al-Cu	-0.055	NaCl solution	44
Cu-65.8Ni	-0.074	NaCl solution	45
Cu-82.0Ni	-0.078	NaCl solution	45
Iron	-0.059	NaCl solution	24
Fe-18Cr-8Ni	-0.088	NaCl solution	35
Fe-18Cr-8Ni	-0.044	Pitlike solution	47
Nickel	-0.071	NaCl solution	45
Titanium	-0.110	KBr/HBr solution	48
Zirconium	-0.058	NaCl solution	46

the highest charge will be preferentially accumulated at the metal-solution interface.

Calculations made for a 0.1M NaCl + 1.0M Na₂SO₄ solution show that the main effect is a reduction of the electrical potential inside the pit due to the presence of the divalent SO₄⁼ ion. In the absence of sulfate ions the electrical potential, ϕ , for $x \cdot i$ equal to 10⁻² A/cm is 0.085V. The addition of 1.0M Na₂SO₄ to the solution reduces the electrical potential ϕ to 0.010V.

More significant effects are found with lower ionic concentrations. For mixtures of 0.1M Na₂SO₄ + 0.01M NaCl solution a remarkable buildup in sulfate ion concentration is found for $x \cdot i$ values higher than 10⁻⁴ A/cm (Fig. 14). Beginning with a SO₄⁼:Cl⁻ concentration ratio of 10:1, ratios as high as 100:1 or higher are easily reached. As soon as a pit is nucleated, a sulfate ion concentration builds up inside the pit, and eventually the pit is repassivated. The pits will not be able to grow any further and sulfate anion would act as pitting inhibitor in NaCl solutions. Figure 14 also explains the potential oscillations, under galvanostatic conditions, found by Szklarska-Smialowska and Janik-Czachor (26) for iron-chromium alloys, and by Szklarska-Smialowska (49) for nickel in NaCl + Na₂SO₄ solutions. As soon as the pits start to grow a buildup in sulfate ions takes place inside the pits, thus deactivating them. Later the diffusion of sulfate ions to the bulk solution reduces the content of sulfate ions inside the pit, and a continuous process of activation and deactivation of the pits is established.

Pitting Potential and Protection Potential

From potentiokinetic measurements, Pourbaix (50) reported two different potentials related to pitting: the pitting potential or rupture potential above which pitting starts, and the protection potential or the potential below which active pits will stop growing. According to Szklarska-Smialowska and Janik-Czachor (26) the real pitting potential is that which Pourbaix calls the protection potential. These authors found that this potential is equal to the galvanostatically measured pitting potential, and concluded that the higher pitting potential potentiokinetically found is the result of the measuring technique.

The present pitting model can be used to explain the existence of two potentials found in the potentiokinetic measurements. As mentioned above, the oxide film on the passive metal will suffer continuous breaks, thus exposing bare metal to the solution. The current density circulating in those fissures will be a function of the electrode potential. At each potential the cracks in the oxide will show a characteristic $x \cdot i$ value given

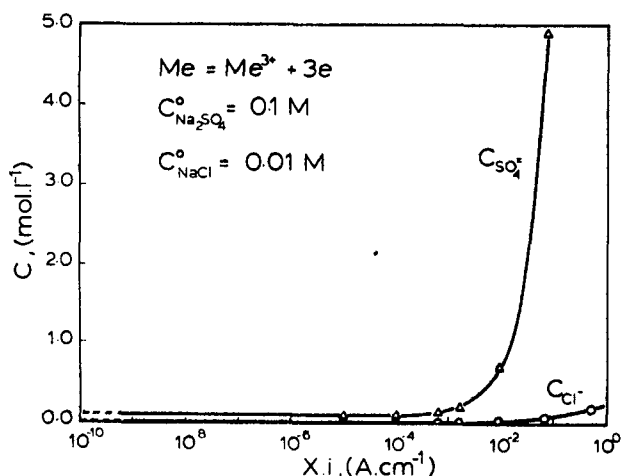


Fig. 14. Concentrations of SO₄⁼ and Cl⁻ as a function of the product of the depth x and the current density i in a unidirectional pit.

by the current density and by the length of the crack (Fig. 15a). As soon as the system reaches the minimum $x \cdot i$ value for pit growth, which is $x \cdot i = 1$ in Fig. 15, the pit will start to grow. If the potential remains constant, the current density will also be constant, but x will increase with time, as will $x \cdot i$ ($x \cdot i = 2$ in Fig. 15). If the potential is then lowered, the current density will drop, but the pit will continue to grow while the $x \cdot i$ value is higher than 1. This means that pitting will grow at potentials lower than the initiation potential. Finally the pit will stop either because the $x \cdot i$ value is lower than the minimum for pit growth, or because the electrode potential is lower than the corrosion potential inside the pit, and the acidification disappears as a result of hydrogen evolution.

Szklarska-Smialowska and Janik-Czachor's results can be used to find out whether the above-mentioned changes could take place during a potentiokinetic measurement. During potentiostatic measurements for Fe-16Cr in 0.7N Na₂SO₄ + 0.7N NaCl solution, pitting could start at potentials as high as +0.50V (SCE). The reported current density inside the pits is about 8 A/cm². Once started, the same pits will continue to grow at lower potentials, and they would stop at -0.05V (SCE). The current density inside the pits at this potential is 0.1 A/cm². Assuming a value for minimum $x \cdot i$ of 10⁻⁵ A/cm, the pits will start to grow at 0.50V (SCE) in defects of about 1.3×10^{-6} cm. When reducing the potential, the pits should have a minimum size of 10⁻⁴ cm to be able to grow at the current density of 0.1 A/cm². With a current density of 8 A/cm² a pit of 10⁻⁴ cm takes less than 0.4 sec to grow. Since the critical $x \cdot i$ values in Fig. 2-6 are lower than 10⁻⁵ A/cm, a much shorter time will be required to obtain the two potentials reported by Pourbaix.

Conclusions

As shown in previous publications (2, 3) there is a potential below which no localized acidification can be maintained on the metal-solution interface. This potential is given by the corrosion potential of the metal in the acidified solution, E_c^* . The alloying elements affect the pitting potential mainly by modifying the corrosion potential inside the pit. When measuring the pitting potential, a positive polarization, η , is added to the corrosion potential, E_c^* , to maintain a net anodic

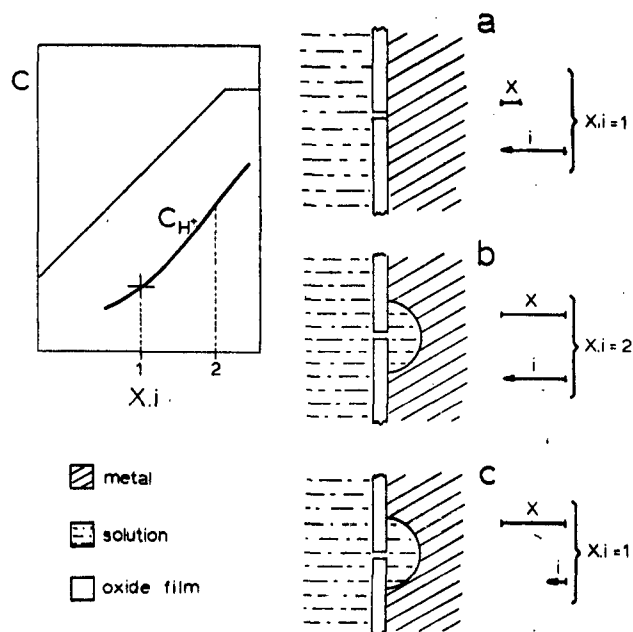


Fig. 15. Events leading to the measurement of pitting protection potentials different from pitting potentials in potentiokinetic experiments.

current density inside the pit, and secure the minimum $\alpha \cdot i$ value. From the present paper it is concluded that a further addition should be made, E_{inh} , when inhibitors like OH^- ions or buffer salts are present.

Since the current density inside the pit is high, another contribution due to the electrical potential, ϕ , must be accounted for. In this way, the measured pitting potential is the total of the above mentioned factors

$$E_p = E_c^* + \eta + E_{inh} + \phi$$

All the observations reported so far in the literature on the pitting potential can be explained by transport phenomena. Processes like competitive adsorption, salt formation, film contamination, etc., even though present during the pitting process, do not play a major role in fixing the pitting potential.

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PITTING POTENTIAL OF HIGH PURITY BINARY ALUMINIUM ALLOYS—I. Al-Cu ALLOYS. PITTING AND INTERGRANULAR CORROSION*

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Abstract—The effect of solute content on the pitting potential of Al-Cu alloys in 1M NaCl solutions was studied. In solution treated Al-Cu alloys the pitting potential of the alloy was found to increase with increasing Cu content. The maximum pitting potential value was limited by the solubility of Cu in the Al. It was found that, while the pitting potential of pure aluminium was *ca.* -0.52 V, the pitting potential of Al-5.22%Cu was -0.33 V.

The ageing of the alloy affected the pitting potential. The pitting potential of the aged alloy was found to be determined by the copper content of the solute depleted zones formed during ageing. The formation of G.P. zones did not modify the pitting potential of the alloy. The formation of θ'' phase, in an Al-3.5 Cu alloy, produced a decrease of 30 mV in the pitting potential, while the formation of θ' phase produced a decrease of > 100 mV.

As ageing was more rapid in the grain boundaries, there was a localized decrease in the pitting potential, which was followed by susceptibility of the alloy to intergranular corrosion.

INTRODUCTION

FROM THE several variables that affect the pitting potential of a metal, the alloy composition is known to be one of the most important. Numerous publications on the effect of the alloying elements on the pitting potential of stainless steels,¹⁻³ for example, show that certain alloying elements would increase the pitting potential of the alloy over the equilibrium potential of oxygen, making it resistant to pitting in aerated NaCl solutions.

In the present work the pitting potential of high purity binary Al-Cu, Al-Zn, and Al-Mg alloys, with solute contents ranging from 0-5% was studied. The aim was to evaluate the corrosion resistance improvement of aluminium alloys, and to get further information on the mechanism of pitting of metals. In this first part the behaviour of Al-Cu alloys was reported.

The binary Al-Cu alloys are of particular interest because of their age hardening properties.⁴ The solubility of copper in aluminium is known to diminish with temperature, going from 5.65%Cu at 548°C to $< 0.04\%$ Cu at room temperature.⁴ If an Al-4Cu alloy is water quenched from 530°C, all the copper remains in solid solution. If the alloy is slowly cooled to room temperature, the excess of copper precipitates as CuAl_2 , leaving a copper-impooverished aluminium matrix. Galvele and De Micheli⁵ found that the pitting potential of the overaged Al-4Cu alloy was *ca.* 0.1 V lower than that of the water quenched alloy.

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By heating the water quenched alloy, at temperatures above room temperature, artificial ageing occurs. Under these conditions intermediate stages of precipitation are found,⁴ leading to important changes in the mechanical properties of the alloy. If ageing takes place at a temperature below 200°C, the precipitation begins with the formation of very small, copper rich, disc shaped zones, known as G.P. zones. Further precipitation leads to the formation of the disc shaped θ'' phase, with a composition close to CuAl_2 . Ageing between 150 and 400°C leads to the formation of θ' phase, and ageing at temperatures over 300°C leads to the precipitation of the equilibrium θ phase.

The effect of the copper content of the solution treated alloy, as well as the effect of the different stages of ageing, on the pitting potential were studied. The pitting potential of the aged alloy was found to be determined by the copper content of the solute depleted zones produced during ageing.

EXPERIMENTAL METHOD

Measurements were made on Al-Cu alloys prepared from 99.99% Al and 99.999% Cu. A master alloy of ca. Al-33.3 Cu was prepared. Further dilutions were made by melting this alloy, with the appropriate amount of Al, in a zirconia crucible. After mixing the melt with a pure graphite rod, the molten metal was poured into graphite moulds. The composition of the alloys thus obtained are given in Table 1.

TABLE 1. ANALYTICAL COMPOSITION OF THE ALLOYS USED IN THE PRESENT WORK

Nominal composition:	Analytical composition:
Al-1% Cu	0.87% Cu
Al-2% Cu	1.97% Cu
Al-3% Cu	2.92% Cu
Al-3.5% Cu	3.33% Cu
Al-4% Cu	4.05% Cu
Al-5% Cu	5.22% Cu

The ingots were annealed for 8 h at 500°C, and hot rolled to 1 mm thick sheet, from which 30 × 10 mm specimens were cut. After the appropriate heat treatment, the specimens were fastened to a copper wire lead. The lead wire, the borders of the specimen, and one of its faces, were covered with epoxy resin, leaving an exposed area of ca. 1 cm². The resin was cured for 24 h at room temperature. The specimens were electropolished for 3 h in a Butyl cellosolvent 10% perchloric acid solution at 0°C and 30 V.

All specimens were solution treated for 2 h at 530° ± 2°C, and water quenched. All but some specimens of the Al-3.5 Cu alloy were used in the solution treated condition. Some of the specimens of the Al-3.5 Cu alloy were aged at 240°C for 5, 10, 15, 30, 45, 72, 120, 144 min, and 24 h. According to Hardy⁶ such a heat treatment would cover all the stages of ageing, from solution treated to over-aged, in a reasonably short time.

Some 2 mm thick specimens of the Al-3.5 Cu alloy were heat treated to obtain coarse grain specimens. After solution treating, these specimens were strained 3% by rolling and heated in a furnace from room temperature up to 530°C, with a heating rate of 100°C/h. They were kept at 530°C for 2 h and then water quenched. By this proceeding coarse grains, ca. 5 mm in dia., were obtained. Part of these coarse grain specimens were aged at 240°C. A second group of coarse grained specimens was aged for 16 h at 110°C, this heat treatment leading mainly to G.P. zones.⁷ Finally, a third group of coarse grain specimens was aged for 6 h at 180°C to obtain mainly θ'' phase.⁸ Before making electrochemical measurements, the grain boundaries of the coarse grain specimens were masked with epoxy resin.

All measurements were made in 1M NaCl solution, prepared from analytical grade reagents and distilled water. The solution was de-aerated with high purity nitrogen, further purified by bubbling

the gas through a solution of reduced chromium sulphate, by the method of Gilroy and Mayne.⁸ A Pyrex glass double-walled cell was used in the measurements, and the temperature was kept constant at $25 \pm 0.1^\circ\text{C}$. The potential was measured with a saturated calomel electrode, through a Luggin capillary. All potentials are reported on the normal hydrogen electrode (NHE) scale. The potential was kept constant with a L.Y.P. potentiostat-galvanostat (L.Y.P. Electronica, La Plata). The current was recorded with a Tacussel EPL-1 recorder, and the potential was measured with a Tacussel Aries 10000 millivoltmeter.

Hardness measurements were made on the coarse grain specimens with a Durimet microdurometer (Leitz-Wetzlar). A load of 1000 g was used, and the mean value of 5 different measurements is reported. The hardness measurements are reported in Vickers Hardness Numbers (VHN).

EXPERIMENTAL RESULTS

Pitting potential of solution treated Al-Cu alloys

Three different methods were used to measure the pitting potential of solubilized Al-Cu alloys. In the galvanostatic measurements a constant, anodic, current density of 1 mA/cm^2 was applied, and the potential changes were recorded. After *ca.* 2 h exposure a quasi-stationary potential was obtained. This potential was recorded as the alloy pitting potential. The measurements were repeated several times for each alloy, and a typical example of the measurements is given in Fig. 1.

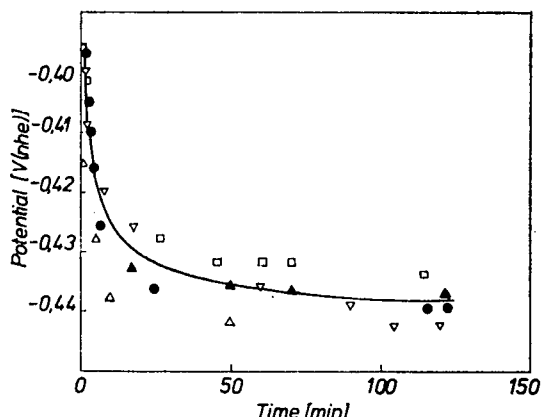


FIG. 1. Galvanostatic pitting potential measurement for solution treated Al-1%Cu in de-aerated 1M NaCl solution at 25°C . Measurements on four different specimens are shown. External current 1 mA/cm^2 .

The second method used was the potentiostatic technique. In this case the potential was gradually changed in steps of 10–20 mV each, with a wait at each potential until a steady current density was reached. Figure 2 shows two typical potentiostatic measurements. As previously reported for pure aluminium⁵ a range of potentials was found where the current density remained in the range of 10^{-6} A/cm^2 . At the pitting potential a sharp increase in the current density was observed.

The third method applied, used only with the Al-4Cu alloy, was the repassivation time technique introduced by Pessal and Liu.¹⁰ By this method the metal surface is scratched with a SiC point, and the repassivation time is measured. A sharp increase in the repassivation time is usually found at the pitting potential. The results obtained with Al-4Cu are shown in Fig. 3. In the case of Al-4%Cu alloy there was no sharp change in the repassivation rate at the pitting potential, as it was reported for instance

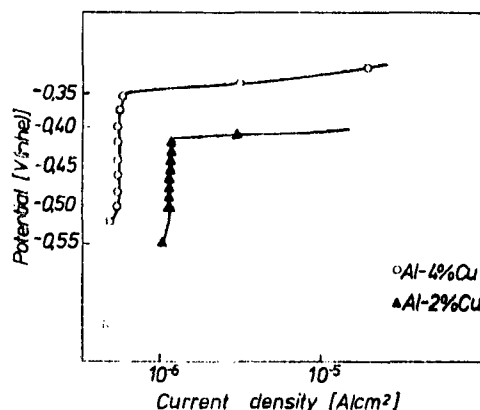


FIG. 2. Typical anodic polarization curves of two solution treated Al-Cu alloys, measured in de-aerated 1M NaCl solution at 25°C.

for stainless steel¹⁰ or for zinc.¹¹ Below the pitting potential, a sharp increase in the current density was observed after scratching the metal surface, and the current returned to the initial value after a few seconds. At the pitting potential, and above, the current was initially high and remained high after scratching. Pitting started before scratching, and the scratch line was not a preferential site for pit nucleation. This proved that the oxide film does not seem to interfere with pitting nucleation in aluminium, while it was reported to do so for stainless steel¹⁰ and for zinc.¹¹ Hence, the disruption of the oxide film by scratching the surface does not help pitting nucleation for Al-4Cu alloys in NaCl solutions.

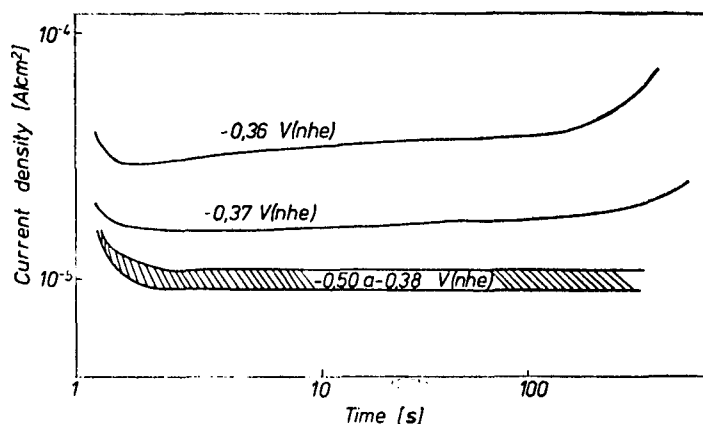


FIG. 3. Potentiostatic current-time curves recorded after scratching the surface of the specimen at various potentials. Solution treated Al-4%Cu in de-aerated 1M NaCl solution at 25°C.

All three methods gave similar pitting potential values. Figure 4 shows the mean pitting potential values for solution treated Al-Cu alloys in 1M de-aerated NaCl solution.

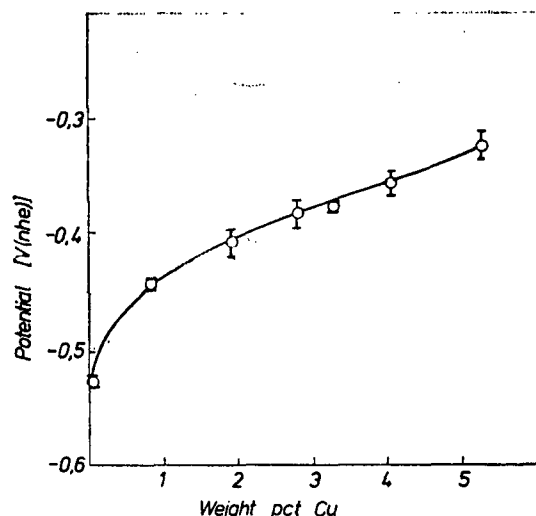


FIG. 4. Effect of the copper content on the pitting potential of Al-Cu alloys. Mean pitting potential values measured on solution treated Al-Cu alloys in de-aerated 1M NaCl solution at 25°C.

Potentiostatic current-time curves

At potentials higher than the pitting potential, the current density, at constant potential, increased with time. A relation of the type:

$$i = A \cdot t^b,$$

was found, where i is the current density measured on the whole specimen, t is the exposure time at constant potential, and A and b are constants. A value of $b = 1.2$ was found at a potential 30 mV higher than the pitting potential, and $b = 1.9$ at a potential 80 mV higher than the pitting potential. Relations of this type have been reported by various authors for pitting of different metals.¹²

The value of the constant A was affected by the pretreatment of the specimens. Figure 5 shows that an exposure of 2 h at a potential below the pitting potential gives afterwards a higher value of A than that without such pretreatment. It seems that the pretreatment increases the number of sites for pit nucleation.

Pitting morphology

At the very early stages of pit growth crystallographically shaped pits were observed, as shown in Fig. 6. After longer exposures the morphology was hidden by the corrosion products, shown in Fig. 7. A tendency to follow certain crystal planes was observed (Fig. 8). Electron microprobe analysis of pitted Al-Cu specimens showed copper enrichment inside the pits, as indicated in Fig. 9.

Effect of ageing on the pitting potential of Al-3.5Cu

The influence of artificial ageing on the pitting potential of Al-3.5Cu in 1M NaCl solution was studied. Galvele and De Micheli⁵ reported that the pitting potential of

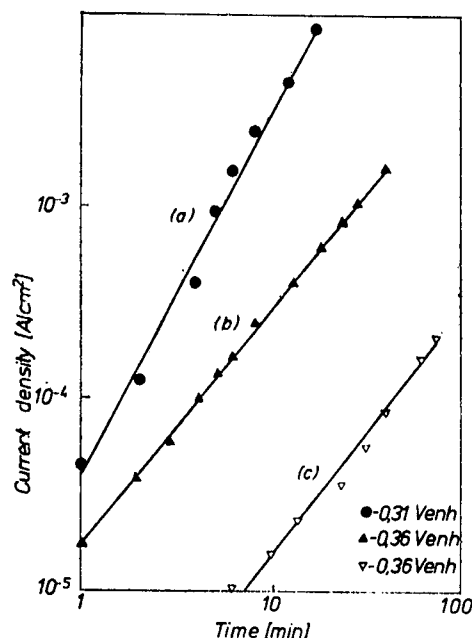


FIG. 5. Kinetics of pit growth at constant potential for solution treated Al-3 Cu in de-aerated 1M NaCl solution at 25°C. (a,b) After prepassivating the specimens for 2 h at a potential below the pitting potential. (c) without prepassivation;

the grain boundaries of an aged Al-Cu alloy was lower than that of the grain interiors. In the present work the development of this difference with time was studied. To measure the pitting potential of the grain bodies, without interference from the grain boundaries, coarse grained specimens with masked grain boundaries were used. The galvanostatic method was used to measure the pitting potentials. Figure 10 shows the results obtained with an alloy aged at 240°C. For the sake of comparison, the same figure shows the results of hardness measurements. The hardness measurements showed a dispersion of less than 5%, and were in good agreement with the values reported by Hardy.⁶

Small changes in the pitting potential value were found at the initial stage of ageing. The pitting potential begins to drop as soon as the hardness of the alloy starts to increase. It remains constant, at *ca.* - 0.38 V, if aged for up to 15 min. At the maximum hardness, 72 min ageing, the pitting potential drops to - 0.49 V, and 24 h later gets down to - 0.51 V.

At the early stages of heat treatment pitting of Al-3.5Cu was localized along certain lines, as shown in Fig. 11. The corroded lines were sensitive to crystallographic orientation, and changed their direction from one grain to another. The back-reflection Laue method¹³ showed that the corroded lines were coincident with the intersection lines of planes {111} and the surface of the specimen.

Intergranular corrosion of Al-3.5Cu

Direct measurement of the pitting potential of grain boundaries presents serious

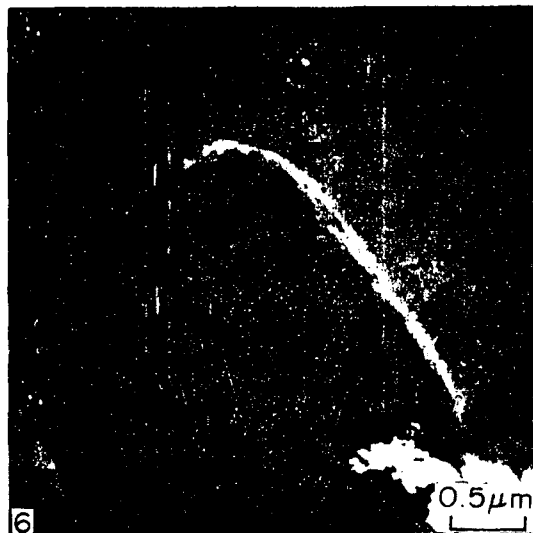


FIG. 6. Initial pitting morphology on solution treated Al-3Cu corroded in de-aerated 1M NaCl solution at 25°C.

FIG. 7. Pits on solution treated Al-3 Cu, occluded by the corrosion products. De-aerated 1M NaCl solution at 25°C.

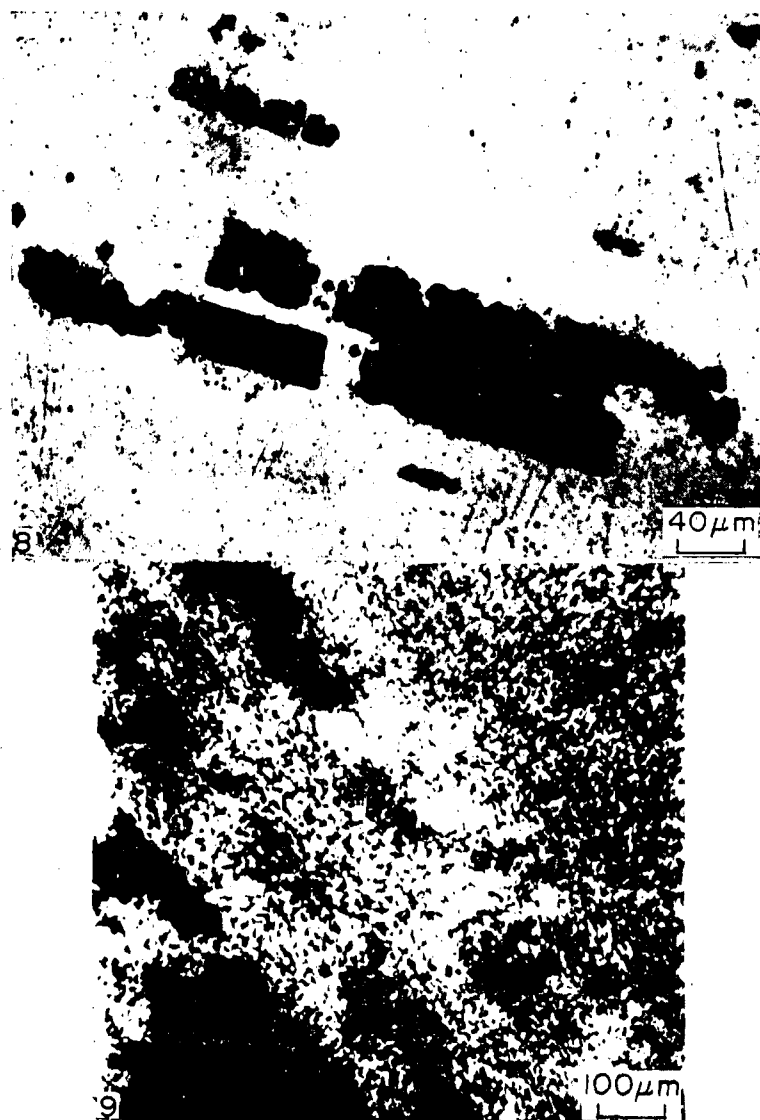


FIG. 8. Pits following certain crystal planes. Solution treated Al-3Cu corroded in de-aerated 1M NaCl solution at 25°C.

FIG. 9. Electron-microprobe analysis of Al-3Cu showing copper enrichment inside the pits. De-aerated 1M NaCl solution at 25°C. CuK α radiation.

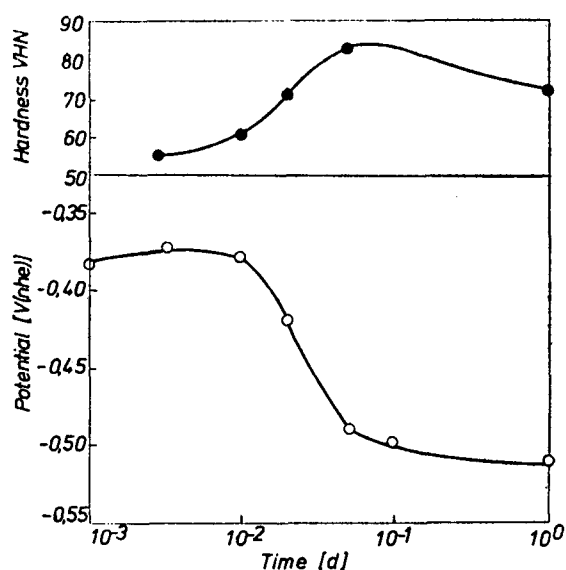


FIG. 10. Effect of ageing time on hardness and on pitting potential of Al-3.33Cu in de-aerated 1M NaCl solution at 25°C. Ageing temperature 240°C.

experimental difficulties. An indirect approach was attempted by studying the intergranular corrosion at constant potential. The aged Al-3.5Cu specimens were exposed in 1M NaCl solution at constant potential. After several hours exposure, the corroded specimens were slightly bent and were observed under the microscope. Evidence of intergranular penetration were looked for. The intergranular corrosion rate was found to be potential dependent, the lower the potential the lower the corrosion rate. A range of potentials below which no intergranular corrosion could be observed was found. This potential range was assumed to be the pitting potential of the grain boundaries. Figure 12 summarizes the observations made, the dotted line being the estimated pitting potential of the grain boundaries. The pitting potential difference between grain boundaries and grain bodies was found to appear at the very early stages of heat treatment. The difference in potentials decreased and eventually disappeared close to the maximum hardness value, as shown in Fig. 12. No intergranular corrosion was found for specimens aged for 72 min at 240°C.

Effect of θ'' phase and G.P. zones on the pitting potential of Al-3.5% Cu

The ageing of Al-3.5Cu at 240°C leads to the direct formation of θ' phase.⁴ At lower temperatures ageing begins with formation of G.P. zones and of θ'' phase.⁸ Coarse grained specimens, with masked grain boundaries, were used to determine the effect of these phases on the pitting potential of the alloy.

Specimens aged for 16 h at 110°C, where G.P. zones would predominate, showed a pitting potential equal to the solubilized alloy. Pits and corrosion product were aligned along {111} plane intersection lines as shown in Fig. 13. Similar results were found with specimens aged during several days at room temperature.



FIG. 11. Pit distribution on Al-3.33 Cu aged 15 min at 240°C and corroded at constant potential in de-aerated 1M NaCl solution at 25°C. The pits follow the {111} planes.

FIG. 13. Effect of G.P. zones on the corrosion distribution. Al-3.33Cu aged 16 h at 110°C, and exposed at constant potential in de-aerated 1M NaCl solution at 25°C. Pitted lines follow {111} planes.

FIG. 14. Pit distribution in presence of θ'' phase. Al-3.33 Cu aged 6 h at 180°C and exposed, at constant potential, to de-aerated 1M NaCl solution at 25°C. Pits follow {111} planes.

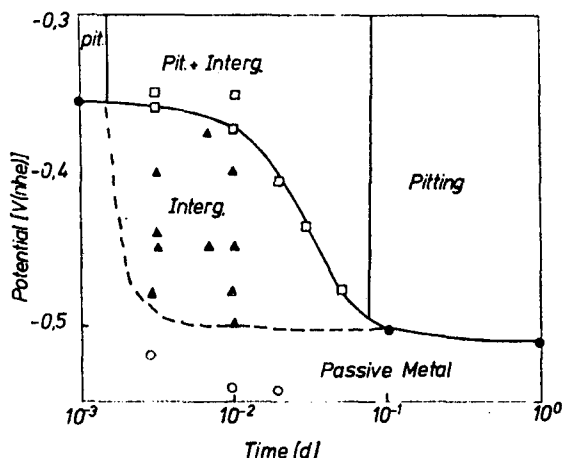


FIG. 12. Effect of ageing time on the corrosion behaviour, at constant potential, of Al-3.33 Cu in de-aerated 1M NaCl solution at 25°C. Ageing temperature 240°C. ○: passive; ▲: intergranular corrosion; □: pitting plus intergranular corrosion; ●: pitting.

Specimens aged for 6 h at 180°C, where θ'' phase should predominate, showed a pitting potential 30 mV lower than that of the solution treated alloy. In these specimens again the pits followed the traces of the $\{111\}$ planes on the metal surface, as shown in Fig. 14.

DISCUSSION

Effect of the alloying element on the pitting potential

Figure 4 shows that the copper content has a strong effect on the pitting potential of solubilized Al-Cu alloys. The higher the copper content, the higher the pitting potential. The effect is stronger for the first 1% of copper, the pitting potential dependence becoming almost linear for higher Cu contents, up to 5% Cu. Copper contents > 5% should not have a noticeable effect on the pitting potential. At higher concentrations the solubility of Cu in Al is exceeded, and a two phase system is formed. The double phase system is composed of a solid solution of Al-Cu with a copper content changing with temperature, but always < 5.65% Cu.⁴ The second phase will be the intermetallic Cu Al_2 , the pitting potential of which was measured by Galvele and De Micheli.⁵ The pitting potential reported for Cu Al_2 was close to the pitting potential of the solution treated Al-4%Cu alloy. The maximum pitting potential obtainable by alloying Al with Cu would be ca. -0.33 V. From a practical point of view no pitting resistant alloy could be produced by alloying Al with Cu, since in the presence of oxygen a pitting potential higher than -0.81 V would be necessary. Nevertheless, the effect of copper on the pitting potential of Al-Cu alloys is of particular interest since it gives a clue for the possible mechanism of pitting. This matter will be discussed more at length in the second part of this work, when comparing the present results with those of Al-Zn and Al-Mg alloys.

Effect of ageing on the pitting potential

Figure 10 shows the change of the pitting potential of Al-3.5 Cu as the alloy is aged at 240°C. By comparing Fig. 4 with Fig. 10 the changes in composition during ageing can be estimated, as shown in Fig. 15. In an alloy aged for up to 15 min no

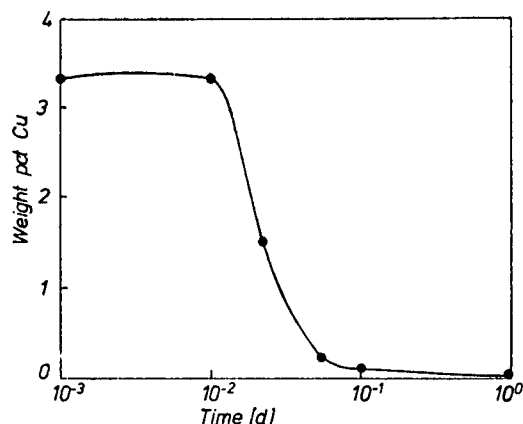


FIG. 15. Calculated copper content in the solute depleted zones formed during ageing Al-3.33Cu at 240°C. Values calculated from the data in Figs. 4 and 10.

important changes in the composition of the alloy are detectable. In the overaged alloy, on the other hand, θ' phase, with a composition of Cu Al₂, will be in equilibrium with a matrix of Al-0.25 Cu⁴. The pitting potential of the overaged alloy should be equal to that of the matrix. The pitting potential measured for an alloy aged for 24 h at 240°C is in good agreement with the value reported by Galvele and De Micheli⁵ for Al-0.2 Cu.

The changes in pitting potential observed between 15 and 144 min should indicate the changes in composition taking place in the alloy during the ageing process. Various authors^{4,14} have reported that during the precipitation process the matrix surrounding the θ' precipitates is depleted of copper. Using electron microscopic techniques Beck¹⁴ could detect a thin layer of depleted alloy surrounding the θ' precipitates. Other evidence that the change in the pitting potential is related to depletion around the θ' precipitates is given by Fig. 11. This picture shows that, for incipient precipitation of θ' phase, the pits are aligned along the slip planes. The literature reports that θ' phase appears in the form of discs orientated along the (100) planes of the matrix.⁴ These θ' particles were found to concentrate along slip planes of the matrix.¹⁶⁻¹⁷ Hence any attack that concentrates around the θ' precipitates should appear macroscopically arranged along the {111} planes, as shown in Fig. 11.

There is no information available on how the composition of the depleted zone changes with time to check the data in Fig. 15. According to Borelius *et al.*,¹⁸ θ' phase would be in equilibrium with a matrix of Al-0.42Cu, but there is no indication of how this composition would evolve with overageing.

Effect of G.P. zones and θ'' phase on the pitting potential

No difference in pitting potential was found for water-quenched specimens and specimens containing G.P. zones. If there were any local changes in the alloy composition, they were not detectable by the present measurements. On the other hand, the presence of θ'' phase caused a drop in the pitting potential of ca. 30 mV. This potential would correspond to an alloy of Al-2 Cu (Fig. 4). According to Beton and Rollason¹⁹, at 240°C the θ'' phase is in equilibrium with a matrix of Al-1.6 Cu, which is in very good agreement with the measurements reported above.

There is not much information available about the macroscopic distribution of these two phases. According to Graf,⁴ who based his views on theoretical considerations, both phases should be distributed at random in the matrix. Figures 13 and 14 show that the pits are distributed along slip lines. Due to the very small dimensions of both phases, it is difficult to find out their macroscopic distribution. Flink *et al.*²⁰ found in ageing the specimens at room temperature, under conditions where G.P. zones should be formed, that there was evidence of precipitation taking place along the slip lines. Silcock²¹ suggests that the conditions leading to a preferential distribution of θ' phase also apply to θ'' phase.

Intergranular corrosion

It is known that in age hardenable alloys the ageing process takes place much faster on the grain boundaries than on the grain bodies.^{22,23} Galvele and De Micheli⁵ showed that there is a difference between the pitting potential of the grain boundaries and that of the grain bodies, this difference being the cause for intergranular corrosion of aged Al-Cu alloys. Figure 12 shows the changes in pitting potential of the grain boundaries and of the grain bodies during ageing. After only 5 min ageing at 240°C the grain boundaries reached the potential of the overaged alloy, while the grain bodies did not show any change in pitting potential. Under further heat treatment the pitting potential of the grain boundaries remained constant. The pitting potential of the grain bodies, on the other hand, remained constant up to the moment when the hardness of the alloy started to increase. Then the pitting potential started to decrease, and, at the maximum hardness, it reached the value of the grain boundaries. At this point, as the difference between the pitting potentials on the alloy and the grain boundary cancels out, the susceptibility to intergranular corrosion disappears. According to Figs. 10 and 11, the most convenient heat treatment would be just at the maximum hardness, or with a slight overaging, since in this way the intergranular corrosion susceptibility would disappear. The results in Fig. 12 are in good agreement with the observations by Robertson,²⁴ who showed that the maximum susceptibility to intergranular corrosion of commercial Al-Cu alloys occurred just before the maximum hardness was reached.

CONCLUSIONS

From the present work it is concluded that:

1. The presence of dissolved copper in a matrix of aluminium increases the pitting potential of the aluminium alloy.
2. The higher the content of copper, the higher the pitting potential of the Al-Cu alloy, the increase in the pitting potential being limited by the solubility of copper in the aluminium.

3. Electron microprobe analysis showed copper enrichment inside the pits. A similar observation was made for Al-Zn alloys, and it will be discussed in the second part of this paper.

4. The heat treatment of the Al-Cu alloys affects the pitting potential because of the formation of copper depleted zones in the aged alloy.

5. When the solute depleted zones are localized along the grain boundaries, the alloy becomes susceptible to intergranular corrosion, the susceptibility being due to the lower pitting potential of the grain boundaries.

6. In the absence of grain boundaries, the pitting potential of the alloy is defined by the composition of the depleted zones formed around the phases precipitated during ageing.

7. Solute depletion around θ'' and θ' phases was detected by pitting potential measurements. The solute distribution change that takes place during the formation of G.P. zones was not detectable by the pitting potential measurement.

8. If an Al-3.5Cu alloy is aged to its maximum hardness at 240°C, the pitting potential of the alloy drops to the value of the grain boundaries, this giving an aged alloy immune from intergranular corrosion.

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Transport Processes and the Mechanism of Pitting of Metals

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ABSTRACT

A pit model was developed on the assumption that the metal ions hydrolyze inside the pits and that the corrosion products are transported by diffusion. Concentrations of Me^{2+} , $\text{Me}(\text{OH})^+$, and H^+ ions, as a function of pit depth and current density, for Zn, Fe, Ni, Co, Al, and Cr were calculated. The main reason for passivity breakdown at the initial stages of pit growth, was found to be the localized acidification due to metal ions hydrolysis. Assuming a critical pH value for pit initiation, the following experimental facts could be explained: (i) the effect of the external pH on the pitting potential of Fe and stainless steel; (ii) the effect of sodium borate concentration on the pitting potential of Zn; (iii) the effect of weak acid salts on the pitting potential of Al; (iv) the oscillations of the electrode potential of stainless steel and nickel in solutions of $\text{Cl}^- + \text{SO}_4^{2-}$ ions; (v) the existence of a pitting inhibition potential; and (vi) the existence of a pitting protection potential. Through analysis of the transport processes inside a pit it was also concluded that the pitting potential of a metal should change with the Cl^- ion concentration according to the equation

$$E_p = E_p^\circ - B \cdot \log [\text{Cl}^-]$$

$B = 0.059\text{V}$ being the slope of the curve at room temperature.

It is a generally accepted fact that pitting starts at a certain critical potential, known as pitting potential (1). Yet the nature of such a potential still remains uncertain. Several explanations have been given, such as zero charge potential, potential-induced ion migration, electrically produced mechanical breakdown, competitive adsorption, salt-formation equilibrium potential, etc. (1). Nevertheless, none of these mechanisms could account for the way in which variables such as pH, ionic concentration, and inhibitor concentration affect the pitting potential. In recent publications, Wexler and Galvele (2) and Alvarez and Galvele (3) reported that the pitting potential was the minimum potential at which localized acidity could be maintained inside a pit. The present paper, based on simple transport equations shows that such acidification can be obtained even at the very early stages of pitting, and that, as was recently reported (4), transport calculations inside the pit explain why variables such as an aggressive anion concentration, nonaggressive anion concentration, external pH, presence of weak acid salts, and alloying elements modify the pitting potential of a metal.

It is concluded that most of the observations made so far on the pitting potential can be explained simply by transport phenomena, and that processes like competitive adsorption, salt formation, film contamination,

etc., even though present during the pitting process, do not play a major role in fixing the pitting potential.

Several authors have shown that the solution inside a pit, as well as that inside a crack or crevice, has a composition quite different from that in the bulk solution (5-10). As early as 1937 Hoar (11) proposed a mechanism of "autocatalytic" pit propagation, which considered that the main cause of pitting was the drop of pH inside the pit. Other authors (12, 13) postulated that the condition for pitting initiation was an increase of chloride ion concentration on the metal-solution interface. In a similar way Kaesche (14) considered the formation of saturated AlCl_3 inside a pit the necessary condition for the pitting of aluminum.

After studying the pitting of iron in various environments, Vetter and Strehblow (15, 16) questioned all mechanisms based on local composition changes. These authors assumed that the causes of pitting should be present in all the stages of pit growth, even in the smallest detectable pits. Pits as small as one micron in diameter, growing with current densities of the order of $1-9 \text{ A/cm}^2$ were detected in iron. According to their calculations, the origin of pitting could not be attributed to changes in pH, in potential, or in ionic concentration, since such changes would be meaningless in the initial stages of pitting. However, the pitting model developed by Vetter and Strehblow cannot be taken as a realistic model; according to their model the pH inside the pit increases during pit growth, while in practice the pH was found to decrease (5-10).

Pickering and Frankenthal (17) developed a much simpler pit model, and they analyzed the changes in

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Key words: pitting of metals, pitting potential, transport processes, pitting inhibitors.

composition to be expected in the pit. Nevertheless, the model by Pickering and Frankenthal could not be applied in its original form to all pitting cases because, again, it would lead to pH increases inside the pit as the pit grew.

Pit Model

In the present paper a pit model similar to that developed by Pickering and Frankenthal is used (Fig. 1). Their model was developed for a metal that would dissolve in an acid solution and consequently always resulted in a decrease in the pH inside the pit. To overcome this difficulty, the model used herein assumes that the pH of the bulk solution can take any value from acid to alkaline values.

The model by Pickering and Frankenthal takes into consideration the transport of ions both by diffusion and by electrical migration. In this way, complex formulae are obtained when the study of the hydrolysis of the metal ions, or modifications of the external pH are attempted. Since, as shown by Vetter and Strehblow (16), pitting initiation takes place with small changes in the electrolyte composition, it is reasonable to assume that the bulk solution acts as a supporting electrolyte for the metal ions and the hydrolysis products produced during pitting initiation. In this way the transport equations are considerably simplified, since only transport by diffusion remains important. The following are the main modifications introduced in the model used in the present paper:

(i) Instead of a single charge transfer reaction, a more general expression is used for the anodic reaction taking place inside the pit



The dissolution reaction is assumed to take place at the bottom of the pit, (Fig. 1) as in the model by Pickering and Frankenthal. No reaction takes place at the walls of the pit. In this way a unidirectional pit model is obtained, with a considerable simplification in the mathematical treatment.

(ii) Reaction [1] is assumed to occur in a sodium salt of an aggressive but noncomplexing anion. The pH of the bulk solution could have any value, and is given as a boundary condition.

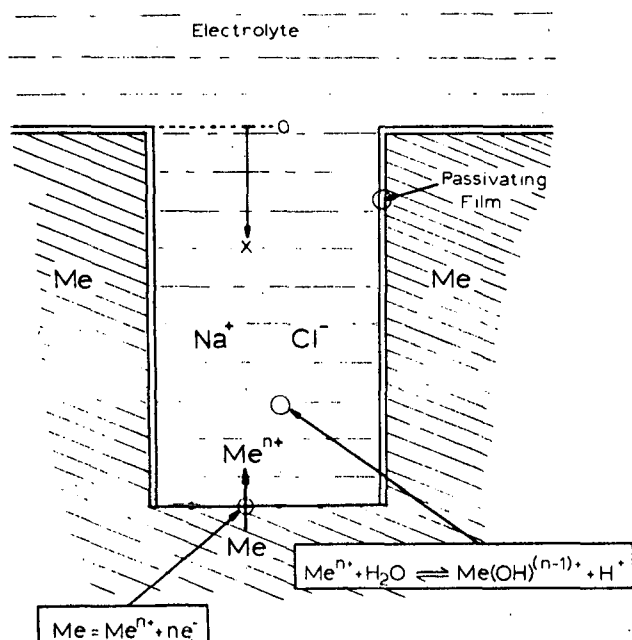
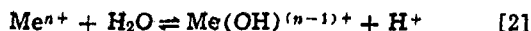


Fig. 1. Unidirectional pit model

(iii) It is assumed that reaction [1] is followed by a hydrolysis equilibrium of the type

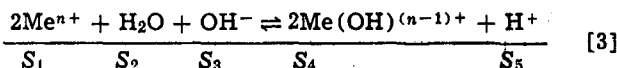


and that this equilibrium is very quickly reached (18).

Reaction [2] is a simplified description of the processes taking place inside a pit. Polynuclear complexes could be formed, or further degrees of hydrolysis could occur. Nevertheless, reaction [2] will give the minimum degree of acidification expected inside a pit. On the other hand, either no polynuclear complexes are reported for the metals used in the present work, or their formation rate is very slow (18, 19).

(iv) The last, and most important, modification introduced to the Pickering and Frankenthal model is the assumption that the aggressive anion salt acts as a supporting electrolyte for the ionic species formed in reactions [1] and [2].²

Since it is assumed that the bulk solution could have any pH value, reaction [2] has to be rewritten to account for the contribution of the OH⁻ ions at pH values higher than 7



From Eq. [3] we find that inside the pit there are five species (S₁-S₅), the concentrations of which should be calculated. The detailed mathematical treatment for a system like this can be found in Vetter's work (20). The five unknown concentrations are calculated by resolution of the five following equations: the flow of the species containing Me atoms will be given by

$$D_1 \frac{dC_1}{dx} + D_4 \frac{dC_4}{dx} = \frac{i}{n \cdot F} \quad [4]$$

the flow of the species containing O atoms will be given by

$$D_2 \frac{dC_2}{dx} + D_3 \frac{dC_3}{dx} + D_4 \frac{dC_4}{dx} = 0 \quad [5]$$

and the flow of the species containing H atoms will be given by

$$2D_2 \frac{dC_2}{dx} + D_3 \frac{dC_3}{dx} + D_4 \frac{dC_4}{dx} + D_5 \frac{dC_5}{dx} = 0 \quad [6]$$

Finally, the two following equilibrium relations must be considered

$$*K_1 = \frac{C_4 \cdot C_5}{C_1} \quad [7]$$

which is the law of mass action applied to reaction [2] and

$$K_w = C_3 \cdot C_5 \quad [8]$$

which is the ionic product of water. In the above equations, D_j is the diffusion coefficient in cm²/sec, C_j is the concentration in mole/cm³ of the species j, n is the charge of the metal ion as given in Eq. [1], F is the Faraday constant, *K₁ is the equilibrium constant of reaction [2], i in A/cm² is the current density of reaction [1], and x is the pit depth in cm where x = 0 at the opening of the pit.

The assumed boundary conditions for x = 0 are C₁ = 0; C₃ = K_w · 10^{-pH} mole/liter; C₄ = 0; and C₅ = 10^{-pH} mole/liter. As a first approximation all the diffusion coefficients, except those for H⁺ and OH⁻ ions, are taken as equal to 10⁻⁵ cm²/sec; therefore D₁ = D₂ = D₄ = 10⁻⁵ cm²/sec, D₃ = 5.3 × 10⁻⁵ cm²/sec, and D₅ = 9.3 × 10⁻⁵ cm²/sec. The equilibrium constants used were taken from the review by Silen and

² This assumption is exact only when the supporting electrolyte is in great excess over the electroactive species. However, it has been shown [Ref. (20), p. 175] that even a minor addition of supporting electrolyte of the order of magnitude of the concentration of the electroactive species reduces to a large degree the influence of the electric field.

Table I. Hydrolysis constants and solubility constants (19)

Metal	Hydrolysis constant ($\ast K_1$)	Solubility constant (K_{so})
Cr ³⁺	10^{-4} (M ¹⁻³)	10^{-80} (M ⁴⁻¹⁻⁴)
Fe ²⁺	10^{-7} (M ¹⁻³)	$10^{-16.1}$ (M ³⁻¹⁻⁹)
Co ²⁺	10^{-10} (M ¹⁻³)	10^{-18} (M ³⁻¹⁻⁹)
Ni ²⁺	10^{-10} (M ¹⁻³)	10^{-18} (M ³⁻¹⁻⁹)
Zn ²⁺	$10^{-9.15}$ (M ¹⁻³)	$10^{-16.6}$ (M ³⁻¹⁻⁹)
Al ³⁺	$10^{-5.05}$ (M ¹⁻³)	10^{-33} (M ⁴⁻¹⁻⁴)

Martell (19), and the values chosen for the calculations are reported in Table I.

By multiplying Eq. [5] by 2 and subtracting from Eq. [6], the terms for S_2 are eliminated

$$-D_3 \frac{dC_3}{dx} - D_4 \frac{dC_4}{dx} + D_5 \frac{dC_5}{dx} = 0 \quad [9]$$

Equation [8] is solved for C_3 , and this expression is substituted for C_3 in Eq. [9]. Equation [7] is solved for C_1 , and the resultant expression is substituted for C_1 in Eq. [4]. By integration, the following two equations are obtained

$$\frac{n \cdot F \cdot D_1}{\ast K_1} C_4 \cdot C_5 + n \cdot F \cdot D_4 \cdot C_4 = x \cdot i + k \quad [10]$$

$$D_5 \cdot C_5 - D_3 \cdot K_w \frac{1}{C_5} - D_4 \cdot C_4 = k' \quad [11]$$

Using the above-mentioned boundary conditions, constants k and k' are calculated. Equation [11] is solved for C_4 , and the resulting expression is substituted for C_4 in Eq. [10]. By giving values to C_5 , the values of the parameter $x \cdot i$ are calculated. With the same values of C_5 , the values of C_4 are calculated in Eq. [11]. Then C_1 is calculated in Eq. [7] and C_3 in Eq. [8]. No calculations are made for C_2 .

Ionic Concentration Diagrams

The above-mentioned calculations were made for the ionic concentration diagrams of the following systems: Zn/Zn²⁺ (Fig. 2); Fe/Fe²⁺ (Fig. 3); Ni/Ni²⁺ (Fig. 4); Al/Al³⁺ (Fig. 5); and Cr/Cr³⁺ (Fig. 6). The diagram in Fig. 4 applies also to Co/Co²⁺, since the same $\ast K_1$ value was used for Ni and for Co (see Table I).

The pH values for the bulk solution were chosen so that the oxide film might be under thermodynamically stable conditions according to Pourbaix diagrams (21). The pH values used were pH 7 for aluminum and chromium, pH 9 for zinc, and pH 10 for iron, nickel, and cobalt.

The straight line C_{Me} in the diagrams indicates the total of the concentrations of all the species containing Me atoms. The line is broken for a concentration of 10 mole/liter to indicate that saturation of the Me salt should be reached. Actually, the present treatment is valid only for diluted solutions, and deviations from the calculated diagrams should be expected for such high concentrations.

The ionic concentration diagrams give the concentrations of Me^{n+} , $Me(OH)^{(n-1)+}$, and H^+ ions as functions of $x \cdot i$. If the current density inside the pit is known, the diagram will show the ionic concentrations along the pit. On the other hand, at a certain given pit depth the diagram will show the current density required to get a certain change in the ionic concentration. For example, let us consider the case of iron in 1.0M NaCl solution at pH 10 (Fig. 3). Let us assume that the iron sample has two pits different in size, one of them 10^{-6} cm deep and the other 10^{-4} cm deep. If the current density inside the pits is 1 A/cm², the $x \cdot i$ values will be 10^{-6} and 10^{-4} A/cm, respectively. From Fig. 3 it is concluded that the composition at the bottom of the shallower pit will be 10^{-5} M Fe²⁺, 5.0×10^{-4} M Fe(OH)⁺, and pH 8.5. On the other hand, the

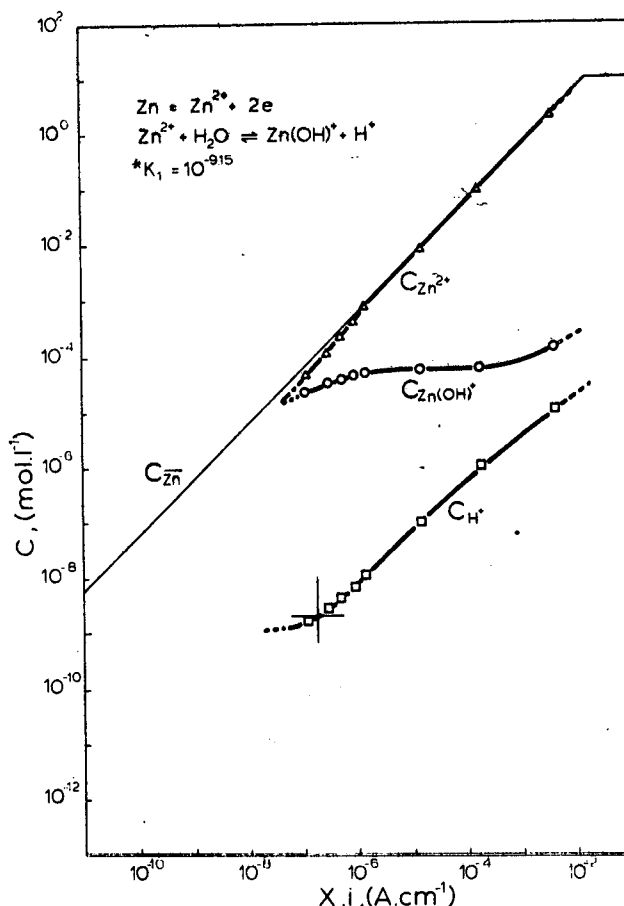


Fig. 2. Concentrations of Zn²⁺, Zn(OH)⁺, and H⁺ as a function of the product of the depth x and the current density i is a uni-directional pit.

composition at the bottom of the deeper pit is going to be: 5.0×10^{-2} M Fe²⁺, 5.6×10^{-4} M Fe(OH)⁺, and pH 5.1. The diagram predicts that the larger changes in composition and in pH will be found at the bottom of the deeper pit.

We can also compare two different specimens, with pits of equal size, but with different current densities inside the pits. For example, if the pits are 10^{-3} cm deep in both specimens, but the current density inside the pits is 10^{-1} A/cm² in one of the samples and 10^{-4} A/cm² in the other, the composition at the bottom of the pits is going to be 5.0×10^{-2} M Fe²⁺, 5.6×10^{-5} M Fe(OH)⁺, and pH 5.1 in the first specimen ($x \cdot i = 10^{-4}$ A/cm), and 5.0×10^{-8} M Fe²⁺, 5.0×10^{-5} M Fe(OH)⁺, and pH 9.95 in the second ($x \cdot i = 10^{-7}$ A/cm). While important changes in composition should occur with current densities of 1 A/cm², virtually no changes should be expected for a current density of 10^{-4} A/cm².

No assumptions are made as to the way in which the current density could be obtained. In practice, it will mean that the electrode potential is properly changed. In most cases of acid solutions, such as those inside a pit, a logarithmic relation between current density and electrode potential should be expected.

Figures 2-6 show that, in spite of what Vetter and Strehlow have indicated, the H⁺ ion concentration inside the pit undergoes important changes when the pit size or the current density inside the pit is changed. It is also shown that, as found in practice, the pH inside the pit is lower than that of the bulk solution. From the data in Fig. 3, the pH along a crevice or a crack in iron can be estimated. It was found (Fig. 7) that the pH predicted by the present model is somewhere between 3 and 4, for an external pH of 10. This

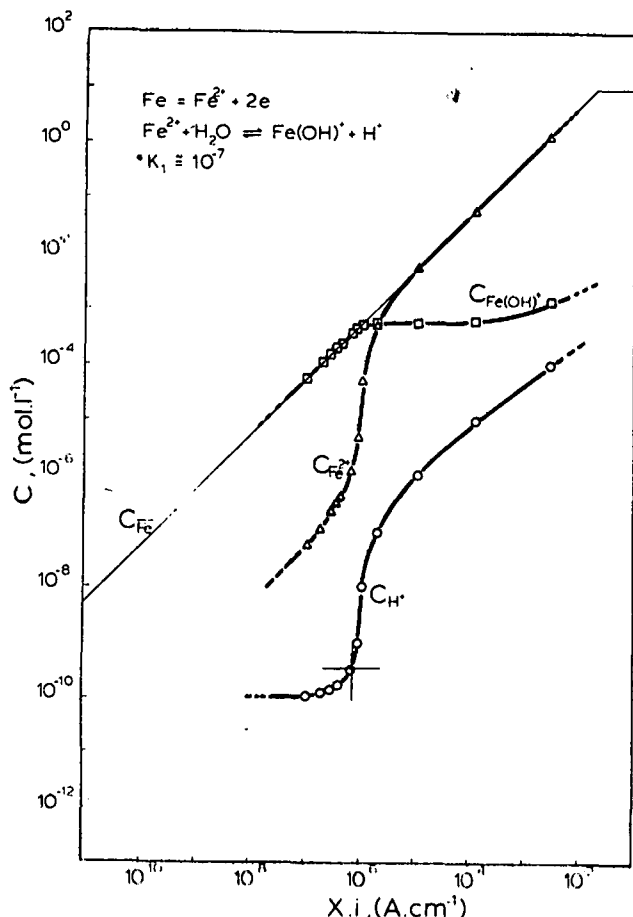


Fig. 3. Concentrations of Fe^{2+} , Fe(OH)^+ , and H^+ as a function of the product of the depth x and the current density i in a uni-directional pit.

prediction is in good agreement with the experimental observations reported by Smith, Peterson, and Brown (6).

Critical H^+ Ion Concentration

To be able to use the present ionic concentration diagrams in the study of pitting it is necessary to find the minimum degree of acidification necessary for sustained pit activity.

As a first approximation, the criterion used by Pourbaix for the potential vs. pH diagrams (21) was applied in the present paper. Pourbaix separates the passivity zones from the corrosion zones as follows. The solubility product of the passivating oxide film being known, the pH value at which such oxide film will be in equilibrium with a solution containing traces of metal ions is calculated. The concentration of the metal ions is arbitrarily taken as equal to 10^{-8} mole/liter. Such pH values are calculated herein by using the K_{so} values reported in Table I. The calculated pH values are indicated in Fig. 2-6 by means of a cross (+) on the H^+ ion concentration line. The pH values calculated are pH 9.5 for iron, cobalt, and nickel; pH 8.7 for zinc; pH 6.0 for chromium; and pH 5.0 for aluminum. All these values are in reasonably good agreement with those reported by Pourbaix (21), with the exception of chromium which, according to Pourbaix, should be somewhere between 3.5 and 4.8.

Due to the scattering of the K_{so} reported values (19), and to the arbitrarily choosing 10^{-8} mole/liter as the metal ion concentration, the calculated critical pH values have an error of at least plus or minus one unit pH. This criterion of choosing the critical pH values is clearly a rough approximation and experimental information is necessary. In the case of zinc,

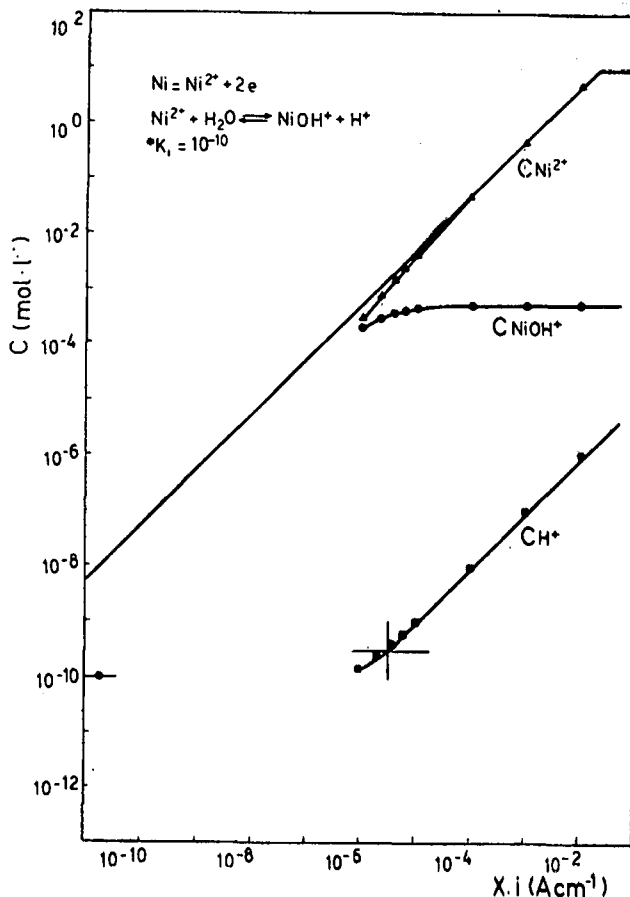


Fig. 4. Concentrations of Ni^{2+} , Ni(OH)^+ , and H^+ as a function of the product of the depth x and the current density i in a uni-directional pit.

the pH value calculated, 8.7, is in good correspondence with the experimental results reported by Davies and Lotlikar (22). These authors found that zinc, in galvanostatic measurements, was passivated in solutions of pH 9.2, 10.0, and 11.0, and did not get passive in solutions at pH 8.2.

For iron the estimated pH value was 9.5. Vetter and Strehblow (23) reported passivity to pitting transitions for iron at pH values as low as 8.0. On the other hand, Alvarez and Galvele (24) found that the pitting potential of iron is pH independent for pH values lower than 10, and pH dependent at values higher than 10. It was then concluded that the critical pH for iron should be around 10.

No experimental information is available for other metals or alloys. Nevertheless, the concept of a critical pH for depassivation was applied to stainless steels by Defranoux and Tricot (25). These authors found that the presence of chloride ions produced an increase in the critical pH for depassivation of stainless steels.

Current Density inside the Pits

To be able to use the ionic concentration diagrams it is also necessary to know the current density inside the pits. For aluminum in NaCl solutions, Kaesche (14) reported that the minimum current density inside the pits was recorded at the pitting potential and had a value of 0.3 A/cm^2 . For aluminum in 4M NaCl solution, the current density inside the pits increased with the electrode potential, following what seemed to be a logarithmic law with a slope of $b = 0.150 \text{ V}$. At a potential 0.100 V over the pitting potential the current density inside the pits was close to 1.1 A/cm^2 .

Szklarska-Smialowska and Janik-Czachor (26) measured the current densities within pits for Fe-16Cr alloy in $0.7N \text{ NaCl} + 0.7N \text{ Na}_2\text{SO}_4$ solution. They

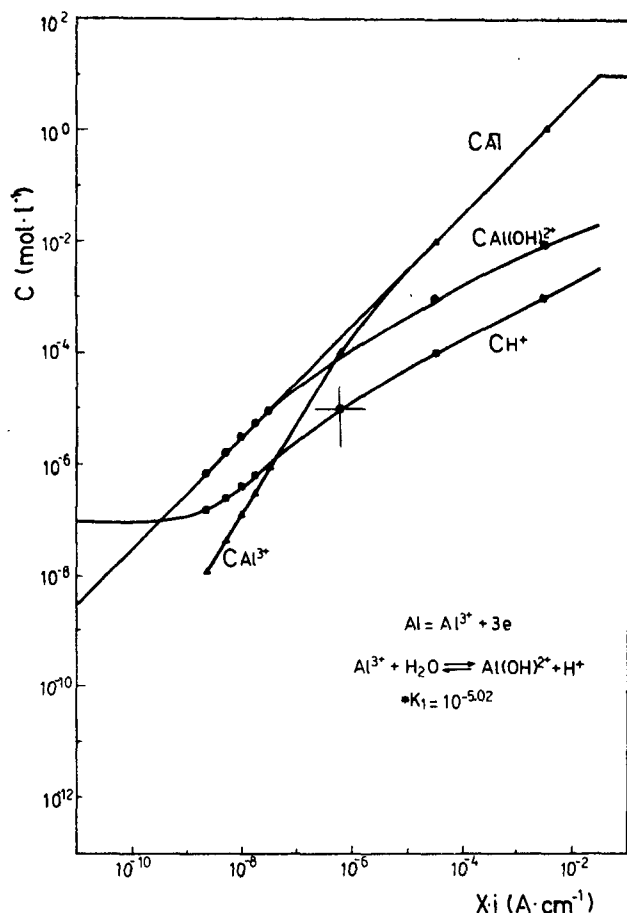


Fig. 5. Concentrations of Al^{3+} , $\text{Al}(\text{OH})^{2+}$, and H^+ as a function of the product of the depth x and the current density i in a unidirectional pit.

found that the current density inside the pits was a function of potential, and according to the interpretation made by Sato *et al.* (27) it would follow a logarithmic law with a slope of $b = 0.220\text{V}$. For the Fe-16Cr alloy Szklarska-Smialowska and Janik-Czachor reported a pit initiation potential of about 0.50V (SCE) and a pit passivation potential of -0.05V (SCE). From Sato's paper it is inferred that the current density at the pit initiation potential was about 8.0 A/cm², while at the pit passivation potential it dropped to 0.1 A/cm².

Sato *et al.* (27) reported that in austenitic stainless steels, for potentials higher than 0.60V (SCE) the current density inside the pits became potential independent, reaching a value of 8 A/cm².

Schwenk (28), working with 18/10 chromium-nickel austenitic stainless steels, reported a current density inside the pits, at the pitting potential, of the order of 0.5 A/cm². He also found that the reaction inside the pit followed a Tafel law, with a slope of $b = 0.087\text{V}$.

For pure iron, Vetter and Strehblow (15) reported pit initiation current densities ranging from 0.9 up to 2.0 A/cm². For nickel pits of 1 μ diameter, Vetter (29) reported current densities as high as 50-70 A/cm².

From the above-mentioned results, it can be safely assumed that the current density inside a pit, at the initiation stage, is of the order of 1 A/cm².

Pit Initiation Conditions

Figures 2-6 show that for most of the metals studied the critical pH is reached with $x \cdot i$ values lower than 10⁻⁶ A/cm. Since at pit initiation conditions the current density inside the pit is at least 1 A/cm², it is concluded that the necessary acidification can be obtained

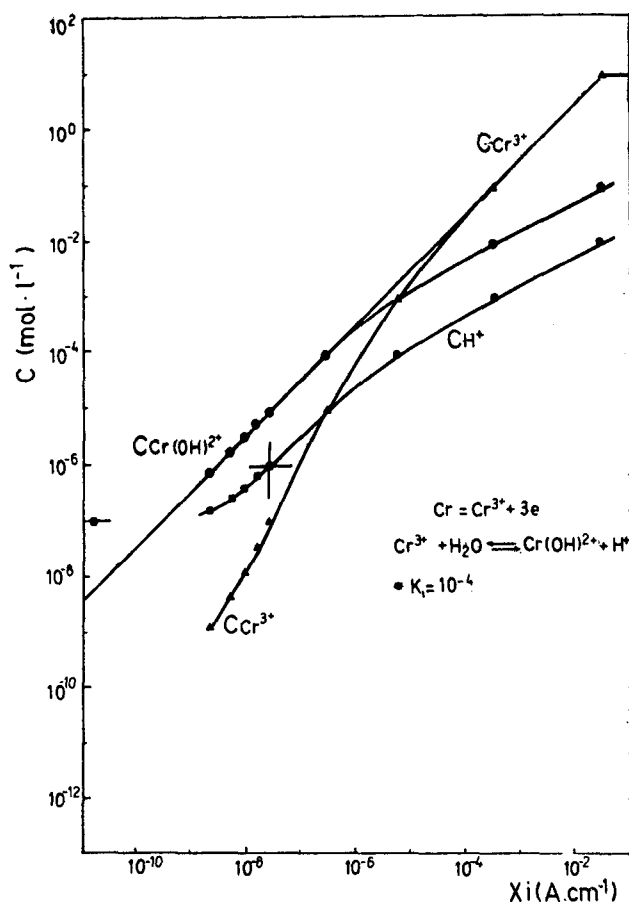


Fig. 6. Concentrations of Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, and H^+ as a function of the product of the depth x and the current density i in a unidirectional pit.

in pits as small as 10⁻⁶ cm. This means that a crack in the passivating oxide film would give a diffusion path long enough to reach the critical pH. If such cracks are present, it would only be necessary to apply a potential high enough to reach the above-mentioned current density.

As for the existence of such cracks in the passive oxide film, there is abundant literature in favor of it. Current oscillations below the pitting potential were reported for aluminum (30), for zinc (31), and for stainless steels (32) showing the presence of a film rupture-reformation process. Vetter and Strehblow (16) reported that a change in the electrode potential, just before the injection of chloride ions, produced a noticeable increase in the pit density in iron. This was interpreted as a production of defects in the oxide film as a result of the potential shift. Sato (33) calculated the tensions induced in the oxide film by electrostriction, and concluded that they were high enough to produce mechanical breakdown of the oxide film. Fromhold (34) also found that the transport of ions through the passive film would produce stresses large enough to cause mechanical breakdown of the oxide film.

It can be concluded that film breakdown is constantly occurring on a passive metal. Nevertheless, the exposure of bare metal does not necessarily lead to localized corrosion. Straining metal experiments (2, 3, 30) have shown that the exposure to bare metal does not lead to pitting, unless the electrode potential is equal to, or higher than, the pitting potential.

Once the crack in the passive film is produced, if the electrode potential is high enough, a net anodic current density will circulate through the fissure. From the diagrams in Fig. 2-6 it should be possible to predict at which current density the critical acidification can be reached, or if the metal will repassivate.

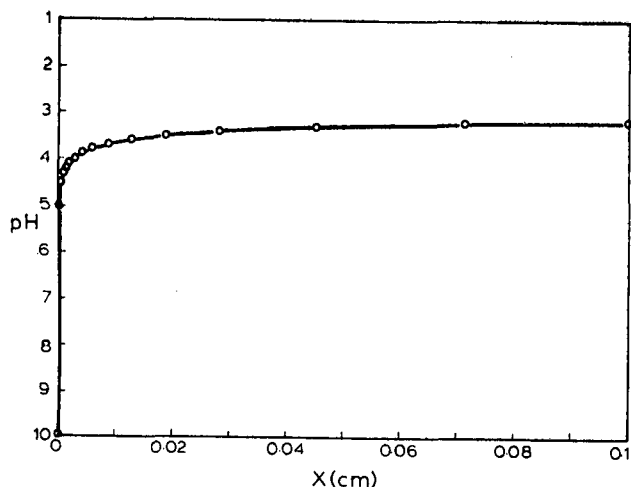


Fig. 7. Calculated pH profile for iron along a pit or crevice. External pH = 10, current density = 1 A/cm², *K₁ = 10⁻⁷ mole/liter.

Figures 2-6 show that the critical acidification varies from metal to metal. For aluminum, for example, it is much higher than for iron or nickel. Nevertheless, in all cases the critical acidification is reached for very low $x \cdot i$ values.

So far it has been assumed that the current density inside the pit is of the order of 1 A/cm². For some metals, as is probably the case with chromium, it might happen that such high current densities could not be reached. Then the metal would not be susceptible to pitting. Nevertheless, the critical $x \cdot i$ value can be reached even with small current densities, provided that a sufficiently long diffusion path is present. That would be the case in a crevice. In this way, a metal could be resistant to pitting, but susceptible to crevice corrosion. From the electrochemical point of view both processes would be equal, the only difference being the length of the diffusion path.

Effect of the External pH on the Pitting Potential

A large increase in the pH of the bulk solution inhibits the pitting process. Leckie and Uhlig (35) reported that the pitting potential of stainless steel was independent of the pH in the range of 1-7, but for pH values higher than 7 the OH⁻ ion acted as pit inhibitor. In the same way, Venu *et al.* (36) and Rajagopalan *et al.* (37) reported that the presence of NaOH inhibited the passivity breakdown of steels in NaCl solutions.

By appropriate modification of the boundary conditions, it is possible to calculate the effect of the external pH on the concentration profiles in the ionic concentration diagrams. Calculations were performed for iron, assuming external pH values ranging from pH 7 to 12 (Fig. 8). The external pH was found to modify the shape of the H⁺ ion concentration curve inside the pit. The critical pH for iron is somewhere between 9 and 10. If the pH of the bulk solution is 10, the critical pH value would be reached with $x \cdot i$ values of about 10⁻⁶ A/cm. By increasing the external pH to 11, $x \cdot i$ values of 10⁻⁵ A/cm are required. For pH 12 the critical acidification is reached only with $x \cdot i$ values of 10⁻⁴ A/cm. The experimental conditions being equal, this means that the current density has to increase one order of magnitude whenever the pH of the bulk solution is increased one unit. If the relation between potential and current density inside the pit follows a logarithmic law, then it should be expected that the pitting potential will follow a law of the type

$$E_p = A + b \cdot \log C_{OH^-} \quad [12]$$

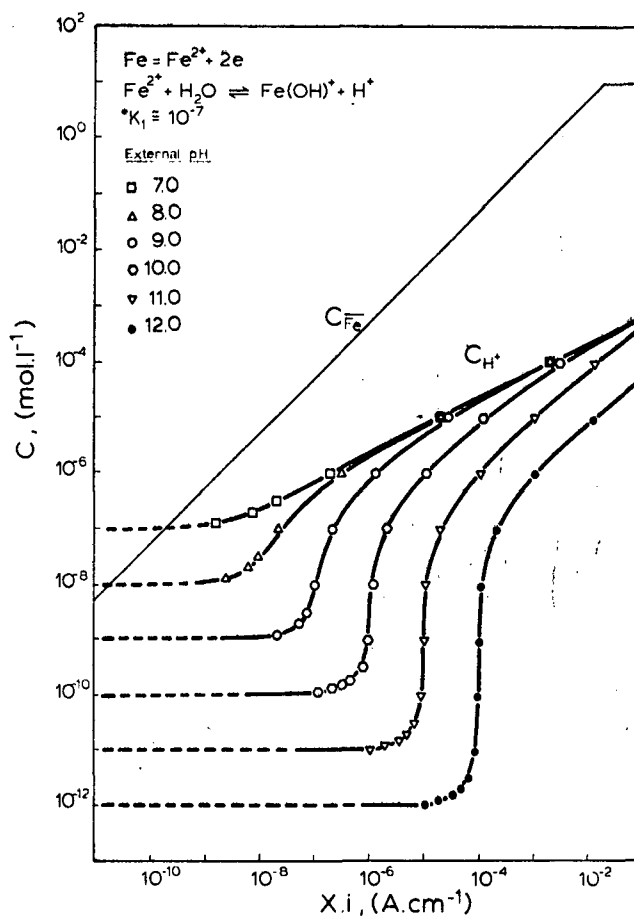


Fig. 8. Effect of the external pH on the concentration of H⁺ as a function of the product of the depth x and the current density i in a unidirectional iron pit.

Through galvanostatic experiments with high purity iron in NaCl solutions, Alvarez and Galvele (24) found that the pitting potential of iron was independent of the pH between pH 7 and 10, but showed a logarithmic relation, as in Eq. [12], from pH 10 to pH 12; the slope of the curve being $b = 0.020V$.

Presence of Anions of Weak Acid Salts

It is known that the presence of weak acid salts inhibits pitting by increasing the pitting potential. The pitting potential of aluminum is increased by the presence of soluble salts of acetate (38), benzoate (38), chromate (38,39) or tartrate (39). Pitting of zinc is inhibited by a borate buffer (40), and the pitting potential of iron in the presence of a borate buffer (23) is more than 100 mV higher than in its absence (41).

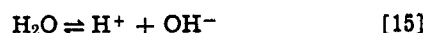
Anions of weak acids, because of their buffer properties, should modify the hydrogen ion concentration profiles in Fig. 2-6. Under these circumstances, the following equilibrium will take place inside the pit



where LH is the weak acid, and L⁻ is the anion of the weak acid. The equilibrium constant of the reaction will be K_a. The other equilibrium reactions are

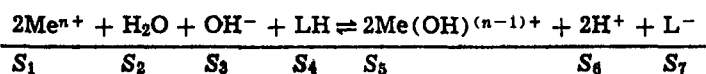


with the equilibrium constant *K₁, and



with the equilibrium constant K_w.

The over-all reaction will be



[16]

The boundary conditions are chosen as above, making allowance for the fact that the concentration of protons in the bulk solution will be related to the concentration of the weak acid (LH) and that of its anion (L^-) through Eq. [13].

Figure 9 shows the ionic concentration diagram for zinc in the presence of 10^{-2}M borax plus 1.0M NaCl solution. By comparison with Fig. 2, the presence of the borate salt is found to shift the hydrogen ion concentration line to higher $x \cdot i$ values. This means that, under otherwise equal conditions, in the presence of borax higher current densities are required to reach the critical acidification. Figure 10 shows the degree of shifting of the hydrogen ion concentration line for various borax concentrations. For borax concentrations lower than 10^{-4} , little effect should be expected from the weak acid salt. For higher borax concentrations an increase of one order of magnitude in the concentration of borax results in an increase of about one order of magnitude in the $x \cdot i$ values. If the relation between potential and current density inside the pit follows a logarithmic law, it follows that the pitting potential of zinc should be related to the borax concentration by an equation of the type

$$E_p = A' + b' \cdot \log C_b \quad [17]$$

C_b being the concentration of the buffer salt. The value of b' should be equal to the Tafel slope of the metal in a pitlike solution.

The results in Fig. 9 are in good agreement with the measurements of pitting potentials for zinc reported by Augustynski et al. (40). These authors found a

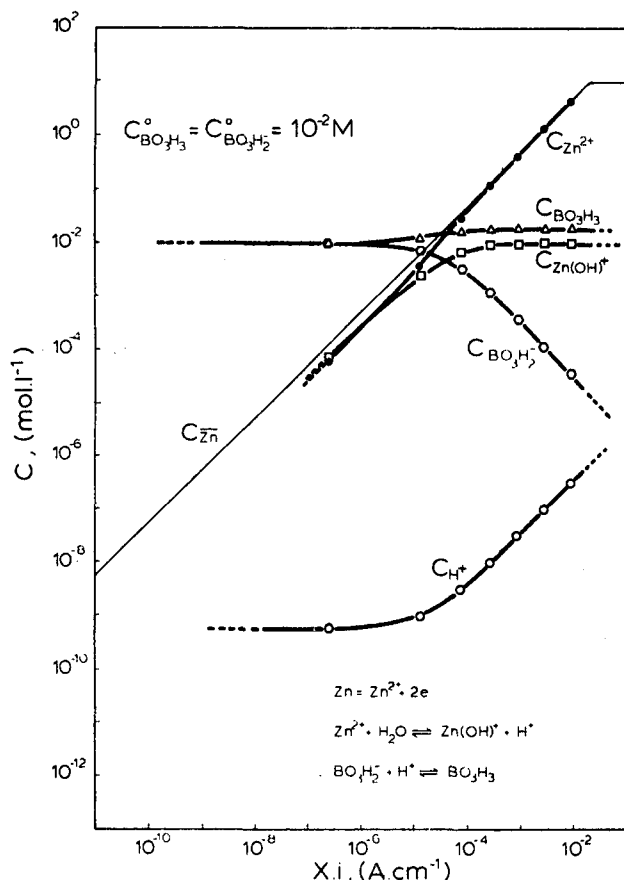


Fig. 9. Effect of 10^{-2}M borax on the concentrations of Zn^{2+} , $\text{Zn}(\text{OH})^+$, and H^+ as a function of the product of the depth x and the current density i in a unidirectional zinc pit.

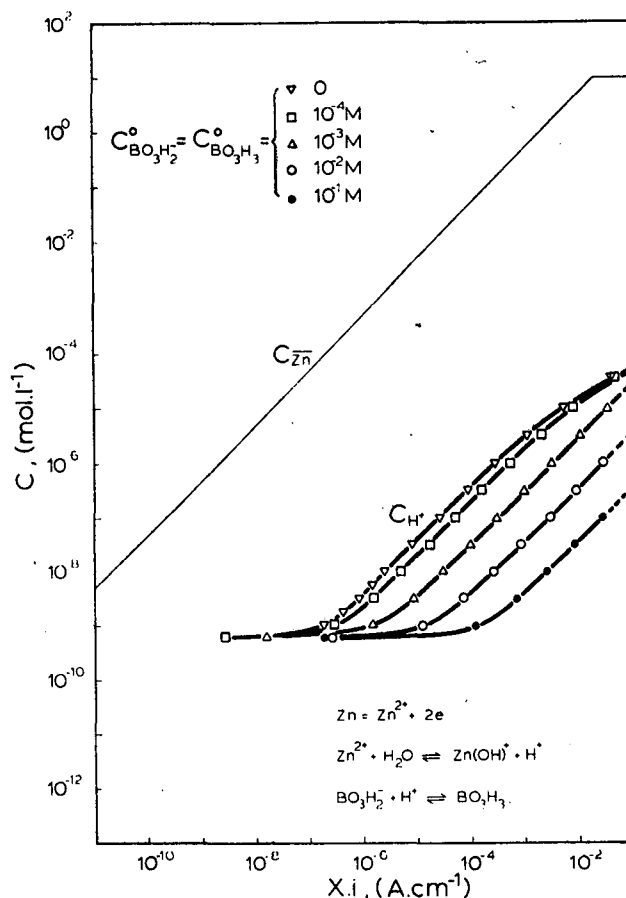


Fig. 10. Effect of the borax concentration on the H^+ concentration as a function of the product of the depth x and the current density i in a unidirectional zinc pit.

logarithmic relation between the pitting potential and the buffer concentration for zinc in NaCl and in NaClO_4 solutions. When the buffer concentration is higher than that of the aggressive anion, the pitting potentials measured by Augustynski et al. are higher than those predicted by Eq. [17]. The reason for this is that under such circumstances the aggressive anion is not acting as a supporting electrolyte, and the concentration buildup of the buffer anion inside the pit must be accounted for.

Diagrams similar to those in Fig. 10 were found for iron in the presence of borax. Vetter and Strehblow (23) reported a pitting potential of -0.17V (NHE) for iron in a 0.1M NaCl solution containing 0.029M KH_2BO_3 + 0.021M H_3BO_3 . In the absence of buffers, Semino and Galvele (41) measured pitting potentials from -0.32 to -0.34V (NHE). A diagram calculated for the solution used by Vetter and Strehblow shows that in their solution the $x \cdot i$ values were about two orders of magnitude higher than in that used by Semino and Galvele. The Tafel slope for iron inside the pit should be somewhere between 0.080 and 0.114V (42). Equation [17] predicts a difference of 0.160 – 0.230V in the pitting potential values, which fits very well with the difference of 0.150 – 0.170V found between the experimental results.

From Eq. [13] one would expect that salts from acids of different strength should have different effects on the ionic concentration diagrams. Figure 11 shows the effect of 0.1M weak acid salt on the proton concentration line inside the pit for aluminum. The calculations were made for four different acid strengths, going from

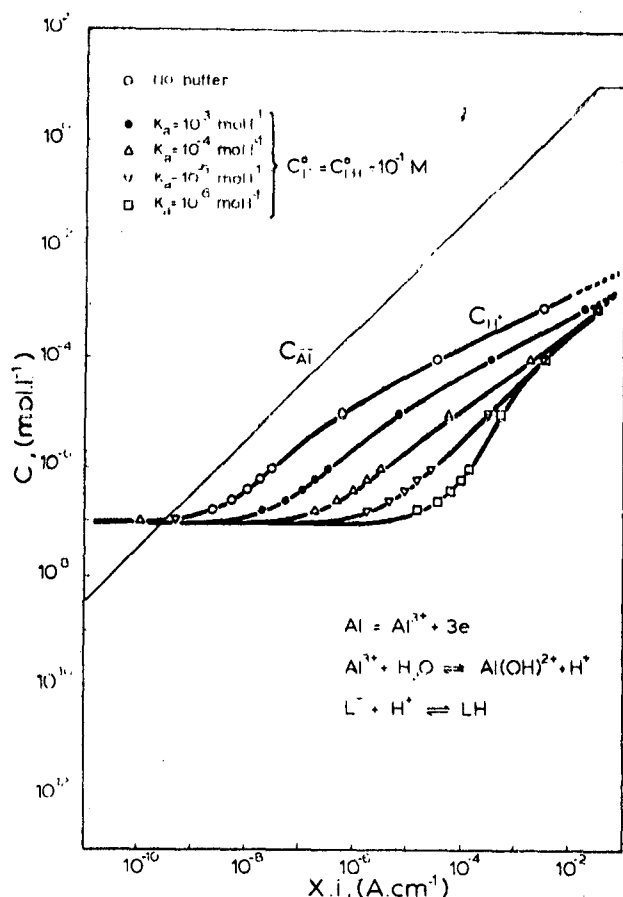


Fig. 11. Effect of the K_a of the buffer on the H^+ concentration as a function of the product of the depth x and the current density i in a unidirectional aluminum pit.

$K_a = 10^{-6}$ up to $K_a = 10^{-3}$ mole/liter. The lower the value of K_a , the higher the $x \cdot i$ values. From Fig. 11 it is concluded that the salt with the lowest K_a should be the most effective pitting inhibitor. Table II shows K_a values for various weak acids. From Table II and from Fig. 11 it can be concluded that from among chromate, acetate, and benzoate, chromate should be the most effective and benzoate the least, in correspondence with the experimental results reported by Böhni and Uhlig (38). Tartrates should be the least effective inhibitors, as reported by De Micheli and Galvele (39). According to Table II silicates and borates should have good inhibitor properties.

The present model does not take into consideration the possibility of formation of insoluble compounds between the metal ions and the weak acid anions. Such precipitates would occlude the pits, thus enhancing the inhibition capacity of the weak acid salt.

Aggressive Anion Concentration

If the concentration of the aggressive anion salt is changed over a wide range of values, the assumption that such salt is acting as a supporting electrolyte is not valid. In this case the electric field inside the pit cannot be ignored, and Eq. [4-6] are not valid. The following equations should be used [Ref. (20), p. 171]

Table II. Ionization constants of weak acids

Aqueous solution	pK _a at 25°C	Reference
Acetic acid	4.76	43
Benzoic acid	4.20	43
Floric acid	9.23	43
Chromic acid	0.00	18
HCO ₃ ⁻ /CO ₃ ²⁻		
Silicate K ₁	11.81	19
Tartaric acid K ₁	3.03	43

$$\frac{i \cdot \nu_j}{n \cdot F} = D_j \left[\frac{dC_j}{dx} + z_j \cdot C_j \cdot \frac{F}{R \cdot T} \cdot \frac{d\phi}{dx} \right] \quad [18]$$

for the reacting species, where ν_j is the stoichiometric factor of the species S_j , and $d\phi/dx$ is the electric field. For the nonreacting species the following equation is used

$$C_j = C_0 \cdot e^{-(z_j \cdot F/RT) \cdot \phi} \quad [10]$$

A further equation used is the condition of electro-neutrality

$$\sum z_j \cdot C_j = 0 \quad [20]$$

The resolution of the above equations for a system where hydrolysis equilibrium is included is quite complex. Nevertheless, the resolution for a simpler system gives very useful information.

Let us assume that the metal is dissolving according to reaction [1]. Neglecting for a while the hydrolysis reaction of the metal ions, we will assume that the only ionic species present are: Me^{n+} ; Na^+ ; and Cl^- . Under these conditions the following set of equations has to be solved

$$\frac{i}{n \cdot F} = D_{Me} \left[\frac{dC_{Me}}{dx} + n \cdot C_{Me} \cdot \frac{F}{R \cdot T} \cdot \frac{d\phi}{dx} \right] \quad [21]$$

for Me^{n+} ions

$$C_{Na} = C_0 \cdot e^{+\psi} \quad [22]$$

for Na^+ ions, where $\psi = F \cdot \phi / R \cdot T$

$$C_{Cl} = C_0 \cdot e^{-\psi} \quad [23]$$

for Cl^- ions, and the electroneutrality condition

$$n \cdot C_{Me} + C_{Na} - C_{Cl} = 0 \quad [24]$$

C_{Na} and C_{Cl} in Eq. [24] are substituted for Eq. [22] and [23]

$$n \cdot C_{Me} = C_0 \cdot e^{+\psi} - C_0 \cdot e^{-\psi} \quad [25]$$

Equation [25] is substituted for $n \cdot C_{Me}$ in Eq. [21]. By differentiating Eq. [25], dC_{Me}/dx is obtained, and it is substituted for in Eq. [21]. By integration of Eq. [22], and taking into account the following boundary conditions for $x = 0$ ($C_{Me} = 0$; $C_{Na} = C_0$; $C_{Cl} = C_0$; and $\phi = 0$), Eq. [26] is obtained

$$i \cdot x = C_0 \cdot D_{Me} \cdot F \cdot [(n+1) \cdot e^{+\psi} + (n-1) \cdot e^{-\psi} - 2 \cdot n] \quad [26]$$

For $n = 1$ the equation developed by Pickering and Frankenthal is obtained (17). By solving Eq. [26] for $n = 3$, $D_{Me} = 10^{-5}$ cm²/sec, and $C_0 = 1.0M$, the diagram in Fig. 12 is obtained. Up to $x \cdot i$ values of 10^{-3} A/cm, the line for C_{Me} in Fig. 12 is the same as C_{Al} in Fig. 5. For $x \cdot i$ values higher than 10^{-3} A/cm a small deviation is found. This indicates that the assumption of a supporting electrolyte, made while drawing Fig. 5 was valid, since the correction for ϕ at low $x \cdot i$ values is negligible.

According to Fig. 12, a measurable electrical potential, ϕ , appears only for high $x \cdot i$ values. For 1.0M NaCl solution at $x \cdot i = 10^{-2}$ A/cm, the electrical potential could get up to some 0.035V. For lower C_0 values higher electrical potentials are found (Fig. 13). In a $10^{-3}M$ NaCl solution at $x \cdot i = 10^{-2}$ A/cm, the electrical potential increases up to 0.200V.

If the value of $x \cdot i$ is known, Fig. 13 can be used to evaluate the electrical potential, ϕ , under the experimental conditions of pitting potential measurement. There is not any precise information available, and only a rough estimation can be made. From the information in the literature, as mentioned above, we can assume that the current density inside a pit is of the order of 1 A/cm². As for the size of the pits, when measuring the pitting potential value they are usually visible under the optical microscope, so they must be at least 10^{-2} cm big. Then, an estimate for $x \cdot i$ value,

under stable pitting growth, would be $x \cdot i \cong 10^{-2}$ A/cm. For such $x \cdot i$ values Eq. [26] is reduced to

$$x \cdot i \cong (n+1) \cdot C_0 \cdot D_{Me} \cdot F \cdot e^{\psi} \quad [27]$$

If the pitting potentials are measured at approximately constant $x \cdot i$ values, then for two different NaCl concentrations we have

$$C_0^I \cdot e^{\psi_I} = C_0^{II} \cdot e^{\psi_{II}} \quad [28]$$

Replacing for the value of ψ , and taking logarithms

$$\ln C_0^I + \frac{F}{R \cdot T} \phi_I = \ln C_0^{II} + \frac{F}{R \cdot T} \phi_{II} \quad [29]$$

reordering and changing to decimal logarithms

$$\phi = \phi_0 - \left[\frac{R \cdot T}{F} \cdot \ln 10 \right] \cdot \log C_0 \quad [30]$$

Equation [30] would give the change of electrical potential inside the pit when the pitting potential is measured as a function of the NaCl concentration. This electrical potential should be subtracted from the measured pitting potential value to get the real pitting potential.

Equation [30] has a negative slope, with a value $b = 0.059$ V at 25°C. Table III shows experimentally measured slopes for pitting potentials vs. aggressive anion concentration. If, as assumed above, the $x \cdot i$ values are close to 10^{-2} A/cm, then the electrical potential inside the pits accounts for all the changes in the pitting potential found for iron (24), aluminum (44), aluminum-copper alloys (44), nickel (45), nickel-copper alloys (45), and zirconium (46), and perhaps for stainless steel (47). It also accounts for half the slope found for titanium (48). The agreement between Eq. [30] and the experimental results in Table III is very good in view of the fact that Eq. [30] is valid only for dilute solutions, and that the results in Table III have not been corrected for ohmic drops outside the pits.

Figure 12 also gives information about pit initiation conditions. According to some authors (12, 13) chloride ion buildup on the metal-solution interface would be the key factor for pit initiation. Figure 5 shows that the critical change in H^+ ion concentration is obtained with $x \cdot i$ values of the order of 10^{-8} A/cm. On the other hand, Fig. 12 shows that to get any significant change in the chloride ion concentration $x \cdot i$ values of the order of 10^{-4} - 10^{-3} A/cm are required. This means that for pit initiation, where x values are of the order of 10^{-6} cm, the critical proton concentration could be reached with current densities of 1 A/cm², while any measurable change in the chloride concentration would require current densities as high as 100-1000 A/cm². This consideration seems to exclude chloride ion buildup as a primary condition for pit initiation.

Mixed Electrolytes: NaCl + Na₂SO₄ Solutions

Sulfate ions are known to inhibit pitting of stainless steels in chloride solutions (35). Equations [18-20] can also be used to study a mixed electrolyte such as NaCl + Na₂SO₄ solutions. Equations [18] and [19] show that for anions of different charge, those with

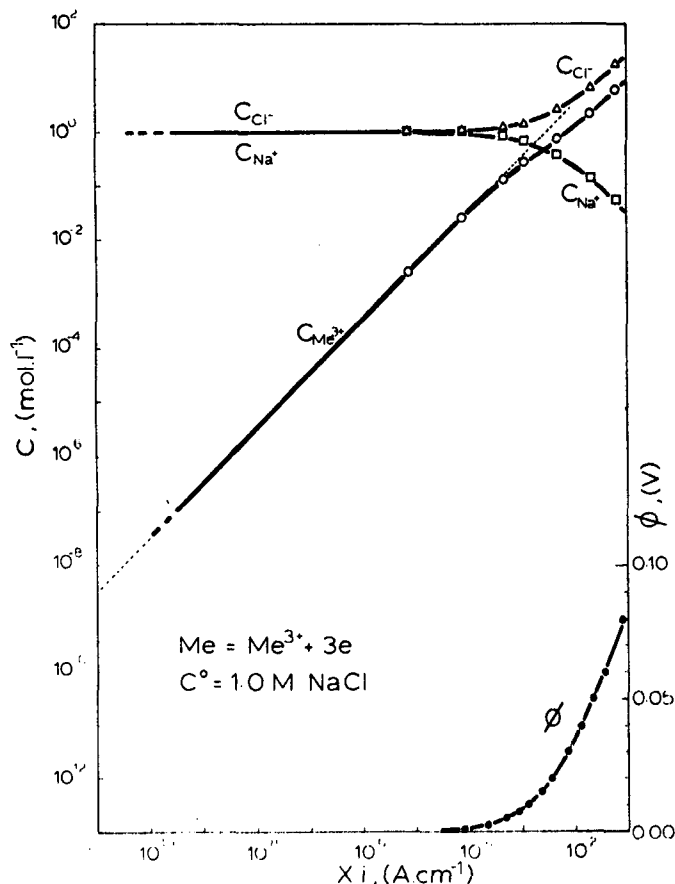


Fig. 12. Concentrations of Me^{3+} , Na^+ and Cl^- , and ϕ as a function of the product of the depth x and the current density i in a unidirectional pit.

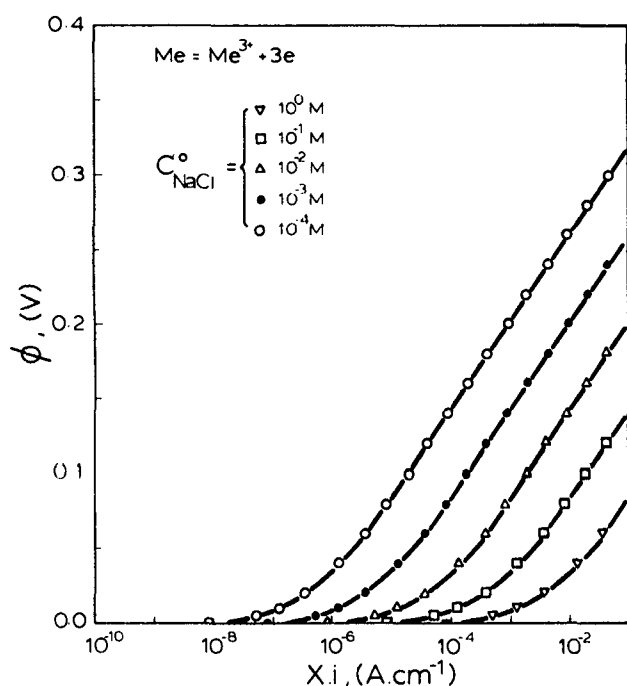


Fig. 13. Value of ϕ for various aggressive anion concentrations as a function of the product of the depth x and the current density i in a unidirectional pit.

Table III. Effect of the aggressive anion concentration on the pitting potential, experimental values for the slope of the curve $E_p = A - B \log C_X$

Metal or alloy	Slope B , (V)	Medium	Reference
Aluminum	-0.073	NaCl solution	44
Al-4% Cu	-0.046	NaCl solution	44
Al-Cu	-0.055	NaCl solution	44
Cu-85.8Ni	-0.074	NaCl solution	45
Cu-82.6Ni	-0.078	NaCl solution	45
Iron	-0.059	NaCl solution	24
Fe-18Cr-8Ni	-0.088	NaCl solution	35
Fe-18Cr-8Ni	-0.044	Pitlike solution	47
Nickel	-0.071	NaCl solution	45
Titanium	-0.110	KBr/HBr solution	48
Zirconium	-0.058	NaCl solution	46

the highest charge will be preferentially accumulated at the metal-solution interface.

Calculations made for a 0.1M NaCl + 1.0M Na₂SO₄ solution show that the main effect is a reduction of the electrical potential inside the pit due to the presence of the divalent SO₄²⁻ ion. In the absence of sulfate ions the electrical potential, ϕ , for $x \cdot i$ equal to 10⁻² A/cm is 0.085V. The addition of 1.0M Na₂SO₄ to the solution reduces the electrical potential ϕ to 0.010V.

More significant effects are found with lower ionic concentrations. For mixtures of 0.1M Na₂SO₄ + 0.01M NaCl solution a remarkable buildup in sulfate ion concentration is found for $x \cdot i$ values higher than 10⁻⁴ A/cm (Fig. 14). Beginning with a SO₄²⁻:Cl⁻ concentration ratio of 10:1, ratios as high as 100:1 or higher are easily reached. As soon as a pit is nucleated, a sulfate ion concentration builds up inside the pit, and eventually the pit is repassivated. The pits will not be able to grow any further and sulfate anion would act as pitting inhibitor in NaCl solutions. Figure 14 also explains the potential oscillations, under galvanostatic conditions, found by Szklarska-Smialowska and Janik-Czachor (26) for iron-chromium alloys, and by Szklarska-Smialowska (49) for nickel in NaCl + Na₂SO₄ solutions. As soon as the pits start to grow a buildup in sulfate ions takes place inside the pits, thus deactivating them. Later the diffusion of sulfate ions to the bulk solution reduces the content of sulfate ions inside the pit, and a continuous process of activation and deactivation of the pits is established.

Pitting Potential and Protection Potential

From potentiokinetic measurements, Pourbaix (50) reported two different potentials related to pitting: the pitting potential or rupture potential above which pitting starts, and the protection potential or the potential below which active pits will stop growing. According to Szklarska-Smialowska and Janik-Czachor (26) the real pitting potential is that which Pourbaix calls the protection potential. These authors found that this potential is equal to the galvanostatically measured pitting potential, and concluded that the higher pitting potential potentiokinetically found is the result of the measuring technique.

The present pitting model can be used to explain the existence of two potentials found in the potentiokinetic measurements. As mentioned above, the oxide film on the passive metal will suffer continuous breaks, thus exposing bare metal to the solution. The current density circulating in those fissures will be a function of the electrode potential. At each potential the cracks in the oxide will show a characteristic $x \cdot i$ value given

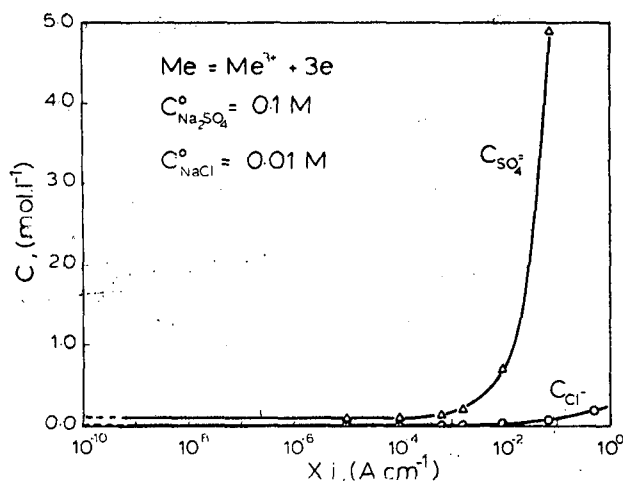


Fig. 14. Concentrations of SO₄²⁻ and Cl⁻ as a function of the product of the depth x and the current density i in a unidirectional pit.

by the current density and by the length of the crack (Fig. 15a). As soon as the system reaches the minimum $x \cdot i$ value for pit growth, which is $x \cdot i = 1$ in Fig. 15, the pit will start to grow. If the potential remains constant, the current density will also be constant, but x will increase with time, as will $x \cdot i$ ($x \cdot i = 2$ in Fig. 15). If the potential is then lowered, the current density will drop, but the pit will continue to grow while the $x \cdot i$ value is higher than 1. This means that pitting will grow at potentials lower than the initiation potential. Finally the pit will stop either because the $x \cdot i$ value is lower than the minimum for pit growth, or because the electrode potential is lower than the corrosion potential inside the pit, and the acidification disappears as a result of hydrogen evolution.

Szklarska-Smialowska and Janik-Czachor's results can be used to find out whether the above-mentioned changes could take place during a potentiokinetic measurement. During potentiostatic measurements for Fe-16Cr in 0.7N Na₂SO₄ + 0.7N NaCl solution, pitting could start at potentials as high as +0.50V (SCE). The reported current density inside the pits is about 8 A/cm². Once started, the same pits will continue to grow at lower potentials, and they would stop at -0.05V (SCE). The current density inside the pits at this potential is 0.1 A/cm². Assuming a value for minimum $x \cdot i$ of 10⁻⁵ A/cm, the pits will start to grow at 0.50V (SCE) in defects of about 1.3×10^{-6} cm. When reducing the potential, the pits should have a minimum size of 10⁻⁴ cm to be able to grow at the current density of 0.1 A/cm². With a current density of 8 A/cm² a pit of 10⁻⁴ cm takes less than 0.4 sec to grow. Since the critical $x \cdot i$ values in Fig. 2-6 are lower than 10⁻⁵ A/cm, a much shorter time will be required to obtain the two potentials reported by Pourbaix.

Conclusions

As shown in previous publications (2, 3) there is a potential below which no localized acidification can be maintained on the metal-solution interface. This potential is given by the corrosion potential of the metal in the acidified solution, E_c^* . The alloying elements affect the pitting potential mainly by modifying the corrosion potential inside the pit. When measuring the pitting potential, a positive polarization, η , is added to the corrosion potential, E_c^* , to maintain a net anodic

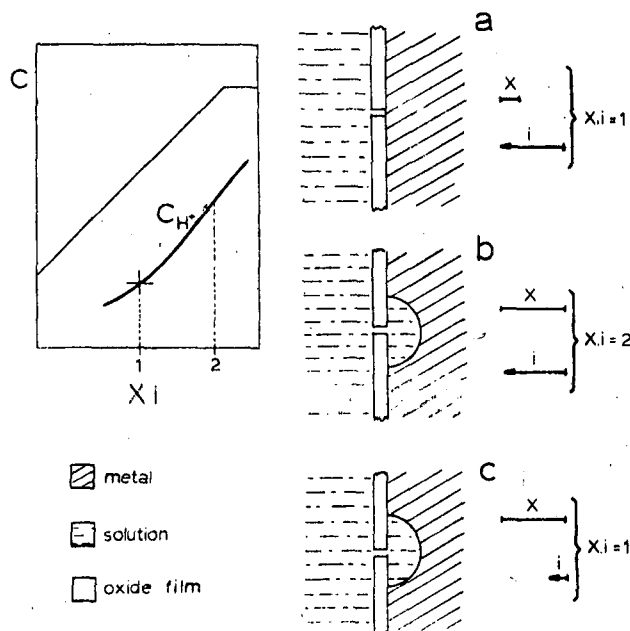


Fig. 15. Events leading to the measurement of pitting protection potentials different from pitting potentials in potentiokinetic experiments.

current density inside the pit, and secure the minimum $x \cdot i$ value. From the present paper it is concluded that a further addition should be made, E_{inh} , when inhibitors like OH^- ions or buffer salts are present.

Since the current density inside the pit is high, another contribution due to the electrical potential, ϕ , must be accounted for. In this way, the measured pitting potential is the total of the above mentioned factors

$$E_p = E_c^* + \eta + E_{inh} + \phi$$

All the observations reported so far in the literature on the pitting potential can be explained by transport phenomena. Processes like competitive adsorption, salt formation, film contamination, etc., even though present during the pitting process, do not play a major role in fixing the pitting potential.

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Pitting of High Purity Zinc and Pitting Potential Significance*

M. G. ALVAREZ and J. R. GALVELE*

Abstract

The passivity breakdown of high purity zinc in aqueous solutions containing different aggressive anions (Cl^- , I^- , SO_4^{2-} , and NO_3^-) was studied. A critical evaluation of different methods for measuring the breakdown potential was made. Reproducible passivity breakdown potential measurements were given only by those methods producing mechanical disruption of the passive film. The passivity breakdown potential of high purity zinc was found to be independent of the nature of the anions tested, except for nitrates, and very close to the equilibrium potential of the reaction $\text{Zn} = \text{Zn}^{2+} + 2\text{e}$. The passivity breakdown potential in all the cases studied was found to be equal to the corrosion potential of zinc in the acid solution formed inside the pits. It is concluded that the pitting potential is the minimum potential at which an acidified solution can be produced and maintained in contact with the dissolving metal.

As early as 1937, Hoar^{1,2} suggested the presence of anions of strong acids as necessary to promote pitting of metals. The mechanism was based on the "consideration of the influence of a nondepositing ion such as Cl^- on the pH of the electrolyte next to the anode".² This mechanism accounted for most of the pitting cases known at the time, but ran into trouble when controlled potential experiments were performed later.^{3,4} The process of pitting was found to occur at a certain potential called the "pitting potential" or the "breakdown potential". Hoar's theory could not account for such a potential. Many theories were proposed later to explain the nature of the pitting potential. They included propositions like competitive adsorption,³ thermodynamic stability of ionic compounds inside the pits,⁵⁻⁷ field-stimulated ion migration through the oxide film,⁴ mechanical breakdown of the oxide film,⁸ metal-solution zero charge potential,⁹ oxide-film-solution zero charge potential,¹⁰ etc.

Nevertheless, none so far has given a satisfactory account of most pitting processes.

The present work is part of a research program in which the behavior of high purity metals and binary alloys in the presence of numerous electrolytes is studied. In the present paper, results on passivity breakdown of high purity zinc are reported. Results on pitting of high purity aluminum,¹¹⁻¹³ high purity cadmium,¹⁴ high purity iron,¹⁵ and binary Al-Cu,^{16,17} Al-Mg,¹⁷ and Al-Zn¹⁷ alloys have been reported elsewhere. The results so far obtained show that a mechanism such as that proposed by Hoar^{1,2} is operative, and that the pitting potential derives from the open circuit potential of the metal in the acid solution inside the pit.

Most of the work reported so far on pitting of high purity zinc was done in NaOH- H_3BO_3 buffers.¹⁸⁻²² According to Davies and Lotlikar,^{18,19} zinc showed a passive behavior in buffer solutions in the pH range from 9.2 to 11. As little as 70 ppm of NaCl was enough to produce pitting in such solutions. For low chloride concentrations, the pitting potential was a function of the chloride

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TABLE 1 — Breakdown Potentials

Solution	Technique	Anodic Polarization Curves	Current-Time Curves	Repassivation Time Measurement
1.0M NaCl, pH = 9.0		-0.79 V	-0.81 V	-0.83 V to -0.84 V
0.1M NaCl, pH = 9.0		-0.78 V to -0.64 V	-0.78 V	-0.80 V to -0.82 V
0.01M NaCl, pH = 9.0		-0.72 V to -0.66 V		-0.79 V
0.5M Na ₂ SO ₄ , pH = 9.0		-0.79 V to -0.74 V		-0.84 V to -0.85 V
1.0M KI, pH = 9.0		-0.78 V to -0.74 V	-0.81 V	-0.83 V to -0.84 V
1.0M NaCl, pH = 7.0		-0.83 V	-0.84 V	No repassivation
0.1M NaCl, pH = 7.0		-0.74 V to -0.81 V	-0.81 V (?)	No repassivation
1.0M NaCl + 0.01M Na ₂ B ₄ O ₇ ·10H ₂ O, pH = 9.2		0.78 V		0.80 V
0.1M NaCl + 0.05M Na ₂ B ₄ O ₇ ·10H ₂ O, pH = 9.2				-0.70 V to -0.66 V
1.0M NaNO ₃ , pH = 9.0		-0.52 V		-0.66 V

concentration. These authors reported no reproducible pitting potential values and pointed out that galvanostatic measurements gave pitting potential values different from potentiostatic measurements. Augustynski, *et al.*,^{10,20} reported a long list of anions capable of producing passivity breakdown of zinc. They also found that the pitting potential was a function of chloride concentration, the effect of the aggressive anion concentration becoming less notorious as it reached the buffer concentration. Augustynski¹⁰ suggested a pitting potential relation to the Zn/Zn²⁺ equilibria, but could not explain the high potential breakdown values found in nitrate solutions. Janik Czachor,²¹ working with Zn single crystals, found that pits were bounded by {0001} planes, and that potentiostatic pretreatment in the passive range, gave very high values in the pitting potentials measured afterwards.

Most of the experiments in our work were made with unbuffered solutions, since the effect of the buffer anion on the pitting potential was unknown. For the sake of comparison, a few experiments with buffered solutions were also performed. It was found that the pitting potential of high purity zinc was equal to the corrosion potential of the zinc in the acid solutions formed inside the pits.

Experimental

Specimens 1.0 x 2.0 and 0.1 cm thick were prepared from "Leico" 99.9995% zinc rods, by hot-rolling. Intermediate washing and etching with 25% HNO₃ were introduced in the preparation sequence to minimize metal contamination. The zinc coupons were annealed for 2 hours at 370 °C in an argon atmosphere. A copper wire lead was soldered to one face of the specimens, and that face and the edges of the specimens were covered with a cured epoxy resin.

Before the electrochemical measurements, the specimens were chemically polished in an aqueous solution of 320 g/l of CrO₃ plus 18 g/l of Na₂SO₄, for about 2 minutes at room temperature.

All the measurements were made at 25 ± 0.5 °C, in an all Pyrex cell, with a platinum counterelectrode. A saturated calomel reference electrode, through a Luggin capillary, was used for the experiments in NaCl solutions. A mercurous sulfate reference electrode (with the Luggin capillary and an intermediate bridge containing the working solution) was used for the other solutions. All the potentials are reported on the normal hydrogen electrode (nhe) scale.

The solutions were prepared with analytical grade reagents and double distilled water, and were deaerated with purified nitrogen.²² The pH of the saline solutions was adjusted by addition of the corresponding acid or base. No buffers were used, unless specifically stated.

The potential was controlled by a Tacussel PRT 40-1X potentiostat. Quasi-stationary potentiostatic curves were obtained by changing the potential in steps of 10 mV, and waiting 10 minutes at constant potential before measuring the current. Current-time curves, at constant potential, were obtained by switching the potential from an open circuit to the chosen value, and recording the current for up to 4 hours. A new specimen was used for each potential. The specimens were cathodically prepolarized for 20

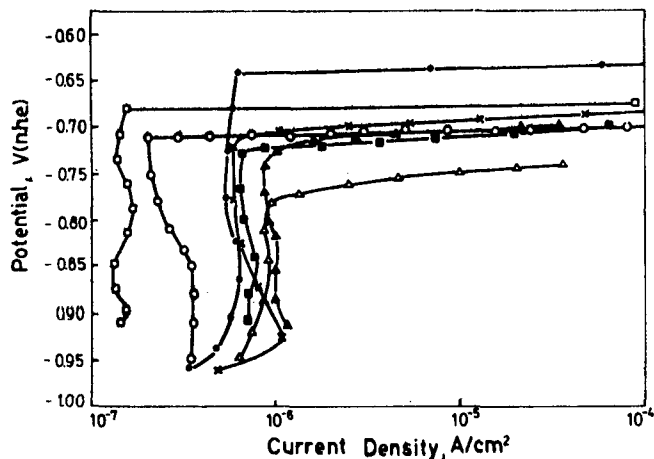


FIGURE 1 — Anodic polarization curves for high purity zinc in deaerated 0.1M NaCl solution (pH = 9.0; t = 25 °C).

minutes at -1.2 V, and then allowed to attain a stationary open circuit potential. It usually required about 15 minutes to reach a stationary potential.

In a third set of experiments, the repassivation time was measured, as described by Passall and Liu.²³ While the specimen was maintained at constant potential, the surface of the specimen was scratched with a SiC point, and the time necessary to return to the initial current was recorded. The potential was changed in steps of 10 or 20 mV, and the specimen was held at constant potential for 10 minutes before scratching the surface. The experiments covered a wide range of increasing potentials, and a single specimen was used for each run. No cathodic pretreatment was applied in the repassivation-rate experiments.

The anodic behavior of high purity zinc was studied in the following solutions: 1.0M NaCl (pH 5.0, 7.0, and 9.0); 0.1M NaCl (pH 7.0 and 9.0); 0.01M NaCl (pH 9.0); 0.5M Na₂SO₄ (pH 7.0 and 9.0); 1.0M KI (pH 9.0); 1.0M NaNO₃ (pH 9.0); buffered 1.0M NaCl (plus 0.01M Na₂B₄O₇·10H₂O, pH 9.1); and buffered 0.1M NaCl (plus 0.05M Na₂B₄O₇·10H₂O, pH 9.2).

Results

Potentiostatic Polarization Curves

Quasi-stationary potentiostatic polarization curves for high purity zinc were determined in all of the above reported solutions.

In alkaline solutions, all the polarization curves showed a passive zone and a breakdown potential at which a high increase in the current density occurred (Table 1). The current density in the passive range was lower than 10⁻⁶ A/cm². In 1.0M NaCl solution (pH 9.0), experiments made in triplicate gave a breakdown potential with a variation less than 10 mV. For less concentrated solutions, on the other hand, a larger variation in the breakdown potential was observed. Figure 1 shows the large variation found in 0.1M NaCl solution (pH 9.0). Substantial variation was also observed in 0.01M NaCl (pH 9.0); 1.0M KI (pH 9.0); and 0.5M Na₂SO₄ solutions.

In acid solution (1.0M NaCl, pH 5.0), no passive range was found. General dissolution of the metal occurred at potentials higher than the corrosion potential. The corrosion potential was -0.80 V.

In neutral solutions, a transition behavior between those in acid and in alkaline solutions was observed. The passive zone showed a higher current density than that in alkaline solutions, and a high dispersion was found in the breakdown potential values.

The morphology of attack observed on high purity zinc, over the breakdown potential, did not show the high localization observed for the passivity breakdown of aluminum and other metals.⁹ Once the breakdown occurred, the attack spread easily all over the surface of the specimen (Figure 2). Dissolution developed along certain preferential planes, giving the appearance of crystal-

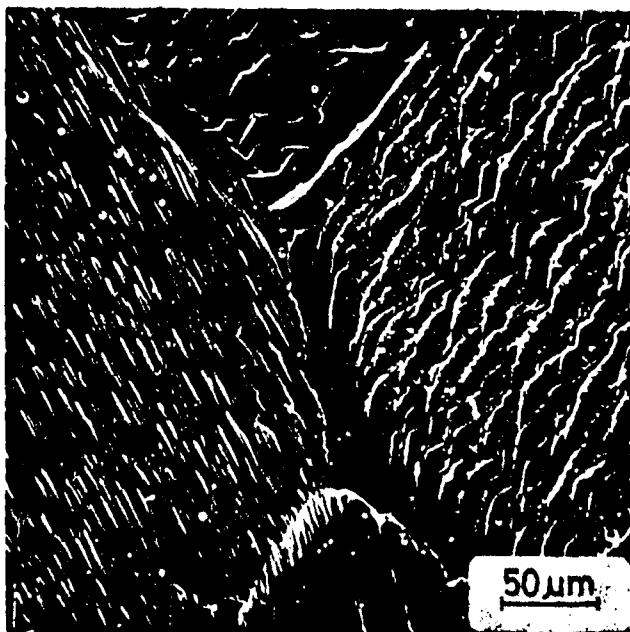


FIGURE 2 — Corrosion of high purity zinc after an exposure of 60 minutes at -0.79 V in deaerated 0.1M NaCl solution, $\text{pH} = 9.0$.



FIGURE 3 — Localized corrosion of high purity zinc in deaerated 0.1M NaCl solution ($\text{pH} = 9.0$). Specimen exposed 18 hours at -0.91 V plus 40 minutes at -0.67 V.

lographic etching. As corrosion proceeded, heavy accumulation of corrosion products was observed on the surface of the metal.

In those solutions where a large variation in the breakdown potential was found, a high breakdown potential was usually followed by high localization in the attack. This suggested the presence of an oxide film acting as an inert barrier and obstructing the propagation of the attack. To confirm this, the effect of the pretreatment of the specimens was studied. Some specimens of zinc were exposed to a 0.1M NaCl solution, $\text{pH} 9.0$, for 18 hours at -0.91 V, then switching the potential to -0.75 V. The current density after such a pretreatment, remained at a very low value (about 10^{-6} A/cm^2) after more than a 2 hour exposure, and the specimens did not show any corrosion under the microscope. If after the pretreatment of 18 hours in the passive zone, the potential of the specimen was switched to -0.67 V, the current density increased after a few minutes, going from 10^{-6} A/cm^2 to about 10^{-3} A/cm^2 , and the surface of the specimen showed very localized corrosion (Figure 3). On the other hand, if instead of allowing the oxide film to grow, the potential was switched from the corrosion potential to -0.75 V, the current density increased to values of 5×10^{-4} A/cm^2 , and the attack spread all over the surface of the specimen, the same as in Figure 2. Figure 4 shows the typical current-time curves observed with and without pretreatment of the specimens.

Pitting Morphology

After passivity breakdown, zinc dissolution did not propagate in a flat front, but developed certain crystallographic planes. When the corrosion had spread all over the surface (Figure 2), it was difficult to attempt any indexing of those planes. With prepassivated specimens, on the other hand, small localized pits with well-developed planes were obtained (Figure 3). By tilting the specimens in the scanning electron microscope (SEM), until two mutually inclined planes just disappeared, the angle formed by those planes was measured.²⁴ Pits like those in Figure 3 were bounded by planes intersecting at 120° (Figure 5), indicating that they were $\{10\bar{1}0\}$ planes. On the other hand, pits like that in Figure 6 contained planes intersecting at 90° (Figure 7). This value corresponds to the intersection of $\{10\bar{1}0\}$ planes with $\{0001\}$ planes. It is concluded that pitting of zinc in NaCl solutions develops not only along $\{0001\}$ planes, as reported by Janik-Czachor,²¹ but also along $\{10\bar{1}0\}$ planes.

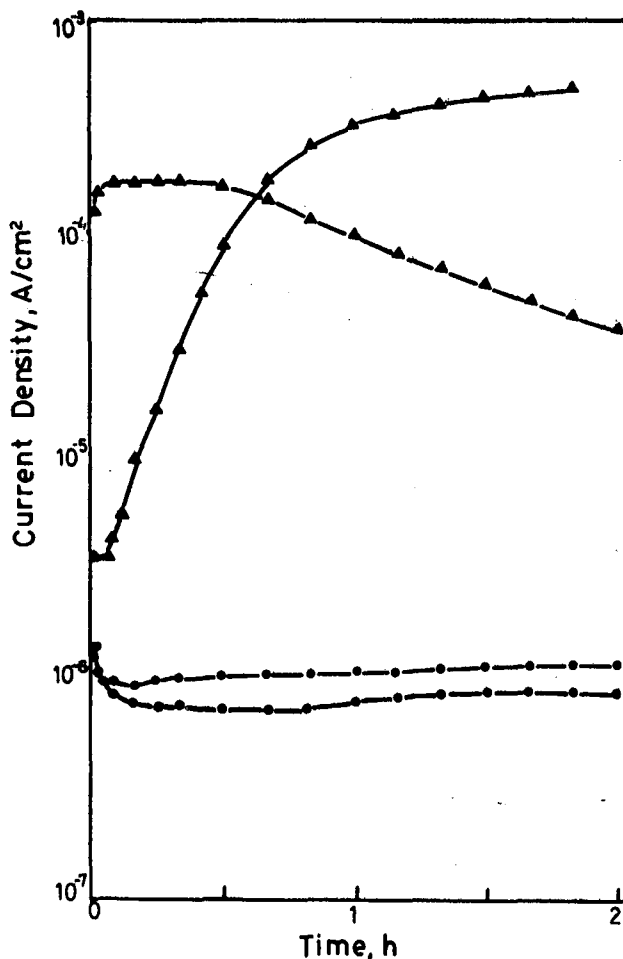


FIGURE 4 — Typical current density time curves for high purity zinc with (●), and without (▲) prepassivation treatment (0.1M NaCl solution, $\text{pH} = 9.0$).

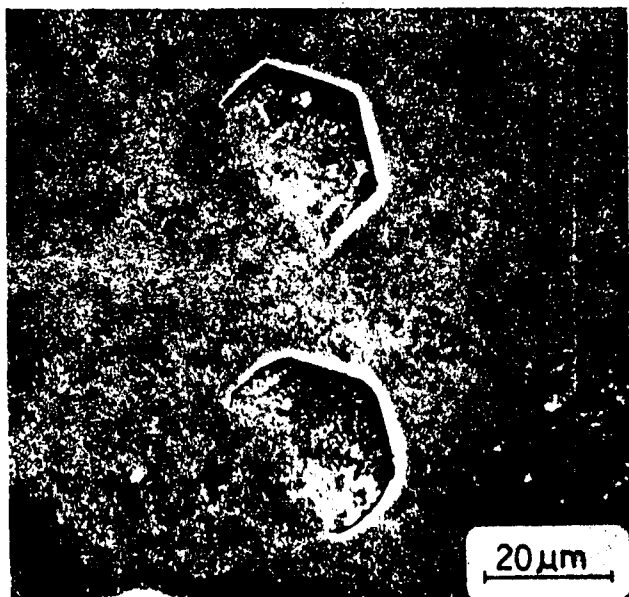


FIGURE 5 – Pits bounded by planes intersection at 120° .

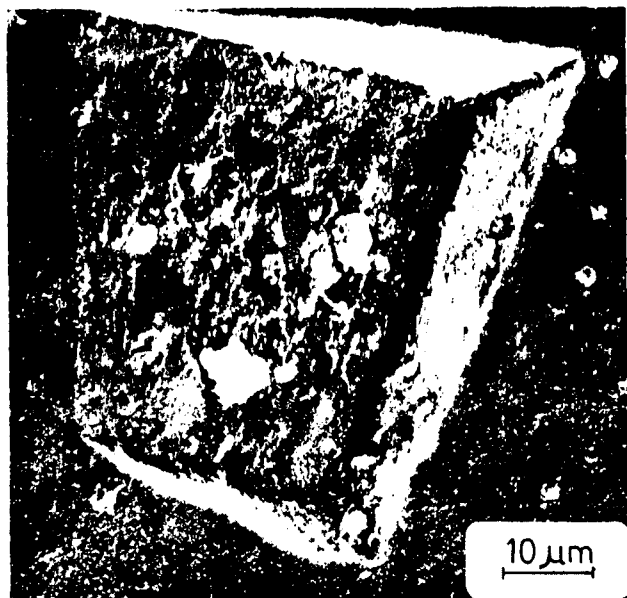


FIGURE 6 – Pit produced on a prepassivated specimen of high purity zinc in deaerated 0.1M NaCl solution, pH = 9.0.

Potentiostatic Current-Time Curves

Current-time curves, at constant potential, were measured for high purity zinc in most of the above mentioned solutions. The potential up to which the current density remained constant and low ($\sim 10^{-6}$ A/cm²), and over which the current density reached high values (10^{-4} A/cm² or more), was taken as the breakdown potential. The values obtained are reported in Table 1.

In 1.0M NaCl (pH 9.0) (Figure 8), the current density remained low and constant below -0.80 V. Light microscope examination of the specimens (after 5 hours exposure) did not show any sign of corrosion. At -0.80 V, the mean value of the current density was low, but frequent oscillations were observed. The optical observation of the specimen showed the presence of small corrosion points, covered with corrosion products. At -0.79 V, the current density reached, after a few minutes exposure, a value three orders of magnitude higher than that observed for a 10 mV lower potential, and the specimen showed extensive corrosion. Similar results were

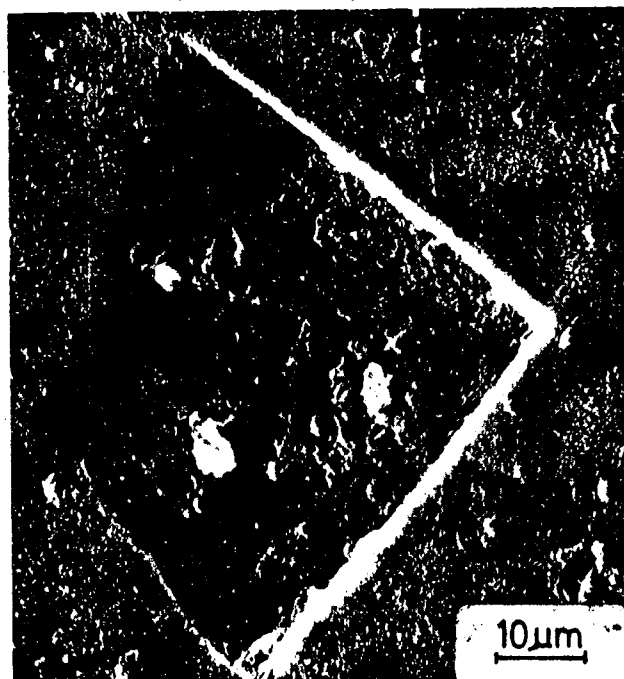


FIGURE 7 – Same conditions as in Figure 6. Pit bounded by planes intersecting at 90° .

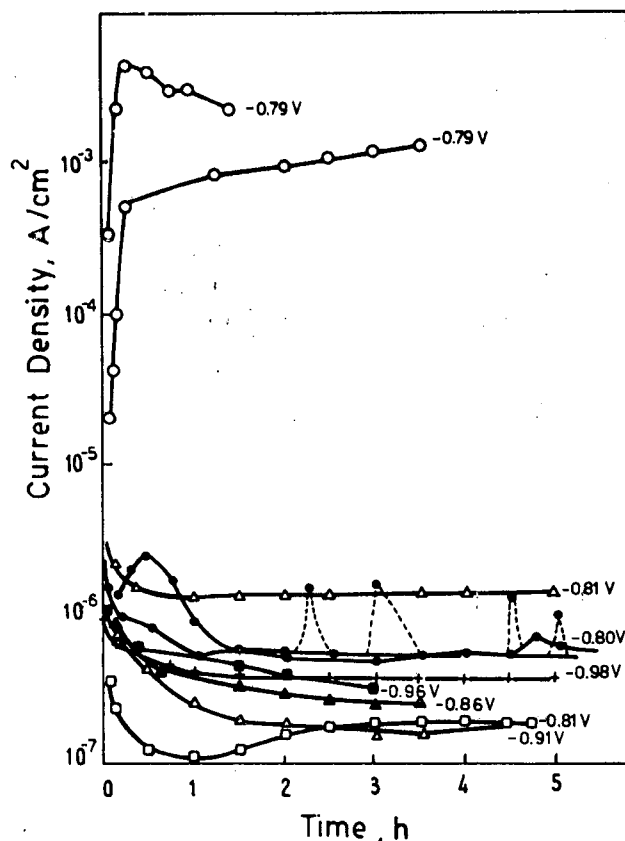


FIGURE 8 – Potentiostatic current density-time curves for high purity zinc in deaerated 1.0M NaCl solution, pH = 9.0.

obtained also with 1.0M NaCl (pH 7.0) and 1.0M KI (pH 9.0). According to these measurements, high purity zinc showed the same breakdown potential in 1.0M NaCl (pH 9.0) and in 1.0M KI (pH 9.0).

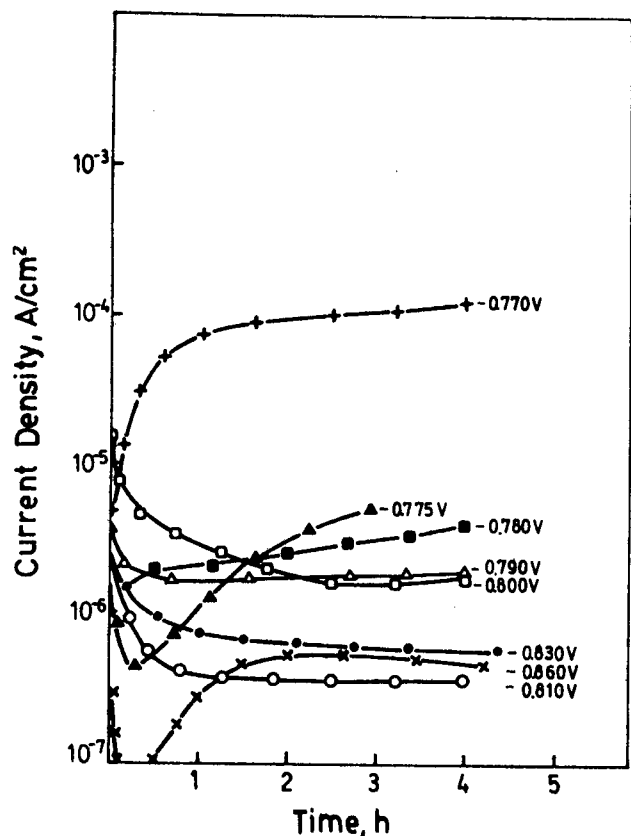


FIGURE 9 — Potentiostatic current density-time curves for high purity zinc in deaerated 0.1M NaCl solution, pH = 7.0.

Less satisfactory results were obtained when applying this technique of breakdown potential determination to more dilute solutions. In 0.1M NaCl (pH 7.0 and 9.0), incipient corrosion of the specimens was detected before noticing any significant change in the current-time curves. Figure 9 shows the results obtained in 0.1M NaCl (pH 7.0). Up to -0.81 V, the current density remained low and no corrosion was found on the surface of the specimens. Between -0.80 and -0.77 V, a small increase in the current density was observed, without any definite change in the shape of the curves. Nevertheless, optical observation of the specimens showed that the passivity breakdown had already occurred. The specimens presented small corroded areas, which became larger as the potential increased. It was only at -0.77 V that the current showed a significant increase, followed by extensive corrosion of the specimens. Similar difficulties were found with 0.1M NaCl (pH 9.0). Experiments at -0.78 V, in this solution, showed a low current density, and no corrosion could be detected on the specimens. On the other hand, at -0.77 and -0.76 V, the current density was still low, but localized corrosion was observed after 4 hours exposure at constant potential.

Repassivation Time Measurements

The third method tested for the determination of the breakdown potential was the repassivation time measurement. Figure 10 shows the repassivation time values found for high purity zinc in 0.1M NaCl (pH 9.0). There was a potential (-0.81 V) over which the repassivation time showed an abrupt increase. This potential was taken as the breakdown potential. In Figure 10, the results of three independent runs were plotted, showing the good reproducibility of the method. Figure 11 shows the current decay curves obtained in one of those runs. The increase in the repassivation time coincided with a change in the shape of the current decay curves. Below the pitting potential, after scratching the surface, the current increased sharply, but returned after a few seconds to the initial value. When the surface scratching was performed at a potential only 10 mV higher than the pitting potential, the current increased and stayed at

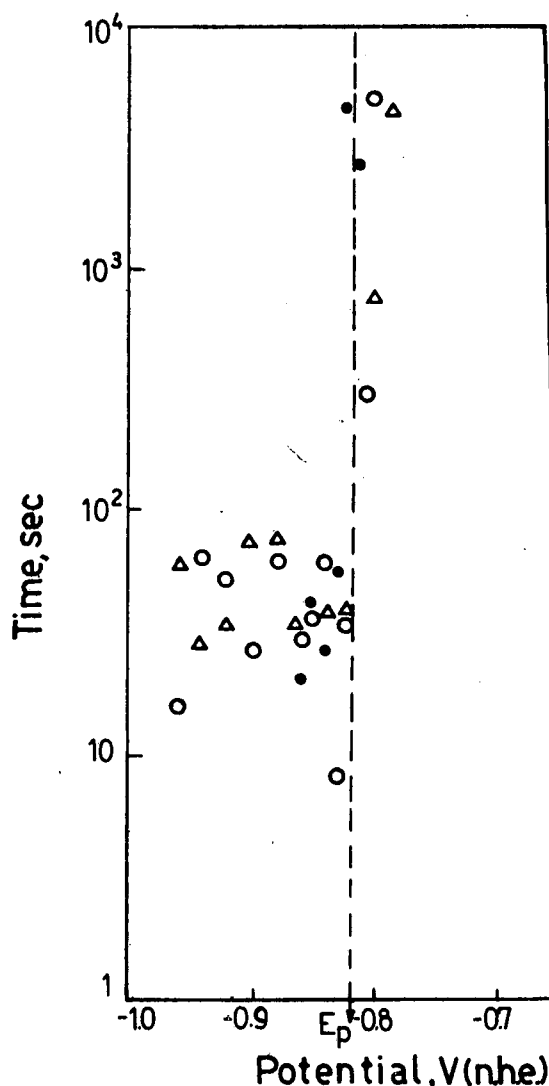


FIGURE 10 — Constant potential repassivation time for high purity zinc after scratching in deaerated 0.1M NaCl solution, pH = 9.0.

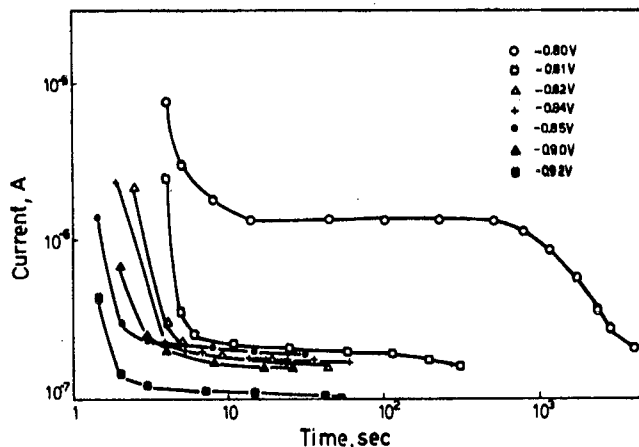


FIGURE 11 — Constant potential current-time curves for high purity zinc after scratching in deaerated 0.1M NaCl solution, pH = 9.0.

a value about one order of magnitude higher than the initial value, and remained at such a value for a long time. After about 500 seconds, the current began to decrease, and it took about 4700

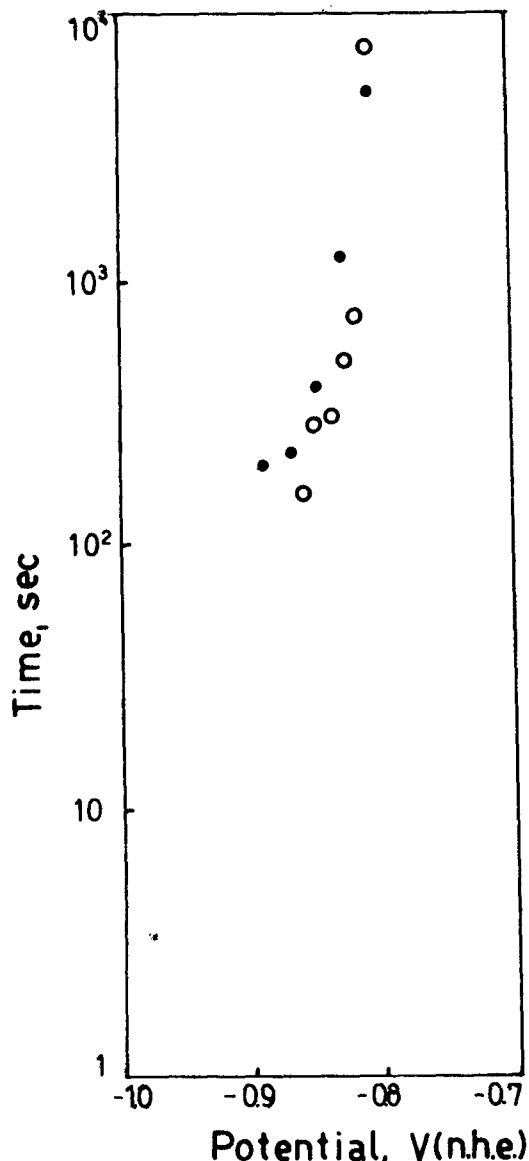


FIGURE 12 — Constant potential repassivation time for high purity zinc after scratching in deaerated 0.1M NaCl solution, pH = 7.0.

seconds to reach a value comparable to the initial current. This final condition, nevertheless, was not the result of the formation of an invisible passivating film, but the result of a heavy accumulation of corrosion products that plugged up the corroding area.

A small dispersion was found in the repassivation time, at potentials below the breakdown potential. This was attributed to differences in the extension and depth of the scratches produced at each potential.

All the alkaline solutions gave similar results. Experiments in duplicate or triplicate gave breakdown potentials reproducible within less than 10 mV. The breakdown potential values measured by this technique are reported in Table 1.

In neutral solutions, the surface scratching technique indicated the absence of real passivity breakdown. It was observed that the apparent repassivation time increased continuously with the potential (Figure 12). The current decay curves (Figure 13), on the other hand, indicated that no real repassivation process was taking place. The current decay curves in neutral solutions showed the same shape as those found in alkaline solutions over the breakdown potential.

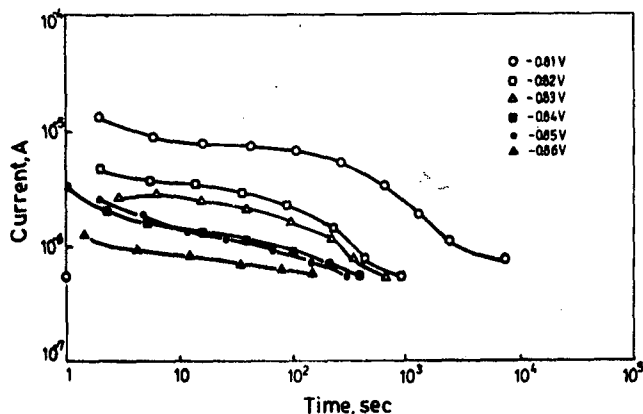


FIGURE 13 — Constant potential current-time curves for high purity zinc after scratching in deaerated 0.1M NaCl solution, pH = 7.0.

Buffered Solutions

Measurements in buffered NaCl solutions (pH 9.2) showed that the effect of the buffer on the breakdown potential varied with the relation of concentrations of the aggressive anion to the buffer, as reported by Augustynski, *et al.*²⁰

In buffered 1.0M NaCl solution (0.01M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, pH 9.2), the polarization curve for zinc was similar to that found in unbuffered solutions. The only noticeable change was an increase in about 30 mV in the breakdown potential. The repassivation-time curves also gave results comparable to those in unbuffered solutions, and here again, the breakdown potential was slightly higher than that in the unbuffered solutions, with 30 to 40 mV difference (Table 1). Another difference observed was that over the pitting potential, the tendency to accumulate corrosion products over the scratches was higher here than in unbuffered solutions.

With a smaller ratio of aggressive anion to buffer anion, 0.1M NaCl plus 0.05M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ solution (pH 9.2), stronger differences were found between buffered and unbuffered solutions. Below the passivity rupture potential, the scratching of the surface did not show any noticeable effect on the current density. When the potential was increased up to the range of -0.70 to -0.67 V, rapid current fluctuations were observed. These fluctuations were of surface scratching. Simultaneously with current fluctuations, points with heavy accumulation of corrosion products were observed on the surface of the specimen, indicating that passivity breakdown had already occurred. Although no precise breakdown potential was detected in these solutions, the potentials at which it occurred were more than 100 mV higher than those for unbuffered solutions.

Passivity Breakdown in Nitrate Solutions

Measurements in 1.0M NaNO_3 (pH 9.0) are reported separately because the results differ considerably from those in the above mentioned solutions. The above described cathodic pretreatment could not be applied to zinc in NaNO_3 solutions. At -1.20 V, a cathodic current density of about 0.2 A/cm^2 was measured, and the surface of the specimens was clearly altered. In these experiments, a constant current cathodic pretreatment with $-5.5 \times 10^{-5} \text{ A/cm}^2$ was adopted. During this pretreatment, the potential of the specimens reached a value of about -1.08 V.

The quasi-stationary potentiostatic polarization curves for high purity zinc in 1.0M NaNO_3 solution showed a passive zone and a passivity breakdown potential. The breakdown potential (-0.52 V) was much higher than those found in all the other solutions used in the present work (Figure 14).

The existence of a breakdown potential for zinc in NaNO_3 solutions was confirmed by scratching technique (Figures 15 and 16). From these results, the most probable value for the breakdown potential was found to be -0.66 V. As in the other solutions tested, the current decay at potentials higher than the breakdown potential

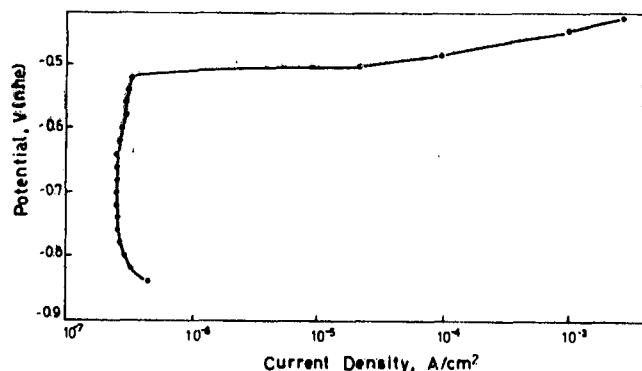


FIGURE 14 — Anodic polarization curve for high purity zinc in deaerated 1.0M NaNO₃ solution (pH = 9.0, t = 25 C).

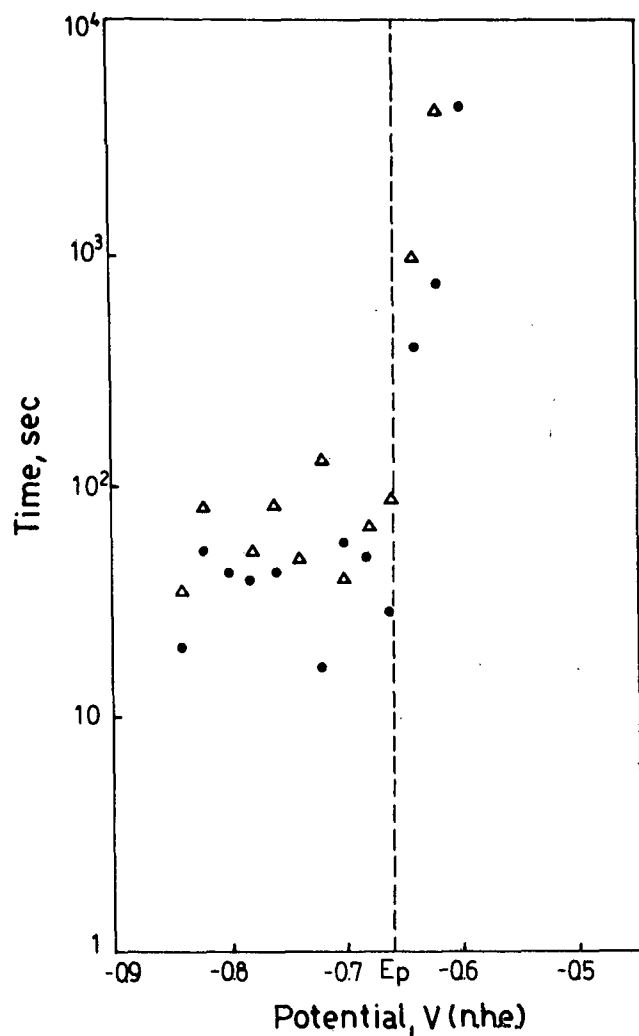


FIGURE 15 — Constant potential repassivation time for high purity zinc after scratching in deaerated 1.0M NaNO₃ solution, pH = 9.0.

was followed by the accumulation of abundant corrosion products over the scratch line.

When zinc was exposed to NaNO₃ solution at potentials higher than the breakdown potential, highly localized corrosion was found (Figure 17). Heavy accumulation of corrosion products was observed over the pits.

To complete the study of zinc in nitrate solutions, the electrochemical behavior in 1.0M HNO₃ solution was measured. It

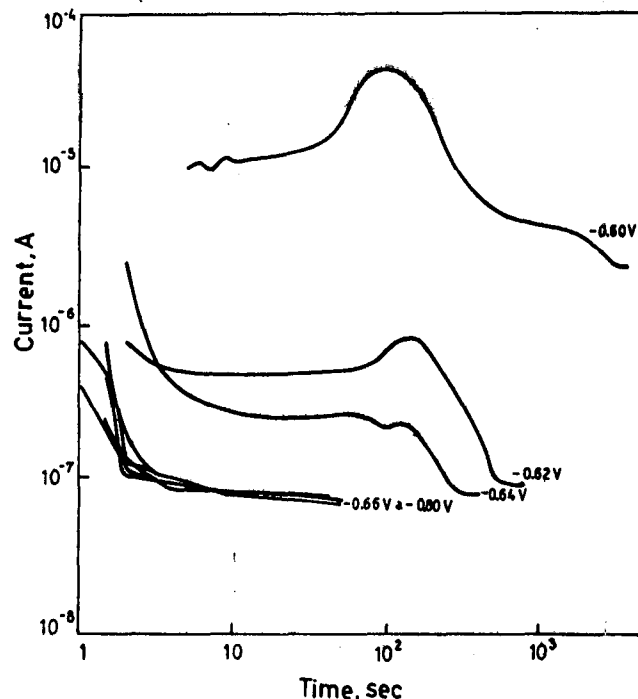


FIGURE 16 — Constant potential current-time curves for high purity zinc after scratching in deaerated 1.0M NaNO₃ solution, pH = 9.0.

was found that in a deaerated solution of nitric acid, zinc showed a corrosion potential between -0.66 and -0.65 V. It was also observed that any small polarization, whether positive or negative, was followed by a very high increase in the anodic or cathodic current, respectively.

Discussion and Conclusions

The potentiostatic polarization measurements showed that pretreatment of the specimens in the passive zone had an important effect on the later pitting propagation rate. It was shown that the longer the time the passive film was allowed to thicken, the more difficult it was to initiate pitting. Comparison of the breakdown potentials obtained through the different methods indicated that the only method that readily gave the correct breakdown values was the one which mechanically disrupted the oxide film. A similar observation was made with other systems where a method of straining wires was applied to determine the pitting potential. This was confirmed for stainless steels,²⁵ aluminum,¹² and zirconium.²⁶ In all those cases, as now with zinc, the exposure of the bare metal to the corrosive environment led to repassivation at potentials lower than the pitting potential. It was only at potentials higher than the pitting potential that the bare metal showed corrosion. This suggests that an oxide film acts as an inert barrier in the process of pitting. From this fact, two conclusions are drawn. First, any method for measuring pitting potentials should assure that the oxide film is disrupted, otherwise high and irrelevant pitting potentials will be measured. Even a method of constant potential current-time curves, as that proposed by Smialowska and Czachor,²⁷ could lead to misleading results, as shown in Figure 9. Second, any theory of pitting potential should explain the fact that exposure of bare metal does not lead to corrosion if the potential is lower than the pitting potential.

For the analysis of passivity breakdown, the following facts should be considered. When a metal dissolves in an electrolyte containing anions of a strong acid, the following reactions will take place:



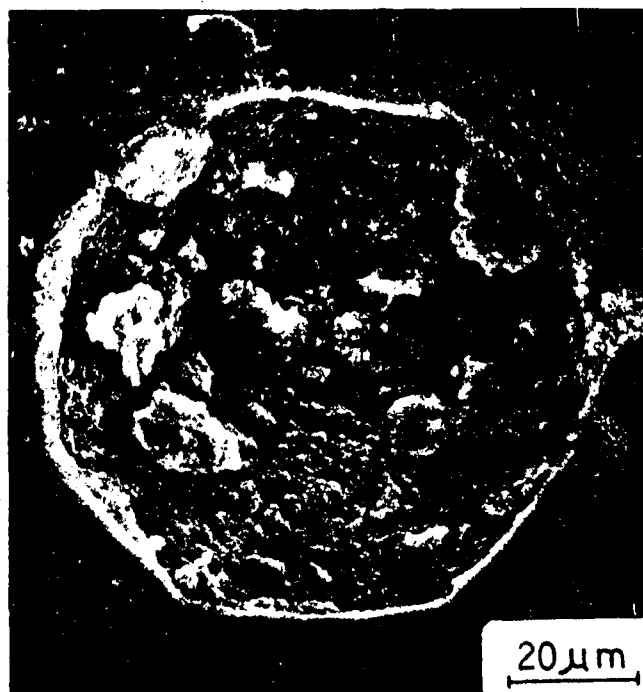
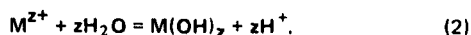


FIGURE 17 — Stereo pair of a pit produced on high purity zinc in deaerated 1.0M NaNO₃ solution, pH = 9.0.

followed by:



If the electrolyte is an alkaline unbuffered solution, the pH of the solution near the anode will drop. The maximum pH drop expected should be given by Reaction (2) at equilibrium, and will depend on the solubility product of the metal hydroxide. Similar results should be obtained if, instead of an hydroxide, an oxide was formed. In the particular case of zinc,²⁸ the pH drop should be somewhere between 5.6 and 8, depending on the Zn²⁺ concentration.

In a in Figure 18 is the initial pH of the solution, and b the pH in the locally acidified zone, pitting will occur only when Reaction

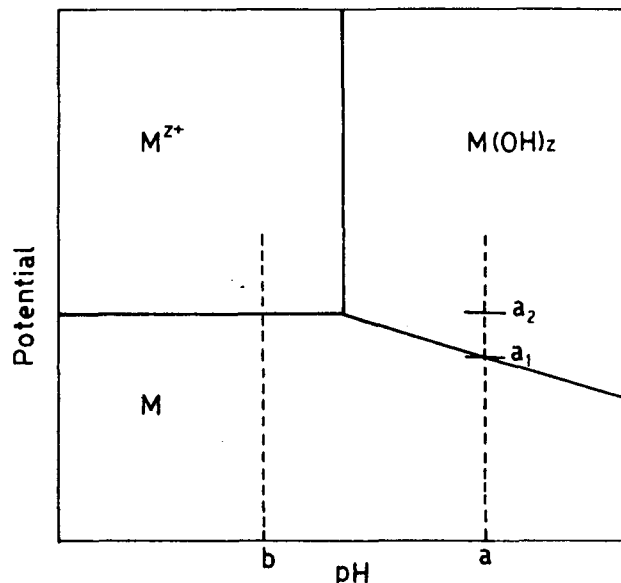
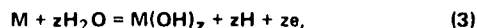


FIGURE 18 — Schematic potential-pH diagram. a: pH of the bulk solution; a₁-a₂: passive zone; a₂: pitting potential, and b: pH of the locally acidified zone.

(1) becomes thermodynamically possible, *i.e.*, pitting will start at a potential higher than a₂. Between a₁ and a₂ only the reaction:



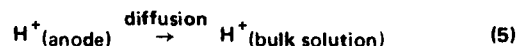
will take place, and the metal will repassivate. Above the potential a₂, the localized acidity produced by Reaction (3) could give the conditions for Reaction (1) to occur. This reaction, followed by Reaction (2), will maintain the acidity near the metal surface. In the particular case of zinc, as soon as the solution close to the metal surface reaches a pH value lower than ~8.5,¹⁸ the metal will not repassivate any more.

According to Figure 18, the passivity breakdown potential, or pitting potential, of the metal will be given by the equilibrium potential of Reaction (1). Such a mechanism was proposed by Pourbaix²⁹ for the pitting potential of copper, but it failed when applied to metals with equilibrium potentials outside the range of stability of water, such as iron, aluminum, zinc, etc., or when reducible anions, such as nitrate, were present in the solution.

The main point in the above described mechanism is that there exists heterogeneity in the solution, close to the dissolving metal surface. The perpetuation of this heterogeneity is a necessary condition to maintain the dissolution process. When the steady state is reached, the rate of proton production, (1) plus (2), will be equal to the rate of proton consumption. In an unbuffered NaCl solution, there will be two processes responsible for the proton consumption. One will be the hydrogen evolution reaction:



and the other will be proton diffusion from the anodic zone to the bulk of the solution:



The rates of Reactions (1), (3), and (4) are potential dependent. If Reaction (2) is fast, Reaction (1) will give the rate of proton production, and the higher the potential, the higher the rate of proton production will be. On the other hand, the lower the potential, the higher the rate of Reaction (4), *i.e.*, the rate of proton consumption. The potential at which the rates of Reactions (1) and (4) are equal is the corrosion potential or open circuit potential of the metal in the acidified solution close to the anode (E_{c,a}). This potential could be measured in a separate experiment, by exposing

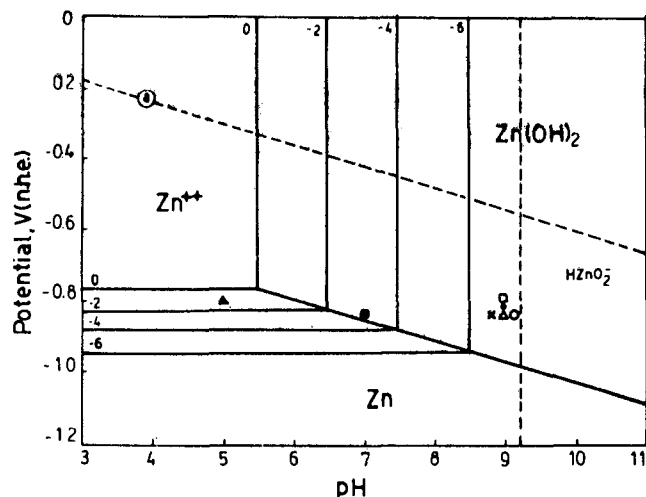


FIGURE 19 — Fragment of the Zn-H₂O potential-pH diagram showing the passivity breakdown potentials measured in the present work. Δ and $\square$: 1.0M NaCl; $\circ$: 0.1M NaCl; $\square$: 0.01M NaCl; $\diamond$: 0.5M Na₂SO₄; $\times$: 1.0M KI; and Δ : corrosion potential of high purity zinc in 1.0M NaCl.

the metal to a solution resembling that near the anode. If the metal in the alkaline, unbuffered solution, is exposed at a potential equal to $E_{c,a}$, No localized acidity could be produced, since at such potential the rate of Reactions (1) plus (2) will equal the rate of Reaction (4), and no net production of protons will take place. Meanwhile, process (5) will dissipate any previously existing localized acidity. Then at any potential up to $E_{c,a}$, the metal will form protective oxide films, and any disruption of the oxide film will lead to its reformation. At potentials higher than $E_{c,a}$, the filmed metal will be under an unstable condition. A disruption of the oxide film could result from a mechanical action, such as scratching or straining, or from changes in the electrode potential, as reported by Vetter and Strehlow.³⁰ Once bare metal is exposed to the solution no protective film will be reformed.

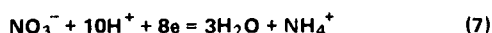
In the case of high purity zinc, as the reaction of hydrogen evolution requires a high overpotential, $E_{c,a}$ will be close to the equilibrium potential of Reaction (1). This is confirmed in Figure 19, where all the breakdown potentials measured in alkaline solutions were close to the equilibrium potential of the reaction:



and equal to the corrosion potential of zinc in an acid solution. Any anion which does not interfere with Reactions (1) and (4) should give the same breakdown potential. No specific effect was observed with Cl^- , I^- , or SO_4^{2-} anions, as shown in Figure 19.

The localization of corrosion on the metal surface will be given by the ease with which the passive film dissolves in the locally acidified solution. The zinc oxide film seems to dissolve very easily, thus explaining the general corrosion observed in Figure 2. On the other hand, if the solubility of the oxide film is reduced by aging of the oxide film, corrosion takes a more localized form (Figure 3).

A different picture is found if instead of working in a solution of an indifferent anion of a strong acid, a reactive anion is used. In NaNO₃ solutions, for instance, not only Reactions (1), (2), (3), and (4) will have to be considered, but also a new reaction:



Reaction (7) is proton consuming, the same as Reaction (4), and localized acidity in NaNO₃ solutions will take place at potentials much higher than in NaCl solutions. A new $E_{c,a}$ value will apply in this case, and it will be the open circuit potential of zinc in acid nitrate solutions. As observed in the present paper, passivity

breakdown of zinc in 1M NaNO₃ solutions only occurs at potentials higher than -0.66 V, while the open circuit potential of zinc in 1M HNO₃ solution was found to be between -0.66 and -0.66 V.

Any other impediment for the formation of the locally acidified zone will produce inhibition of the pitting process. This is the case when buffers are present in the solution. In this case, the higher the concentration of the buffer, the higher the pitting potential will be. The pitting potential will result from a competition between the transport of buffer anions to the surface of the metal and the production rate of metal ions on the metal, as described by Augustynski, *et al.*²⁰

From the present paper, it is concluded that:

1. High purity zinc shows, in unbuffered solutions, a pitting potential close to the equilibrium potential of the reaction:



2. Pitting starts as a result of local acidification of the solution close to the metal surface.

3. The pitting potential is the minimum potential at which such local acidification could be maintained.

Acknowledgments

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Ellipsometric Studies on Iron Oxide Film Growth at 100 to 350 C[★]

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Abstract

Ellipsometric measurements of oxide film formed at 100 to 350 C in air were performed on a steel specimen. The complex indices of refraction of individual layers in the multilayer oxide film and their thicknesses were determined. The kinetics of oxide film formation was studied and the activation energy for film formation was calculated.

Iron oxide formation depends on oxidation temperature. It is generally accepted that at low temperatures, Fe_3O_4 (and $\gamma\text{-Fe}_2\text{O}_3$) is formed, whereas above 220 C, a cubic spinel type of oxide (either $\gamma\text{-Fe}_2\text{O}_3$ or Fe_3O_4) is formed at the oxide/metal interface and $\alpha\text{-Fe}_2\text{O}_3$ at the oxide/gas interface. The composition and thickness of the oxide film was also found to be dependent on oxidation conditions, surface preparation, and the presence of impurities.¹ On the basis of electron diffraction and electrochemical evidence, Sewell and Cohen^{2,3} suggested that an intermediate oxide some 50 Å thick separates Fe_3O_4 from $\alpha\text{-Fe}_2\text{O}_3$. This oxide consists of an array of oxygen planes with cubic close packing and has a distribution resembling that of $\gamma\text{-Fe}_2\text{O}_3$. Considering this structure together with the stacking fault mode of nucleation of $\alpha\text{-Fe}_2\text{O}_3$, they proposed the following model for the composition of the thin oxide film:

metal/ Fe_3O_4 /cpc $\gamma\text{-Fe}_2\text{O}_3$ /stacking faults/ $\alpha\text{-Fe}_2\text{O}_3$

The results of studies carried out by Sewell and Cohen,³ indicate that the composition and structure of the oxide film on iron is more complex than was previously believed.

The present work was carried out in order to elucidate the kinetics of oxide film growth (in the range 100 to 350 C) and to determine the thickness and the optical constants of oxide film grown at different temperatures.

Experimental

The experiments were performed on a steel of the following composition: C, 0.305%; Mn, 0.35%; Si, 0.16%; P, 0.19%; and S, 0.41%. The specimens had the form of cylindrical steel discs with a 3 cm² exposed area. They were prepared by polishing with line emery metallographic papers to 800-grit finish, annealing for 3 hours in vacuum (10⁻⁵ mm Hg) at 640 C, and polishing with 1 μ diamond abrasive. After mechanical polishing, the specimens were cleaned, degreased, and cathodically treated in a solution of borate buffer of pH 8.4 (0.11M H_3BO_4 + 0.025M $\text{Na}_2\text{B}_2\text{O}_7$) at the potential of -0.66 mV/NHE. The specimens prepared in this way have on the surface an oxide film formed in air at 20 C. The

complex index of refraction of such iron was 3.0(1 - 1.32i). After determining the optical parameters of iron, the specimens were oxidized in air at 100, 150, 200, 250, 300, and 350 C for 30 to 1000 minutes as follows: the specimens were placed in a furnace heated to the required temperature in air atmosphere. The required temperature in the furnace was established after 5 to 10 minutes and was maintained with an accuracy of ± 2 C during oxidation. Then, the specimens were furnace cooled to room temperature in an argon atmosphere.

The ellipsometric measurements were performed in air by the Archer-Winterbottom method with the compensator situated in the incident beam. The vacuum wave length of light was 5461 Å, and the angle of incidence was 60°. The optical constants of iron and of films on its surface, as well as film thickness, were calculated using the McCrackin computer program.⁴

The semiconductive properties of oxide layers obtained in various ways were determined from the kinetics of the redox reaction: $\text{Fe}(\text{CN})_6^{-3}/\text{Fe}(\text{CN})_6^{-4}$.^{5,6}

Results

The results of the ellipsometric measurements are given in Figures 1 through 4. In Figures 1 and 2, the points represent the values of the readings of analyzer (A) and polarizer (P) at the extinction condition and the curve shows the theoretical relationship between A and P for the film with the index of refraction indicated on the figures. It follows that, depending on the oxidation temperature, one or more oxide layers having different properties are formed on the metal surface. The results of measurements of P and A for the specimens oxidized at 100, 150, and 200 C are given in Figure 1. At these temperatures, only one oxide film is formed with complex index of refraction 2.55(1 - 0.14i). This value is close to the values of complex index of refraction found by various authors for magnetite obtained by gaseous oxidation and by anodic oxidation.⁷

Figure 2 shows the same relationship also for specimens heated at 250, 300, and 350 C, as well as the optical constants corresponding to the experimentally found curves of dependence of A upon P. It can be inferred from this figure that the oxide layer formed at 250 C consists of two layers: (1) an inner layer [2.55 (1 - 0.14i)] and (2) an outer layer having the refraction index 2.8 (1 - 0.2i). However, the specimens oxidized in air at 300 and 350 C can consist of three or four oxide layers. The third one has optical

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Anodic Behavior of Aluminum Straining and a Mechanism for Pitting

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ABSTRACT

The anodic behavior of pure aluminum during straining at a constant potential in various electrolytes was studied. In sodium sulfate solutions, up to 1.84V, and both in sodium chloride solutions and in sodium nitrate solutions below the pitting potential, the exposure of bare metal to the solution leads to repassivation. At potentials higher than the pitting potential, pitting localization depends on the rate of pitting nucleation. Under conditions of fast pitting nucleation generalized pitting was observed, while under conditions of slow pitting, pits nucleated preferentially on the slip lines and might eventually have led to transgranular stress corrosion cracking. Pitting is the result of localized acidification on the metal-solution interphase due to metal dissolution and hydrolysis of the metal ions. To maintain such acidification, compensation for the loss of protons by hydrogen evolution and by diffusion to the bulk of the solution is necessary. Such compensation will occur if the electrode potential of the metal is higher than its corrosion potential in the locally acidified solution. No pitting will propagate at or below that corrosion potential, which is, for aluminum in chloride solutions, $-0.64V$.

The study of anodic behavior of straining metals has been widely applied to the investigation of the mechanism for stress corrosion cracking (SCC) (1-4). In the present work, the same technique has been used to study the mechanism for the pitting of aluminum. It was found that the exposure of bare metal to a solution, at a potential lower than the pitting potential, leads to the repassivation of the metal. It is only at potentials higher than the pitting potential that the reaction changes from repassivation to anodic dissolution. The change in behavior is correlated to the type of anodic and cathodic reactions occurring on the bare metal.

The above results have also been used to propose a mechanism for transgranular SCC initiation. In many cases the SCC of a metal starts at the pitting potential (5). The reason for this correlation is clear for high strength steels (5, 6) and for aluminum alloys (5), but it is not so in cases where transgranular SCC is observed as is the case with stainless steels in hot chloride solutions.

Experimental

The straining experiments were made with aluminum wires. "Analar" 99.9% aluminum wires, 0.6 mm diameter, and "Leico" 99.999% aluminum wires, 1 mm, diameter, were used. The specimens were about 10 cm long. The wires were previously annealed for 20 min at 400°C in an argon atmosphere, and water quenched. Before the straining experiments the wires were electropolished in a solution of Butylcellosolve, 10% $HClO_4$, at 0°C and 25V. The cell used for the straining experiments was described in a previous publication (5).

Static experiments were performed on 99.99% aluminum coupons of 10×30 mm. The heat-treatment of these specimens was the same as for the wires. The edges and the surface of the specimens were covered with a cured-epoxy resin, leaving an uncovered area of about 1 cm^2 . These specimens were electropolished in the same way as the wires.

The solutions were prepared with analytical grade reagents and were deaerated with purified N_2 (7). A saturated calomel reference electrode was used for the experiments in NaCl solutions, and a mercurous sulfate reference electrode in $NaNO_3$ and in Na_2SO_4 solutions. All the potentials are reported on the normal

hydrogen electrode (NHE) scale. The straining experiments were done at room temperature ($20^\circ \pm 2^\circ C$) and at constant potentials, the current changes were recorded during the experiments.

Polarization of aluminum specimens was controlled by a Tacussel PRT 20-2X potentiostat, and the potential was measured with a Tacussel Aries 10000 electronic millivoltmeter. The current was recorded on a Tacussel EPL2 multirange recorder.

The straining of the wires was done with a motor-driven Hounsfield Tensometer at constant rate of cross head displacement, using initial strain rates of 1.6, 5, 21, and 90%/min. Before straining the wires, they were prestressed below the yield stress and kept at a desired passive potential until a constant current was attained. For the experiments at higher than the pitting potential the specimens were kept for 10 min at a constant potential below the pitting potential, and switched to the working potential simultaneously with the straining machine.

Results

Straining aluminum in neutral 1.0 NaCl solution.—The anodic current was observed to increase significantly when 99.9% aluminum was strained in 1.0M NaCl solution at a constant potential. As soon as the plastic deformation of the wire started, the current began to increase but attained a steady-state value after about 5% elongation. Over a wide range of potentials the steady-state current density observed during deformation was independent of the potential but varied with the strain rate. Figure 1 shows typical results obtained with wires yielding at a constant strain rate of 90%/min with potentials ranging from -0.80 to $-0.56V$. The mean value of the steady-state current density observed at this strain rate was $2.5 (\pm 0.5) \times 10^{-5} A/cm^2$. Wide scattering of the steady-state current density was found in experiments at $-0.53V$ (Fig. 2). The current density measured at this potential was $5 (\pm 2) \times 10^{-5} A/cm^2$. At potentials higher than $-0.53V$ the steady-state current density became potential dependent, and a potential increase of 20 mV produced a 100 times increase in the current density. The potential at which steady-state current density became potential dependent was the same for all the strain rates tested, and was equal (8) to the pitting potential of aluminum in the test solution (Fig. 3).

Below the pitting potential, the steady-state current density during straining depended on the strain rate

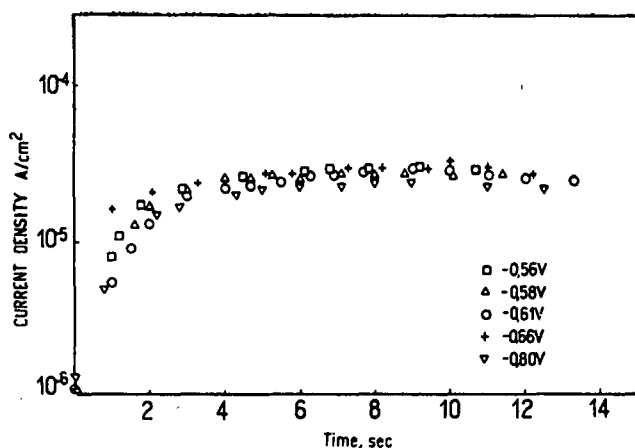


Fig. 1. Potentiostatic current density/time curves at various potentials for aluminum straining at 90%/min in 1M NaCl solution.

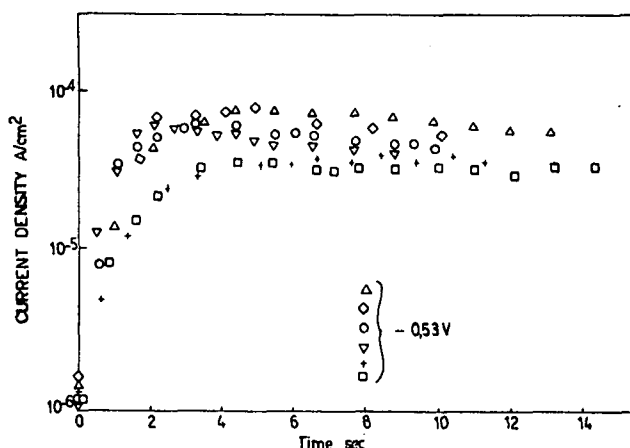


Fig. 2. Potentiostatic current density/time curves near the pitting potential for aluminum straining at 90%/min in 1M NaCl solution.

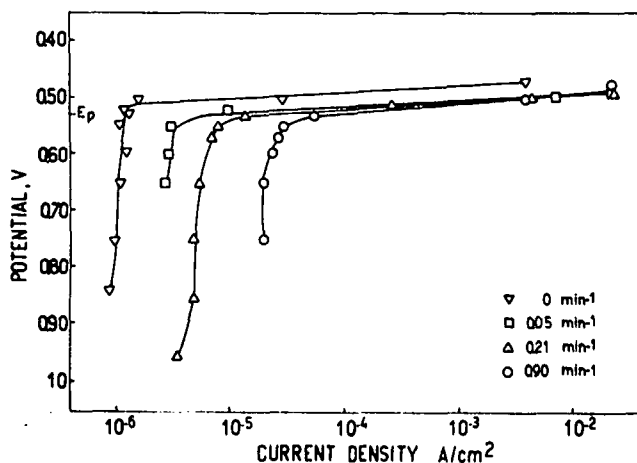


Fig. 3. Steady-state current densities for aluminum during straining in 1M NaCl solution at different potentials and at different strain rates.

(Fig. 4). Above the pitting potential this current was practically independent of the strain rate (Fig. 3).

At potentials lower than the pitting potential, interruption of straining caused a drop in the current density which after a couple of seconds reached the value observed before straining. At the pitting potential and above, interruption of straining also caused a drop in the current, but the drop was less severe than in the previous case. At potentials 100 mV higher than the

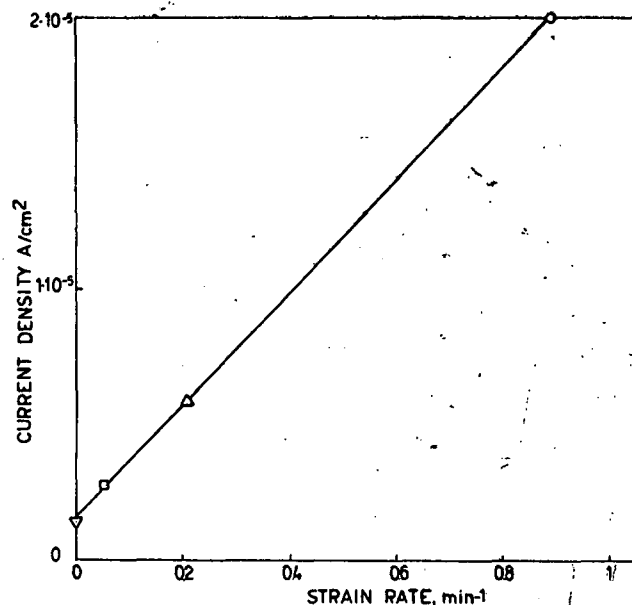


Fig. 4. Relation between steady-state current density and strain rate for aluminum straining in 1M NaCl solution.

pitting potential no current drop was observed after interruption of straining.

After the tests all the wires were examined under both an optical and a scanning electron microscope. No evidence of corrosion was observed on wires strained below the pitting potential. On the other hand, extensive pitting was found on wires which were potentiostated above the pitting potential. The density of the pitting observed was much higher than usually observed on nonstrained or static specimens, but the pits were smaller. Pitting on aluminum in NaCl solutions is known to nucleate very easily without showing any induction time (8). The straining of the metal does not introduce any change in the type of attack except that it offers more sites for pit nucleation, leading to higher density of pits.

Straining aluminum in neutral 0.5M Na₂SO₄ solution.—Figure 5 shows the typical results of the anodic behavior of straining 99.9% aluminum in 0.5M Na₂SO₄ solution. Up to a potential of above 0.9V the steady-state current density was independent of the potential and of the same order of magnitude as that found during straining in 1M NaCl solution below the pitting potential (Fig. 1). At higher potentials a slight potential dependence was observed probably due to

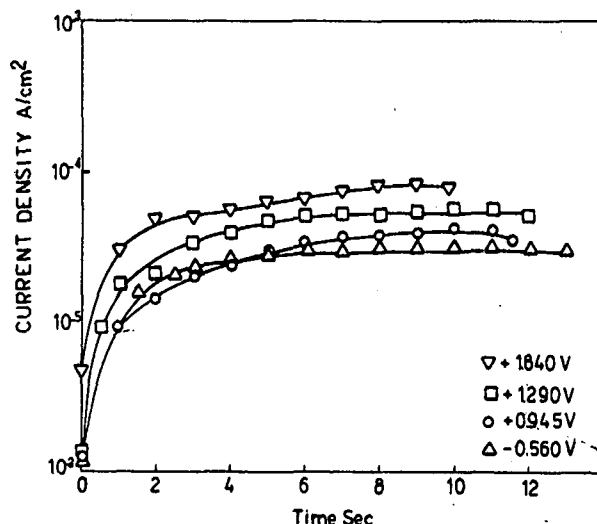


Fig. 5. Potentiostatic current density/time curves at various potentials for aluminum straining at 90%/min in 0.5M Na₂SO₄ solution.

oxygen evolution on the bare metal. The strained wires did not show any sign of corrosion, and no passivity breakdown was detected at potentials up to 1.84V.

Straining aluminum in 0.9M Na₂SO₄ plus 0.1M NaCl solution.—The anodic behavior of 99.9% aluminum during straining at constant potentials was studied in a mixture containing 0.9M Na₂SO₄ plus 0.1M NaCl. The results were similar to those found in 1M NaCl solution, with a potential independent region and a potential dependent region. The transition potential, -0.35V, coincided with the pitting potential reported for aluminum in the same solution (9).

Straining aluminum in 1.0M NaNO₃ solution.—The anodic behavior during straining at a constant potential in deaerated 1.0M NaNO₃ solution was studied with 99.9% aluminum and 99.999% aluminum wires. Similar results were obtained with both grades of purity.

Below the pitting potential of aluminum in nitrates, $E_p = 1.70V$, the current density after about 5% elongation reached a steady-state value, as found in the previous solutions (Fig. 6.). The values of current density, however, are slightly higher than those found in chloride or in sulfate solutions. The steady-state current density was also observed to be slightly dependent on the applied potential. No traces of corrosion were to be found on the strained wires below the pitting potential. Interruption of straining at those potentials caused a rapid drop in the current, which in a couple of seconds reached the same value observed before straining.

When aluminum was strained in nitrate solutions, at potentials higher than 1.70V, the current did not reach a steady value, but kept increasing all through the experiment. The rate of current increase was a function of the potential, and it became higher as the potential increased. No pitting was observed on the strained metal up to potentials 100 mV higher than the pitting potential, provided that the exposure time was not too long. However white corrosion products covering the slip lines could be observed under a microscope.

As described in a recent paper (5), the rate of current increase for aluminum straining in nitrate solu-

tions at potentials higher than the pitting potential followed a square root law (Fig. 7). It was then explained that such a law was the result of pitting nucleation on the slip lines. Recent electron microscopy done in our laboratory confirmed that semicylindrical channels are formed on the slip lines under conditions of the square root law behavior (10).

The rates of current increase for static aluminum and for straining aluminum in nitrate solutions at constant potential are shown in Fig. 8 and 9. It was ob-

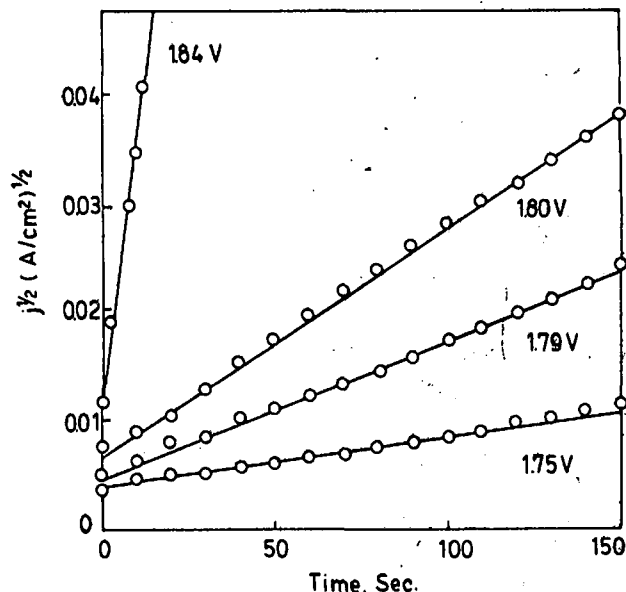


Fig. 7. Potentiostatic current density/time curves for aluminum straining at 1.6%/min in 1M NaNO₃ solution at potentials higher than the pitting potential.

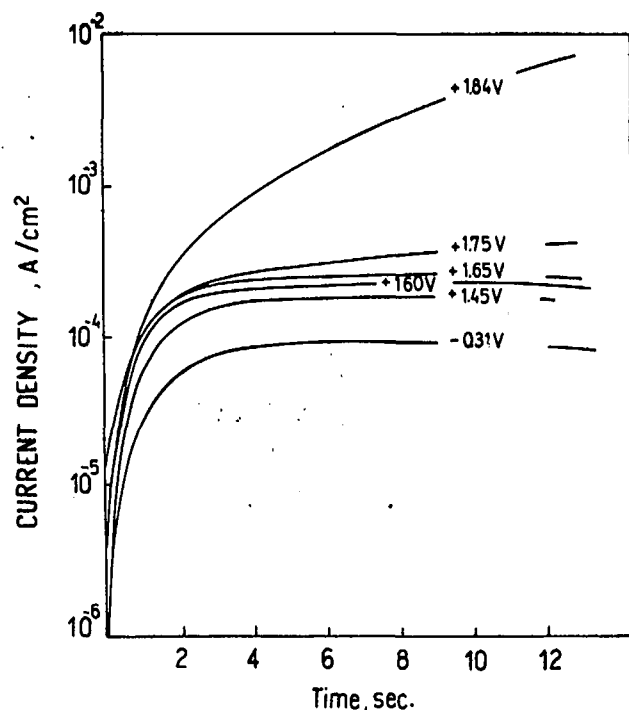


Fig. 6. Potentiostatic current density/time curves at various potentials for aluminum straining at 90%/min in 1M NaNO₃ solution.

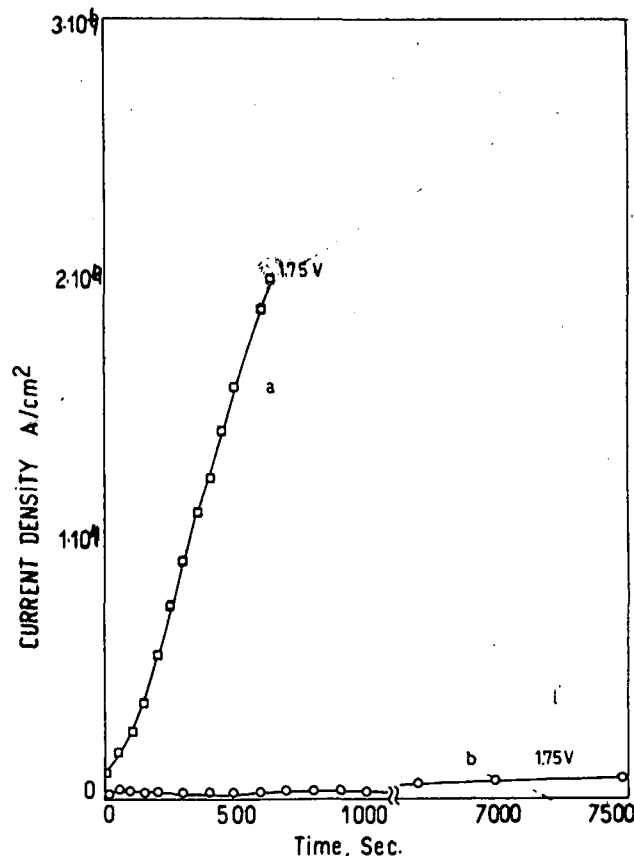


Fig. 8. Potentiostatic current density/time curves for aluminum in 1M NaNO₃ solution at a potential 50 mV higher than the pitting potential. a, Specimen straining at 1.6%/min; b, static specimen.

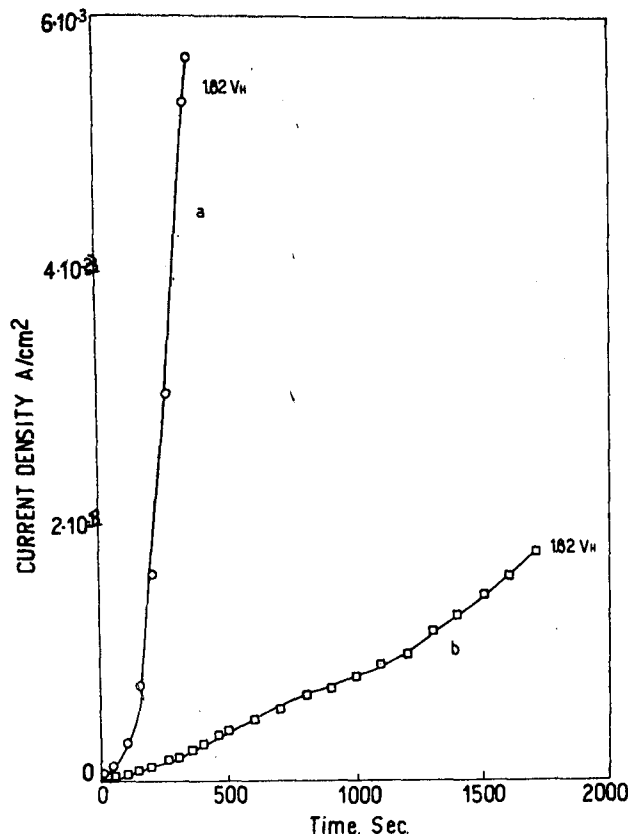


Fig. 9. Potentiostatic current density/time curves for aluminum in 1M NaNO₃ solution at a potential 120 mV higher than the pitting potential. a, Specimen straining at 1.6%/min; b, static specimen.

served that there was a great difference between the anodic behavior of the static metal and that of the straining metal. A slow strain rate of 1.8%/min was used to minimize the contribution of the repassivation process, as described above (Fig. 4). The straining metal showed a much faster current increase than the static metal. The difference in behavior was more pronounced at potentials slightly higher than the pitting potential. At 1.75V the current density for the static metal, after an exposure of several hours, is only a small fraction of that obtained after a few minutes of straining. The rate of current rise for the static metal increased with the potential, and at 1.82V the current density for the static metal became significant. If the current density for the static metal corresponds to hemispherical pitting, and that for the straining metal to the corrosion on slip lines, assuming that both processes do not interfere with each other, Fig. 8 shows that compared to corrosion at slip steps, very little pitting should be expected on the metal at fracture time. On the other hand, at 1.82V, the strained metal should have corrosion on slip lines and also hemispherical pits on the surface at fracture time (Fig. 9).

Discussion

Mechanism of the pitting of aluminum.—After a comparison of the several mechanisms proposed for the pitting initiation on aluminum, the most conflicting point appears to be the role assigned to the oxide film. In one line of thought, supported mainly by Pryor *et al.* (11-16), it is considered that a very important step for pit initiation is the contamination of the oxide film by chloride ions. This contamination increases the conductivity of the oxide film leading to enhanced localized dissolution (pitting). While these authors do not elaborate on the effect of the potential, Hoar *et al.* (17, 18) suggest that the migration of the chloride ions should start at the pitting potential. On the other hand, Wood and Richardson (19, 20), taking into consideration observations with the scan-

ning electron microscope, suggest that the oxide film acts mainly as an inert barrier, with no effect on the mechanism of pitting. According to them the pits will start in flaws always present in the oxide film. The existence of such flaws has been questioned by Pryor (15, 16).

The straining method, as used in the present work, avoids discussion of the existence of flaws in the oxide film, since these flaws are continually produced during straining. Before straining, the aluminum wire carries an air-formed oxide film of the order of 30Å (15). The plastic deformation of the aluminum produces slip displacements of the order of 600Å (21). As the aluminum oxide film is very fragile (22) in deformation the film breaks easily, and the bare metal is exposed to the solution.

In the potentiostatic straining experiments it was observed that there is a range of potentials at which the anodic behavior of aluminum is independent of the electrolyte used. The current density observed during straining in Na₂SO₄ solution (Fig. 5) was similar to that found below the pitting potential in NaCl solution (Fig. 1) and in a mixture of aqueous NaCl plus Na₂SO₄ solution. Similar values were obtained by Bubar and Vermilyea (22) for straining aluminum at -0.06V in ammonium borate solutions. The similarity of anodic behavior in the different electrolytes, as well as the absence of any sign of corrosion on the slip steps, suggest that the exposure of bare metal to a NaCl solution, below the pitting potential, leads to the reformation of an oxide film as the only reaction. The linear relation between the steady-state current density and the strain rate, in Fig. 4, as expected from the straining of passive metals (4), confirms this supposition. These results suggest that if there are flaws in the oxide film below the pitting potential, they will not last long, since the bare metal will quickly repassivate.

The straining experiments show that the behavior of aluminum in NaCl solution is similar to that in a NaNO₃ solution. In both cases repassivation occurs below the pitting potential, and the attack of the metal starts only at the pitting potential. In the case of nitrates, because of its large size, it is doubtful whether the nitrate ion could migrate through the aluminum oxide film. The migration of chloride ions in the aluminum oxide film, as found by Pryor, could produce weak points in the film which would account for the ease at which the pitting in NaCl solutions starts.

As for the changes in behavior observed at the pitting potential, they are visualized as follows. When an oxide-free metal is exposed to the solution a rapid dissolution of the metal will occur



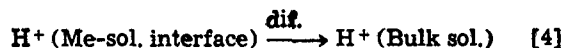
In solutions of weak acid salts, like ammonium borate, the solubility point of the aluminum hydroxide will be quickly exceeded, and it will precipitate on the bare metal inhibiting further dissolution.

In the presence of a strong acid salt, like NaCl, a localized acidification will occur as the result of hydrolysis of the metal salt, which allows further dissolution



The existence of local acidity will be favored if the rate of metal dissolution is increased.

Two other important processes occurring in the acidified zone will be hydrogen evolution and proton diffusion to the bulk of the solution

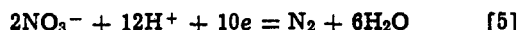


These two processes will oppose the existence of the localized acidity. The rate of metal dissolution, and hence acidity production, has to be high enough to

compensate the loss of protons by diffusion and by reaction.

Reactions [1] plus [3] will give aluminum a certain corrosion potential, or mixed potential. If the potentiostatically controlled potential of the specimen is higher than the corrosion potential of the metal in the acidified solution, the anodic dissolution of the metal will lead to localized corrosion, reactions [1] plus [2]. On the other hand, if the potential of the specimen is maintained below the corrosion potential the reaction of hydrogen evolution, reaction [3], will predominate. In addition there will be no localized acidity, and the oxide film will precipitate on the bare metal. According to this, the pitting potential of aluminum in sodium chloride solutions should be higher than the corrosion potential of aluminum in AlCl_3 solutions, so that reactions [1] and [2] might maintain the localized acidity in spite of [3] and [4]. The corrosion potential of aluminum in saturated AlCl_3 solutions was found to be -0.640V (23), and the pitting potential in 1M NaCl solution was reported as -0.530V (8). The same relation between corrosion potentials and pitting potentials was found for several aluminum binary alloys (24).

The high pitting potential of aluminum in nitrate solutions is attributed to the interference by a cathodic reaction with the localized acidification process, i.e., reduction of the nitrate ions. Gas evolution was observed during the pitting of aluminum in sodium nitrate solutions. Analysis by explosion showed that this gas was neither hydrogen nor oxygen. Preliminary results of gas chromatography suggested that the main component of this gas was nitrogen. Such a cathodic reaction will produce a high consumption of protons, thus preventing the formation of localized acidity



In this case the anodic reaction will predominate only at potentials at which the nitrate reduction becomes negligible. According to Pourbaix diagrams (25), in an acidic solution the nitrate ion will become stable at potentials higher than 1.0-1.2V. It is only at such high potentials that the current density during straining in nitrate solutions becomes potential dependent (Fig. 6) indicating an increasing contribution of the anodic reaction.

Basically the pitting mechanism described above is similar to the "autocatalytic" process for localized corrosion proposed by Edeleanu and Evans in 1950 (26). The main difference is that these authors did not make any reference to the electrode potential. In the present work an explanation for the existence of a pitting potential is given.

Anodic behavior of straining metals.—The above-described results show that the anodic behavior of a straining metal varies substantially with the composition of the media and with the electrode potential. The differences in behavior can be classified into three different categories: (i) repassivation of the metal, (ii) fast pitting nucleation, and (iii) slow pitting nucleation. When repassivation of the metal is the dominant reaction, straining will have little effect on the anodic behavior of the metal. An increase in the anodic current density will be observed as a result of the rupture and reformation of the oxide film, but no localized corrosion will be detected. This is the case for aluminum in sodium sulfate solutions from -0.56 to $+1.8\text{V}$, in ammonium borate solutions at -0.06V (22), or at potentials lower than the pitting potential in solutions containing NaCl or NaNO_3 . This type of behavior was also observed by Muratta and Staehle for nickel in sulfuric acid solutions (4).

The second type of behavior corresponds to those cases where pitting nucleation occurs very easily. In such cases the straining of the metal will have little effect on the anodic attack, and pitting will be observed over the whole surface on the metal. An example of this behavior is that of aluminum in NaCl solutions above

pitting potential as observed in the present work. Another example of this behavior is the one reported by Muratta and Staehle for stainless steel in KCl plus H_2SO_4 solutions at potentials much higher than the pitting potential. This type of behavior is also observed when straining aluminum in nitrate solutions at potentials much higher than the pitting potential.

The third type of behavior corresponds to the conditions of difficult pitting nucleation. In the present work it was found that aluminum in nitrates, at potentials slightly higher than the pitting potential, is one of those cases. Another very well-known instance of difficult pitting nucleation is stainless steel in chloride solutions. This case is well documented in the literature and leads to different pitting potentials under different conditions of measurement (27-29). In these cases straining produces a high increase in the current density. The oxide film acts as an inert barrier, but anodic dissolution on the bare metal exposed at slip steps leads to pitting. When the metal is strained at the pitting potential, pitting will start at the slip steps thus creating conditions that will eventually lead to transgranular SCC initiation.

Acknowledgments

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MECANISMO DE PICADO DE CADMIO DE ALTA PUREZA

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RESUMEN

Se describen los resultados obtenidos estudiando el comportamiento anódico y la ruptura de la pasividad de cadmio de alta pureza en soluciones de distintos electrolitos. En las experiencias realizadas se utilizaron dos métodos potenciostáticos diferentes: trazado de curvas de polarización y medición de tiempos de repasivación.

En soluciones alcalinas de NaCl y Na₂SO₄ el cadmio presenta el fenómeno de picado, siendo necesario superar un cierto valor de potencial, correspondiente al potencial de ruptura del metal en la solución ensayada, para que se inicie la disolución de la superficie pasiva. En solución de KI 1M, pH = 11, el óxido de cadmio es inestable, observándose en estas condiciones la disolución del metal, debido, aparentemente, a la formación del ión $\text{CdI}_4^{=}$.

Los resultados obtenidos se analizan en base a los diagramas de equilibrio electroquímico de los sistemas Cd-H₂O, Cd-I⁻-H₂O y Cd-Cl⁻-H₂O, verificándose que el potencial de ruptura de la pasividad del cadmio en las soluciones estudiadas corresponde al potencial de equilibrio de la reacción:

$$\text{Cd} = \text{Cd}^{+2} + 2 \text{e}^{-}.$$

INTRODUCCION

El picado es una forma de ataque localizado que presentan los metales pasivos cuando el medio corrosivo contiene ciertos iones que suelen clasificarse como "agresivos" (haluros, sulfatos, nitratos, etc.) y cuando el potencial del metal es superior a un cierto valor crítico denominado potencial de picado o potencial de ruptura.

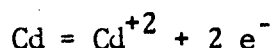
A pesar de las numerosas teorías que se han propuesto hasta el presente intentando explicar el fenómeno de picado y su relación con un potencial determinado, la verdadera naturaleza del potencial crítico de ruptura es

aún incierta. Las discrepancias que existen en este sentido llevaron a iniciar un estudio sistemático del comportamiento anódico y la ruptura de la pasividad de una serie de metales puros con el objeto de determinar cuáles son las condiciones que en cada caso llevan a la aparición de picado.

Para el cinc de alta pureza se encontró(1) que el potencial de ruptura no dependía del anión agresivo presente ni era modificado en forma apreciable por la concentración del mismo, correspondiendo su valor al potencial de equilibrio de la reacción: $\text{Zn} = \text{Zn}^{+2} + 2 e^-$. Esta correspondencia entre el potencial de ruptura medido y el potencial de equilibrio se atribuyó a que la reacción catódica de desprendimiento de hidrógeno no se produce sobre el cinc puro en estas condiciones y, en consecuencia, no interfiere con el equilibrio Zn/Zn^{+2} que se establecerá en el interior de las picaduras como resultado de la acidificación proveniente de la disolución del metal y posterior hidrólisis de los productos de disolución.

Como el diagrama de equilibrio electroquímico del cadmio(2) es muy parecido al del cinc, lo cual indica que ambos metales deberán tener similar comportamiento en soluciones acuosas, y la reacción catódica de desprendimiento de hidrógeno tampoco se producirá sobre el cadmio puro en el rango de potenciales correspondientes al equilibrio Cd/Cd^{+2} , se comenzó a investigar si el cadmio presenta una relación entre el potencial de ruptura y el potencial de equilibrio del metal en medio ácido semejante a la encontrada para el cinc. Los resultados de Kadyrov y col.(3), quienes encuentran que en soluciones de NaCl y NaCl-NaOH el cadmio presenta picado a un potencial de -0,50 V apoyan esta suposición. También Augustynsky(4) encuentra para cadmio, cinc y manganeso en soluciones de tampón borato con diferentes iones agresivos, valores del potencial de picado relativamente próximos al potencial normal Me/Me^{+2} .

En el presente trabajo se estudió el comportamiento anódico del cadmio en las siguientes soluciones: NaCl 1M (pH=11, pH=12,5 y pH=9), NaCl 0,1M (pH=11), NaCl 0,01M (pH=11), KI 1M (pH=11) y Na_2SO_4 0,5M (pH=11). Comparando los resultados obtenidos con los diagramas de equilibrio electroquímico de los sistemas $\text{Cd}-\text{H}_2\text{O}$ (2), $\text{Cd}-\text{I}^- - \text{H}_2\text{O}$ (5) y $\text{Cd}-\text{Cl}^- - \text{H}_2\text{O}$ (5) se comprobó que el potencial de ruptura de la pasividad del cadmio en las soluciones estudiadas corresponde al potencial de equilibrio de la reacción:



MATERIALES Y METODO EXPERIMENTAL

Se utilizó cadmio de alta pureza, 99,999%, laminado en caliente con de capados intermedios, hasta un espesor de 1 mm. Del material laminado se cortaron probetas rectangulares de 20 x 10 mm, que fueron recocidas durante 2 horas en atmósfera de Ar a 270°C. El contacto eléctrico se realizó mediante un alambre de cobre soldado en un extremo de las probetas. El contacto eléctrico, los bordes y una cara de las probetas fueron cubiertos con resina epoxy curada a 70°C, dejando libre una superficie de aproximadamente 1 cm². Las probetas fueron pulidas químicamente con una solución de la siguiente composición: 5 c.c. de HNO₃ conc., 5 c.c. de H₂O₂ (100 vol.) y 30 c.c. de alcohol etílico.

Todas las soluciones fueron preparadas con reactivos de pureza analítica y deaireadas con N₂ purificado(6), manteniéndose el burbujeo de N₂ durante los ensayos. El ajuste de pH de las soluciones se realizó mediante el agregado de la base correspondiente.

Todas las experiencias se hicieron a $25 \pm 0,5^\circ\text{C}$, en una celda de vidrio pyrex con contraelectrodo de Pt. Los potenciales se midieron en relación a un electrodo de sulfato mercurioso en las soluciones de sulfato de sodio y en relación a un electrodo de calomel saturado en las demás soluciones, siempre a través de un capilar de Luggin. Todos los valores de potencial están dados en la escala normal de hidrógeno.

Para realizar las mediciones se utilizó un circuito compuesto por un potenciostato Tacussel PRT 40-1X, un milivoltímetro Tacussel S6ZR2 y un registrador Sefram tipo BS.

Antes de iniciar las mediciones las probetas fueron sometidas a una reducción catódica, manteniéndolas durante 20 minutos a un potencial de -0,86 V, esperando luego 30 minutos la estabilidad del potencial de corrosión.

Las curvas de polarización fueron trazadas en forma potenciostática, variando el potencial a razón de 20 mV cada diez minutos.

La determinación de los potenciales de ruptura se realizó por medición de tiempos de repasivación. En estos ensayos el potencial del metal, controlado potenciostáticamente, se fue variando en escalones de 10 mV, esperando 10 minutos a que se estabilice la corriente antes de raspar la superficie de las probetas con un trozo de carburo de silicio pegado en el extremo del capilar de Luggin.

RESULTADOS EXPERIMENTALES

Las curvas de polarización anódica del cadmio obtenidas en soluciones de aireadas de NaCl 1M, NaCl 0,1M, NaCl 0,01M y Na₂SO₄ 0,5M, todas de pH=11, muestran la existencia de un rango de potenciales para los cuales las densidades de corriente son bajas, menores que 10^{-6} A/cm², y no varían significativamente con el potencial, permaneciendo el metal pasivo en estas condiciones. Para un valor de potencial determinado se produce un decidido aumento de la densidad de corriente, y hay aparición de picado sobre la superficie metálica. En la Figura 1 se ven ejemplos de dichas curvas de polarización, mostrando así mismo, que los valores del potencial de ruptura obtenidos por este método pueden ser marcadamente diferentes, aún cuando las curvas sean trazadas en las mismas condiciones experimentales.

Esta dispersión en los valores de los potenciales de ruptura obtenidos por trazado de curvas de polarización condujo a efectuar la determinación de los mismos por medición de tiempos de repasivación. Este método, propuesto por Pessal y Liu(7) para determinar el potencial de picado del acero inoxidable en agua de mar y que dió resultados satisfactorios en el estudio del cinc, consiste en raspar la probeta, mantenida a potencial constante, de modo de romper la película pasivante para exponer a la solución una superficie de metal libre de óxido, y medir el tiempo de repasivación, considerando como tal el tiempo en que la corriente vuelve al valor inicial. Se encuentra que existe un valor de potencial por encima del cual se produce un marcado aumento del tiempo de repasivación, asociado a un comportamiento diferente de la corriente luego del raspado. Este valor de potencial corresponde al potencial de ruptura del metal en la solución ensayada. La Figura 2, en la que se ha representado la variación del tiempo de repasivación con el potencial en solución de NaCl 0,1M, pH=11, muestra un ejemplo de la aplicación de este método. Se observa que a partir de un valor de potencial de -0.48 V el tiempo de repasivación aumenta un orden de magnitud respecto a los potenciales inferiores. Análogamente, en la Figura 3, que muestra la variación de la corriente con el tiempo luego del raspado para cada valor de potencial, se ve que para potenciales inferiores a -0,48 V la corriente, luego de un brusco aumento inicial, vuelve en pocos segundos a valores correspondientes a la zona pasiva, mientras que para un valor de potencial 10 mV más alto no sólo aumenta el tiempo de repasivación, sino que la corriente presenta frecuentes oscilaciones antes de alcanzar nuevamente el valor inicial. Finalmente, para potenciales más elevados la corriente no disminuye luego del raspado, alcanzando valores varios órdenes de magnitud

mayores que los correspondientes al rango pasivo; simultáneamente se observa la aparición de puntos de ataque sobre la superficie raspada.

Se han encontrado resultados similares en soluciones de NaCl 1M, NaCl 0,01M y Na₂SO₄ 0,5M. Los valores de los potenciales de ruptura correspondientes se han reunido en la Tabla I.

TABLA I - Potenciales de ruptura

SOLUCION	Ep (Ve.n.h.)	SOLUCION	Ep (Ve.n.h.)
NaCl 1M, pH=11	-0,53	NaCl 0,1M, pH=11	-0,48
NaCl 1M, pH=12,5	-0,50	NaCl 0,01M, pH=11	-0,38
Na ₂ SO ₄ 0,5M, pH=11	-0,45		

En solución deaireada de KI 1M, pH=11, la curva de polarización del cadmio (Fig.4) es semejante a las ya descritas, con la presencia de un potencial crítico que separa la zona pasiva de la zona donde se produce el picado. Sin embargo, la densidad de corriente en la zona pasiva es más alta y el valor del potencial de ruptura (-0,64 V) es marcadamente inferior a los valores obtenidos por el mismo método en presencia de cloruros o sulfatos.

Cuando se aplica el método de medición de tiempos de repasivación se encuentra que el comportamiento del cadmio en este medio es distinto al observado en las otras soluciones ensayadas. La Fig.5, en la que se ha representado la variación de la corriente con el tiempo luego del raspado, evidencia claramente esa diferencia pues muestra que en soluciones de ioduros no existe ningún valor de potencial para el cual se produzcan variaciones significativas en el comportamiento de la corriente cuando se raspa la superficie metálica. La misma no experimenta el marcado aumento inicial que indicaría la ruptura de un óxido pasivante pero su valor aumenta prácticamente en forma continua a medida que aumenta el potencial, lo que permite concluir que en estas condiciones no se produce la pasivación del metal.

MORFOLOGIA DEL ATAQUE

Respecto a la morfología del ataque, el cadmio presenta un ataque poco profundo que se extiende rápidamente cubriendo grandes áreas de la superficie metálica. La Fig.6 muestra el ataque observado en solución de NaCl 1M, pH=11, pero la misma morfología del ataque fue encontrada en todas las soluciones ensayadas. El ataque permite diferenciar los granos pues se extiende siguiendo ciertos planos cristalinos, originando una especie de facetado cristalográfico, que puede observarse con más detalle en la Fig.7. Esta morfología del ataque, que difiere marcadamente de la localización característica del picado en otros metales, también fue encontrada para el cinc en soluciones de distintos electrolitos(1).

DIAGRAMAS DE EQUILIBRIO

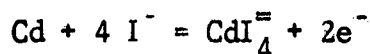
En la Fig.8 se comparan los potenciales de ruptura encontrados en las distintas soluciones ensayadas con el diagrama de equilibrio electroquímico del sistema Cd-H₂O(2). En la misma figura se ha señalado el valor de potencial para el que se observa aumento de la densidad de corriente al trazar la curva de polarización en solución de KI 1M. Se encuentra que existe buena coincidencia entre los valores obtenidos en presencia de cloruros y sulfatos y el potencial de equilibrio del metal en medio ácido. Sin embargo, este diagrama no permite interpretar los resultados obtenidos en presencia de ioduros pues, de acuerdo al mismo, la zona pasiva que aparece al trazar la curva de polarización correspondería a un rango de potenciales para los cuales la única especie termodinámicamente estable es el metal.

Sabiendo que el cadmio forma complejos estables con el ión I⁻, lo cual modifica las condiciones de equilibrio, se construyó el diagrama de equilibrio potencial-pH del sistema Cd-I⁻-H₂O a 25°C para una solución que contenga 1 ión-gramo de ioduro total disuelto por litro (Fig.9)(5).

Se encuentra que la presencia de ioduros modifica sensiblemente el diagrama. En particular, para bajas concentraciones de ión Cd⁺² total (Cd⁺² + CdI₄⁼) en solución se ha producido un marcado desplazamiento del potencial de equilibrio en medio ácido hacia potenciales más bajos y prácticamente ha desaparecido el dominio de estabilidad del óxido, quedando reducido a un rango de pH muy estrecho, comprendido entre 13,2 y 13,5.

Cuando se comparan los resultados obtenidos con el nuevo diagrama se

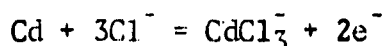
verifica que la zona pasiva que aparece en la curva de polarización corresponde a un rango de potenciales para los cuales habrá gran competencia entre disolución del metal y formación de un óxido pasivante. Dicha zona desaparece cuando se raspa la superficie metálica pues se promueve la disolución del metal de acuerdo a la reacción:



Como el cadmio también forma complejos con el ión Cl^- , se verificó el efecto de este último sobre las condiciones de equilibrio construyendo el diagrama de equilibrio electroquímico del sistema $\text{Cd}-\text{Cl}^--\text{H}_2\text{O}$ a 25°C para una solución que contenga 1 ión-gramo de cloruro total disuelto por litro (Fig.10)(5). Si bien se produce un corrimiento del límite superior de estabilidad del cadmio hacia potenciales más bajos y un estrechamiento del dominio de estabilidad del $(\text{OH})_2\text{Cd}$, estos desplazamientos son menos marcados que en presencia de ioduros.

Como para bajas concentraciones de ión Cd^{+2} total ($\text{Cd}^{+2} + \text{CdCl}_3^-$) en solución el valor de $\text{pH}=11$ coincide prácticamente con el límite del dominio de estabilidad del óxido, se realizaron experiencias en soluciones de diferente pH con el objeto de verificar cómo se modifica el comportamiento del metal dentro y fuera de dicho rango. En solución de NaCl 1M, $\text{pH}=12,5$, condiciones que de acuerdo al diagrama corresponden al rango de estabilidad del óxido, el comportamiento del metal es semejante al encontrado a $\text{pH}=11$, sólo que el valor del potencial de ruptura ($-0,50 \text{ V}$) es ligeramente más alto (Tabla I). En solución de NaCl 1M, $\text{pH}=9$, condiciones en las que existirá gran competencia entre disolución del metal y formación de un óxido pasivante, el comportamiento del metal coincide con el encontrado en iguales condiciones en presencia de ioduros: mientras la curva de polarización indica la existencia de una zona pasiva y un potencial de ruptura (indicado en el diagrama de la Fig.10), cuando se aplica el método de raspado y repasivación la corriente aumenta prácticamente en forma continua a medida que aumenta el potencial poniendo de manifiesto la inestabilidad del óxido.

En el diagrama de la Fig.10 se han representado los potenciales de ruptura obtenidos en soluciones de NaCl 1M, encontrándose que sus valores coinciden con el potencial de equilibrio de la reacción:

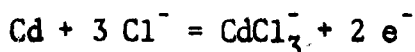


DISCUSION Y CONCLUSIONES

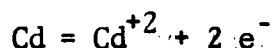
A diferencia de lo que ocurre con el cinc, para el cual el potencial de ruptura tiene el mismo valor en soluciones de cloruros, ioduros y sulfatos de la misma normalidad(1), en el caso del cadmio se encuentra una cierta especificidad del ión agresivo presente, pues el potencial de ruptura hallado en solución de Na_2SO_4 0,5M es 80 mV más alto que el potencial de ruptura en solución de NaCl 1M, mientras que en solución de KI 1M no se encuentra un potencial de picado medible debido a la inestabilidad del óxido.

También el efecto de la concentración de ión Cl^- sobre el potencial de ruptura es más marcado para el cadmio que para el cinc: para el primero se ha encontrado que la transición de una solución de NaCl 0,1M a una solución de NaCl 0,01M produce un aumento de 100 mV en el potencial de ruptura, mientras que en el cinc dicho aumento es de sólo 30 mV.

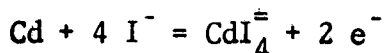
Sin embargo, cuando se comparan los resultados obtenidos con los diagramas de equilibrio electroquímico de los sistemas $\text{Cd}-\text{Cl}^--\text{H}_2\text{O}$, $\text{Cd}-\text{H}_2\text{O}$ y $\text{Cd}-\text{I}^--\text{H}_2\text{O}$ (Figs.10, 8 y 9) se encuentra que el potencial de ruptura del Cd en solución de NaCl 1M coincide con el potencial de equilibrio de la reacción:



mientras que en soluciones más diluidas de cloruros y en solución de Na_2SO_4 0,5M el potencial de ruptura coincide con el potencial de equilibrio de la reacción:



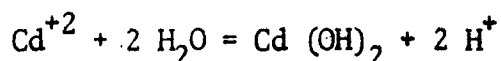
Finalmente, en solución de KI 1M se observa disolución del metal en un rango de potenciales que corresponden al equilibrio de la reacción:



Estos resultados indican que para el cadmio de alta pureza, ~~igual que~~ para el cinc, el potencial de ruptura corresponde al potencial de equilibrio del metal en medio ácido. Además, permiten explicar las diferencias en el comportamiento de ambos metales pues, según lo visto, las variaciones del potencial de ruptura del Cd con la naturaleza del ión agresivo son el resultado de las modificaciones que como consecuencia de la formación de complejos con los iones Cl^- e I^- se producen sobre el potencial de equilibrio. Por su parte el cinc no forma complejos estables con ninguno de estos iones.

Respecto a la influencia de la concentración de cloruros, es evidente que la disminución de la misma dificultará la formación de complejos y, consecuentemente, variará el potencial de equilibrio Cd/Cd^{+2} al hacerse menos marcado el efecto sobre el mismo de la presencia de cloruros.

Las condiciones que determinan la existencia de una relación como la hallada entre el potencial de ruptura y el potencial de equilibrio del metal en medio ácido serán, en el caso del cadmio, semejantes a las descritas para el cinc. Dentro de las picaduras se producirá la disolución activa del metal de acuerdo a las reacciones arriba mencionadas, estableciéndose dichos equilibrios al acidificarse la solución presente en el interior de las mismas como resultado de la reacción:



Por otra parte, la reacción catódica de desprendimiento de hidrógeno no interfiere con el equilibrio establecido dentro de las picaduras pues la misma requiere sobre el cadmio puro un sobrepotencial relativamente elevado y, tal como muestran los diagramas de las Figs. 8, 9 y 10, el potencial de equilibrio del cadmio es muy cercano al potencial de equilibrio de la reacción de hidrógeno. En estas condiciones el potencial de ruptura medido corresponde al potencial de equilibrio del cadmio en la solución ácida presente en el interior de las picaduras. Sólo cuando el potencial aplicado externamente sea superior a dicho valor será posible mantener las condiciones de disolución y, por consiguiente, de acidificación necesarias para que el proceso sea estable.

Esta relación entre potencial de picado y potencial de equilibrio también fue hallada por Pourbaix(8) para el cobre en soluciones de cloruros. Tampoco en este caso existe una reacción catódica que interfiera con el equilibrio dentro de las picaduras pues la reacción de desprendimiento de hidrógeno no es termodinámicamente posible en el rango de potenciales correspondientes al potencial de equilibrio de este metal.

Si se modifica la reacción catódica, el potencial de ruptura ya no corresponderá al de equilibrio sino al potencial mixto del metal en la solución presente en el interior de las picaduras. Esto se verificó en el caso del cinc, para el cual se encuentra que el potencial de ruptura en soluciones de NaNO_3 1M (-0,66 V) es marcadamente superior al de equilibrio, coincidiendo su valor con el potencial de corrosión o potencial mixto del metal en solución de aireada de HNO_3 1M. Este resultado se atribuye a la interfe-

rencia de la reacción catódica de reducción de ión NO_3^- que se produce sobre el cinc en el interior de las picaduras.

También para metales como el hierro, el aluminio, el titanio, etc., en los que se produce desprendimiento de hidrógeno en las picaduras (8,9,10), el potencial en el interior de las mismas corresponderá a un potencial mixto que tenga en cuenta la reacción catódica.

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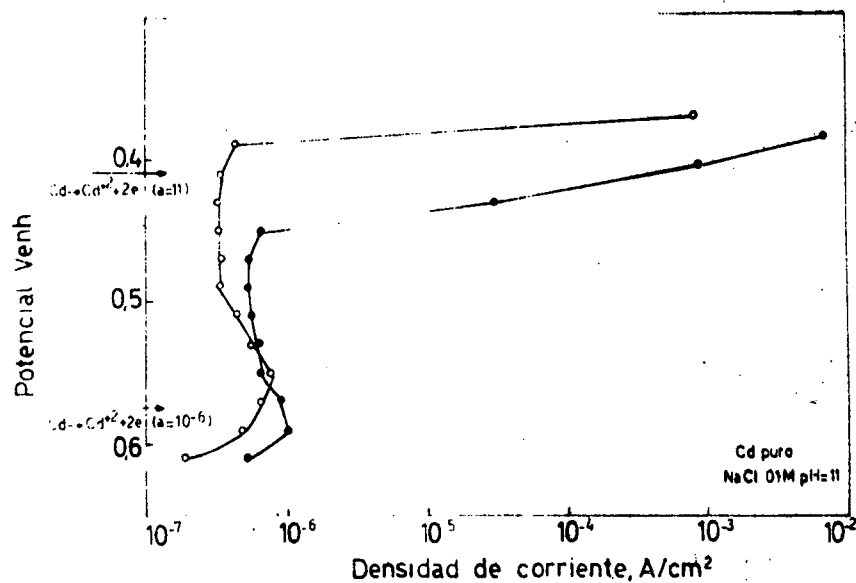


Figura 1 - Curvas de polarización del cadmio en solución deaireada de NaCl 0,1M (pH=11).

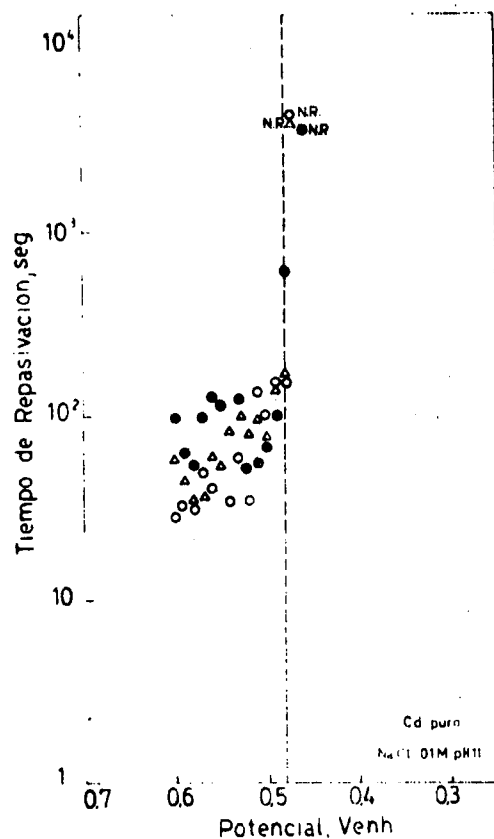


Figura 2 - Variación del tiempo de repasivación con el potencial para Cd puro en solución de NaCl 0,1M, (pH=11)

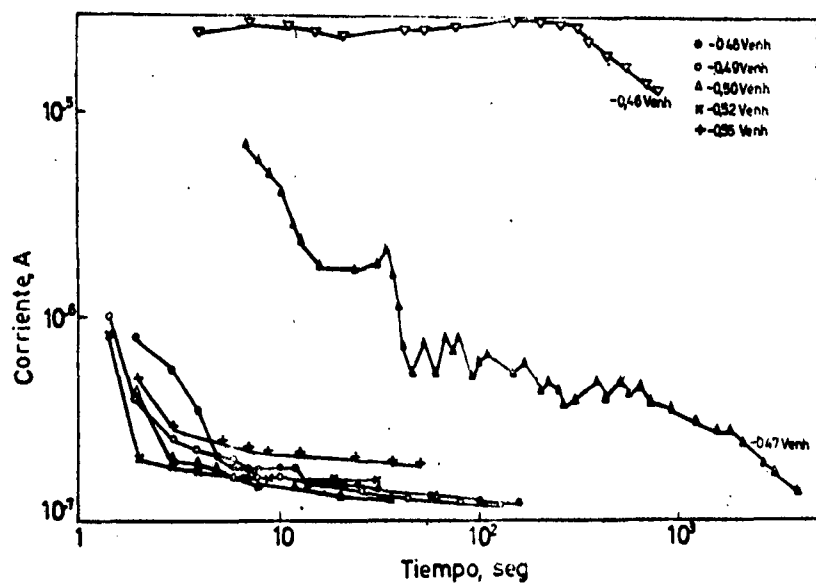


Figura 3 - Curvas I vs. t luego del raspado. Cd puro en solución de NaCl 0,1M (pH=11).

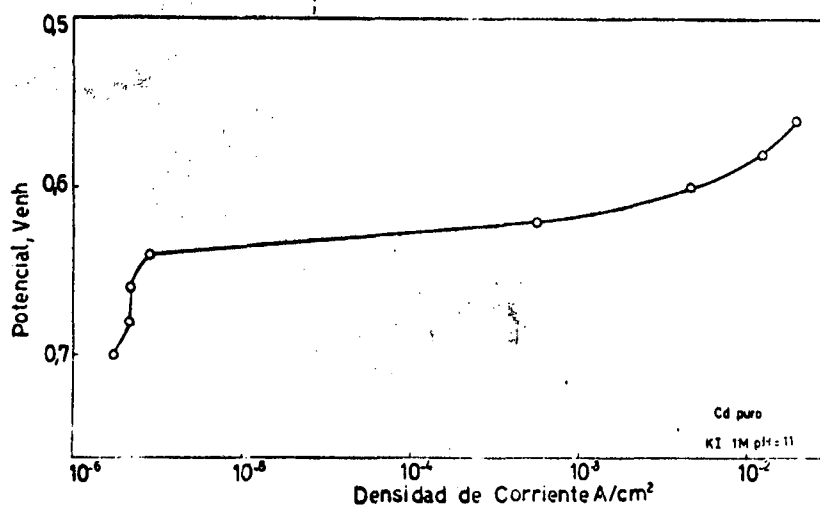


Figura 4 - Curva de polarización del Cadmio en solución de KI 1M (pH=11).

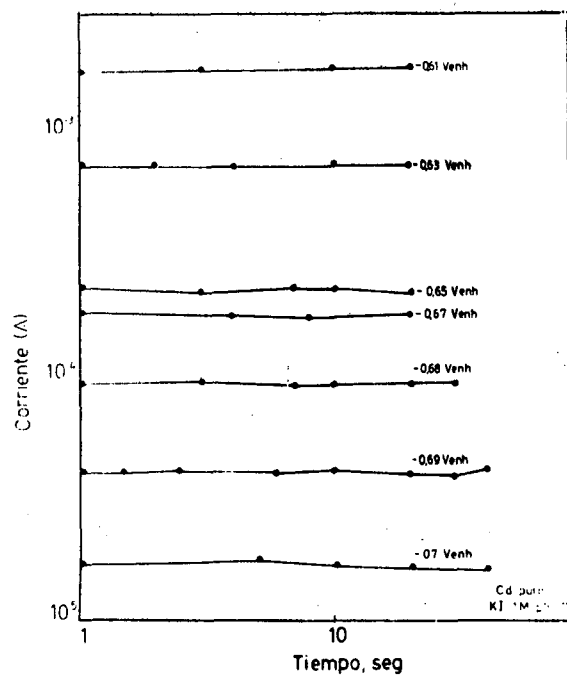


Figura 5 - Curvas I vs. t luego del raspado. Cd puro en solución de KI 1M (pH=11).

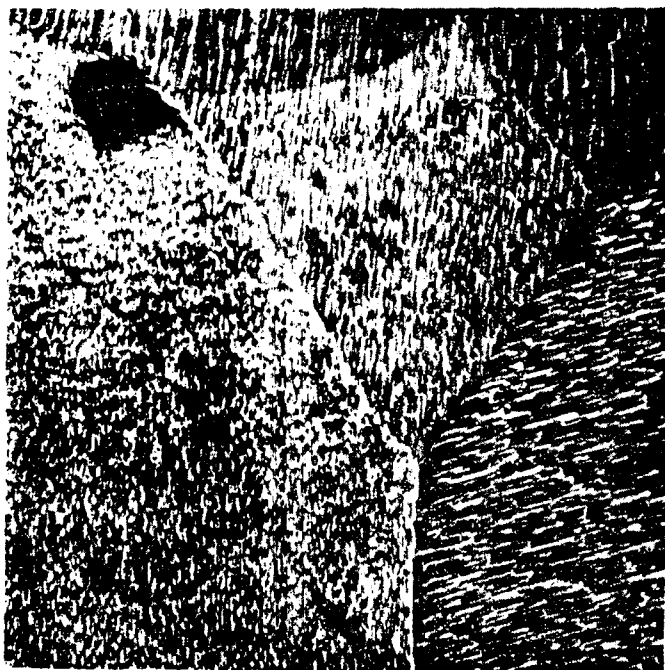


Figura 6 - Ataque del Cd en solución deaerada de NaCl 1M (pH=11) (300X)



Figura 7 - Ataque del Cd en solución deaerada de NaCl 1M (pH=11) (3000X)

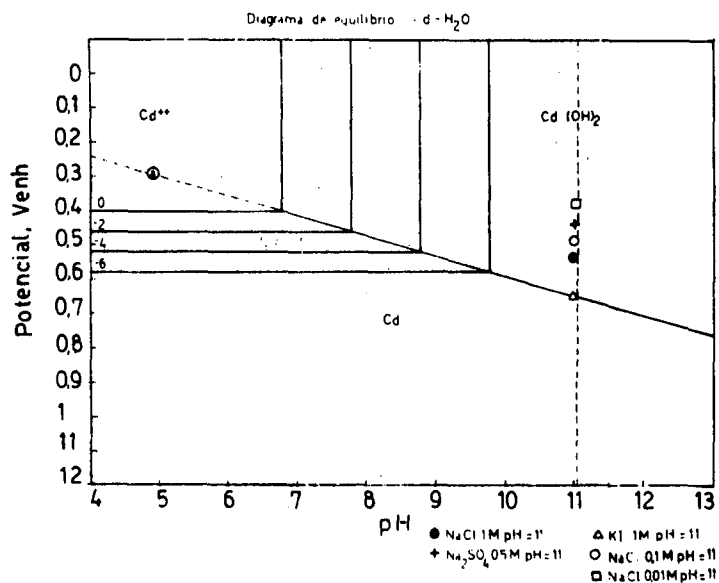


Figura 8 - Diagrama de equilibrio electroquímico del sistema Cd-H₂O a 25°C (2)

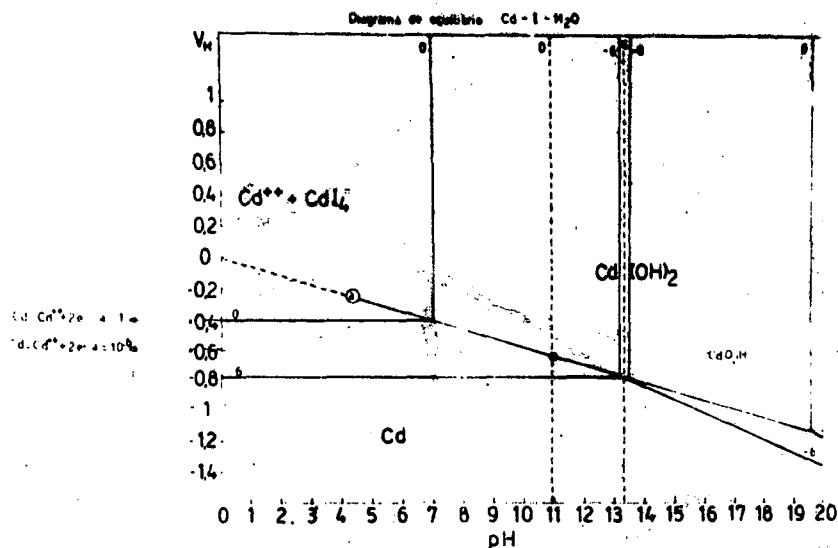


Figura 9 - Diagrama de equilibrio electroquímico del sistema $\text{Cd-I-H}_2\text{O}$ a 25°C para una solución que contenga 1 ión-gramo/litro de yoduro total(*)).

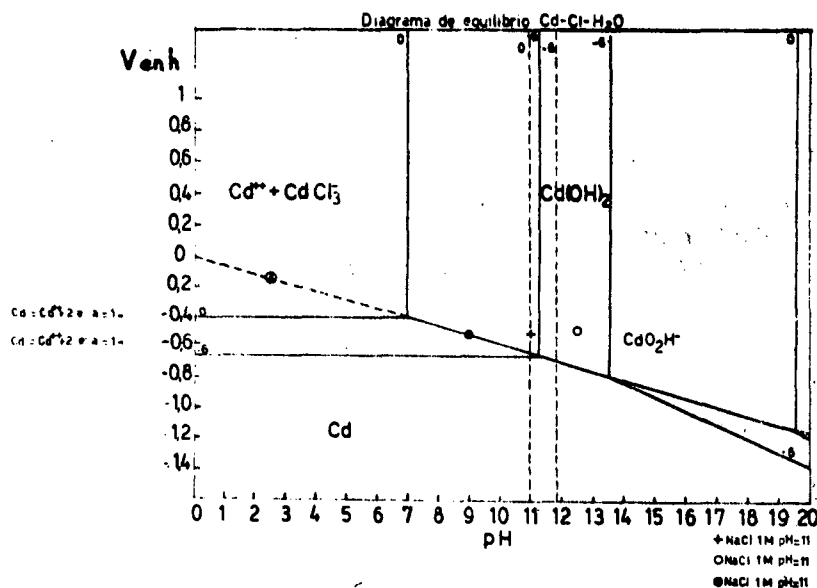


Figura 10 - Diagrama de equilibrio electroquímico del sistema $\text{Cd-Cl-H}_2\text{O}$ a 25°C para una solución que contenga 1 ión-gramo/litro de cloruro total(**).

(*) Las líneas indicadas con los números -6 y 0 representan dos concentraciones de especies solubles ($\text{Cd}^{+2} + \text{CdI}_4^{2-}$ o CdO_2H^-) diferentes: 10^{-6} ión-gramo/litro y 10^0 ión-gramo/litro respectivamente.

(**) Las líneas indicadas con los números -6 y 0 tienen el mismo significado anterior.

CRITICAL POTENTIALS FOR LOCALIZED CORROSION OF ALUMINUM ALLOYS

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Introduction

The present paper describes current research in our laboratory. Emphasis was put on the electrochemical behavior of metals as related to pitting and stress corrosion cracking. In the particular case of Al-Cu alloys, it was found that there is a good correlation between pitting of Al with intergranular corrosion and with SCC of Al-Cu alloys.

The anodic behavior of yielding metals, usually applied to study SCC, was found very useful in the study of the mechanism of pitting of Al. These same studies gave evidence of the way pitting could lead to SCC.

Considering the importance of the anion concentration to the anodic behavior of metals, the determination of potential/concentration diagrams for various metal/aqueous solution systems was initiated. The first results obtained are reported.

Morphology of Pitting in Aluminum

The study of pitting morphology in Al is of particular interest because, on the one hand, not all the reports available in the literature seem to agree, and on the other hand, because although it shows an electrochemical behavior similar to that of other pitting systems,¹ the shape of the pits in Al is not the usual hemispherical electropolished one found in other systems. The confusion in the literature comes from the fact that while some authors reported tunnel-like pitting in Al,^{2,3} others described the pitting in Al as hemispherically shaped.⁴ On the other hand, while some authors^{1,4,5} described pitting of Al in chloride solutions as a typical high potential passivity breakdown, others^{6,7} associated pitting only with bright electropolished pits. According to the last authors, crystallographic etching, as found in Al, should occur only below the Flade potential, as happens in the case of Fe-Cr alloys in sulfuric acid.⁸

During the present work, the morphology of the pitting of pure Al in Cl^- solutions, in NO_3^- solutions, and in mixtures with different anions was studied. Measurements were performed on Al 99.99% specimens annealed for 2 hours at 600 C (1112 F) and water quenched. The edges and the surface of the specimens were covered with a cured epoxy resin, leaving an uncovered area of about 1 sq cm. The specimens were electropolished in a HClO_4 -acetic anhydride bath, and stored in a desiccator for a few days

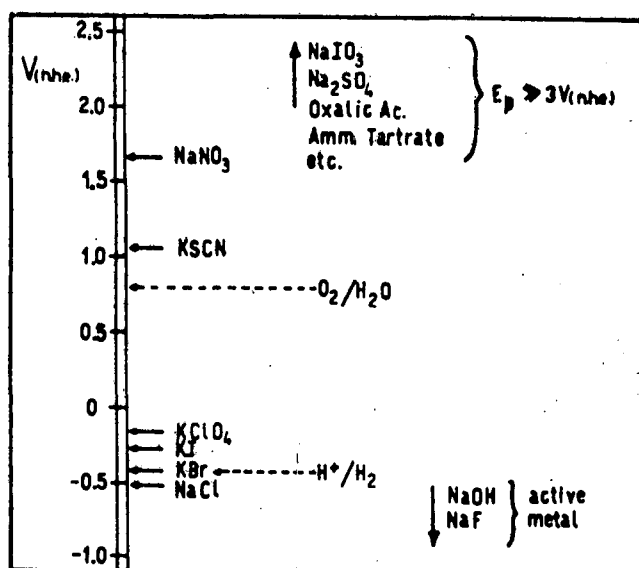


FIGURE 1 — Comparison of the pitting potentials of Al in various electrolytes. The solutions were neutral and of 1M concentration, except for KClO_4 where 0.1M solution was used. The standard potentials for hydrogen evolution and for oxygen reduction in neutral solutions are included as a reference.

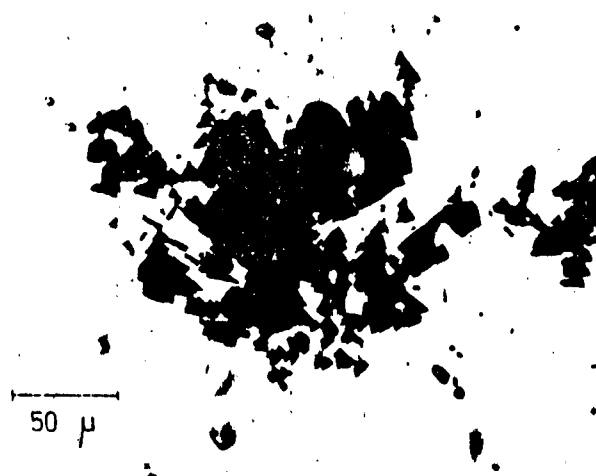


FIGURE 2 — Pitting of aluminum in neutral deaerated 1M NaCl solution. The pits take different geometrical forms according to the orientation of the metal grains. In the figure, predominance of triangular pits is observed.

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before the experiments. The solutions were prepared with analytical grade reagents and were deaerated with purified N_2 . The potential was controlled with a Tacussel PRT 20-2-X potentiostat. All measurements were made at 25 C (77 F).

Pitting of Al is known to occur in solutions of NaCl,^{1,4,5,9} KBr,^{1,4,5} KI,^{1,4} $NaClO_4$,^{1,5} and $NaNO_3$.¹ During the present experiments, it was found that the pitting of Al also occurred in 1M NaSCN at 1.2 V (NHE). The pitting potentials in the different solutions are compared in Figure 1.

The pitting of Al in neutral deaerated NaCl solutions was found to develop clearly geometrical forms (Figure 2). This type of behavior is similar to that reported by Edeleanu² in constant current experiments. Hemispherical pits, as those found by Kaesche⁴ in pH 11 NaCl solutions were not found in neutral NaCl solutions. As reported below, hemispherical pits were found in pH 11.0 deaerated 4M NaCl solutions but, if the pits were allowed to propagate long enough, they developed crystallographic planes similar to those found in neutral NaCl solutions.

Apart from the geometrical shape mentioned above, very well developed crystallographic planes were observed inside the pits formed in neutral NaCl solutions (Figure 3). According to Edeleanu,² these crystallographic planes are the (100) planes. It was also observed, as previously reported by the same author, that the pits formed in neutral NaCl solutions propagated deep into the volume of the metal. Crystallographic pitting similar to that observed in NaCl solutions was found in pits produced by KBr, KI, $NaClO_4$, and NaSCN solutions.

The pits produced in $NaNO_3$ solutions, on the other hand, showed a completely different morphology. In deaerated 1M $NaNO_3$ solutions, the pitting of pure Al occurred at potentials higher than 1.7 V (NHE). In those solutions, the pits were found to be of a circular shape and they were frequently covered by a poorly adherent corrosion product. This corrosion product, amorphous to the electron diffraction, is supposed to be $Al_2O_3 \cdot n H_2O$. Removing the corrosion product, hemispherical electropolished pits could be observed (Figure 4). Inspected with the scanning electron microscope (SEM), the bottom of the pits showed the typical "dried mud" structure (Figure 5).

With more diluted solutions, i.e., 0.1M $NaNO_3$, the pits tended to lose their hemispherical shape, and flat surfaces developed inside the pits. By plastically deforming the pitting specimens and comparing the orientation of the flat surfaces in the pits with the slip lines produced by deformation, those surfaces appeared to correspond to (111) planes (Figure 6).

Measurements made in mixtures of NaCl plus $NaNO_3$ solutions showed that the pitting potentials and the morphology of the pits were strongly affected by the composition of the solution.

Up to a relation of 1 to 9 of NaCl to $NaNO_3$ the pitting potential was the same as for pure $NaNO_3$ solutions (Figure 7). For small contents of NaCl, the morphology of the pits corresponded to that of $NaNO_3$ solutions (Figure 8). In a 0.9M $NaNO_3$ plus 0.1M NaCl solution, the pitting was still



FIGURE 3 — SEM picture showing the (100) planes developed inside pits of aluminum in 1M NaCl solution.

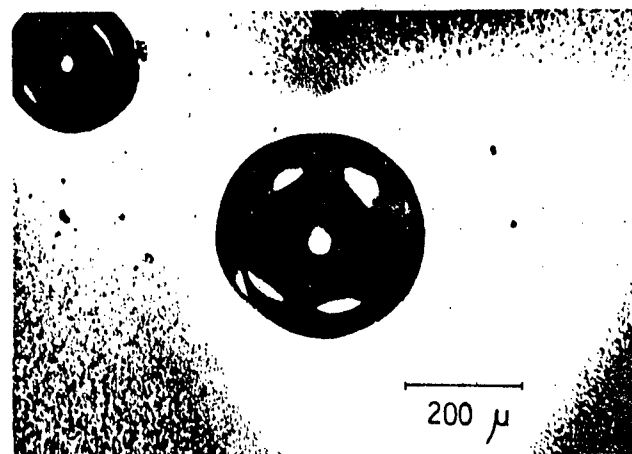


FIGURE 4 — Hemispherical brightened pits of Al produced in deaerated 1M $NaNO_3$ solution.



FIGURE 5 — SEM picture of the interior of a pit of Al produced in a 1M deaerated $NaNO_3$ solution. The bottom of the pit is covered with corrosion products showing a "dried mud" structure.

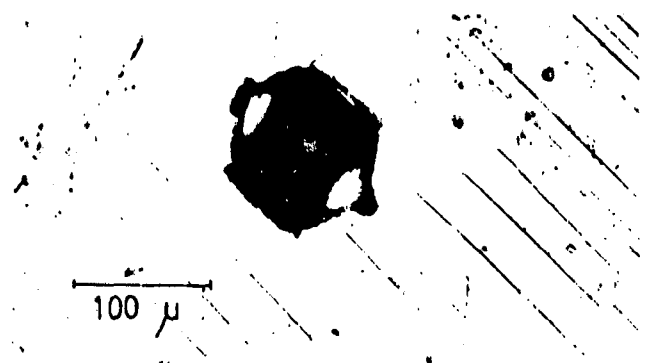


FIGURE 6 - Geometrical pit produced on pure Al in a deaerated 0.1M NaNO_3 solution. The pitted specimen was plastically deformed after polarization to compare the orientation of the pit with the slip lines. Pitting developed flat surfaces which were found to be (111) planes.

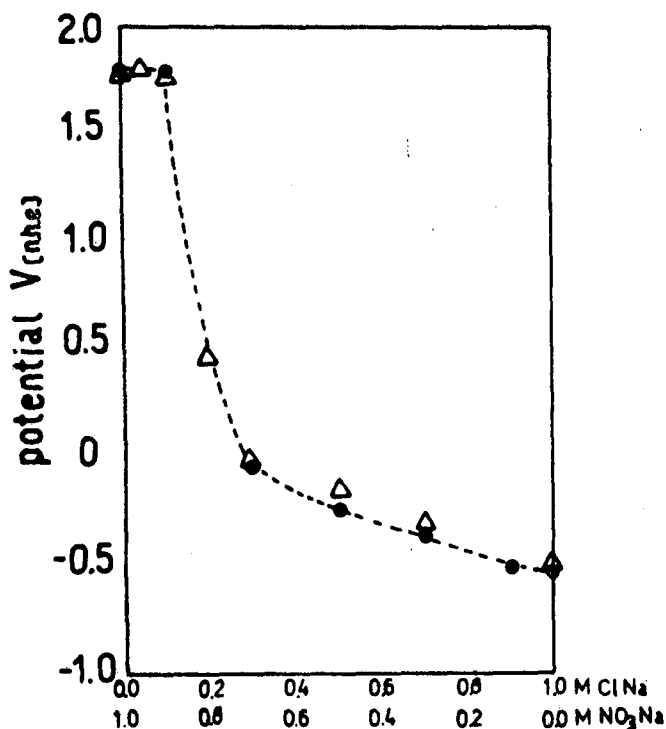


FIGURE 7 - Pitting potentials of Al 99.99% in mixtures of NaCl plus NaNO_3 solutions. Δ : galvanostatic measurements; $\circ$: potentiostatic measurements.

equal to that in a pure NaNO_3 solution, but the morphology of the pits showed an important change. The round shaped pits were replaced by the arrow shaped ones observed in Figure 9. For higher NaCl contents, the pitting potential showed a sharp drop and the pits became of the NaCl type.

In mixtures of NaCl plus NaClO_4 solutions, the pitting potential of Al showed a smooth transition from the pitting potential in pure NaCl solutions to the pitting potential in pure NaClO_4 (Figure 10). In the whole range of compositions tested, the morphology of the pits was of the NaCl type.

The pitting potential of Al in mixtures of NaCl plus Na_2SO_4 solutions (Figure 11) showed the same dependence on the NaCl concentration as in the case of pure NaCl solutions.¹ Only at very low Cl^- concentrations, was a deviation observed, and with a concentration of 0.003M NaCl in 0.5M Na_2SO_4 , no pitting was detected up to a potential of 3 V (NHE). The morphology of the pits was of the NaCl type. At low Cl^- concentrations, pitting appeared as clusters of small pits (Figure 12), but the bottom of the pits showed the same crystallographic etching found in pure NaCl solutions.

From the results so far obtained it can be concluded that, in pitting, brightened hemispherical pits are not a general rule. The pits can have clearly defined crystallographic planes, as in the case of Al in NaCl solutions, or incipient geometrical planes, as in the case of Al in dilute NaNO_3 solutions, or they can be brightened hemispherical pits, as in concentrated NaNO_3 solutions. Crystallographic

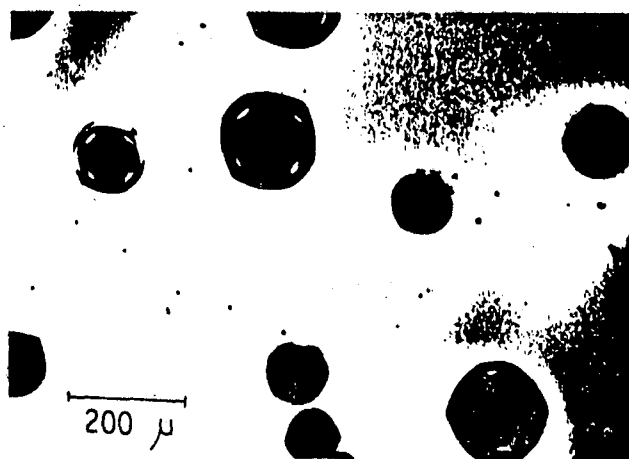


FIGURE 8 - Pitting of pure Al in a 1M NaNO_3 plus 0.05M NaCl solution. The morphology of the pits is the same as for pure NaNO_3 solutions.



FIGURE 9 - Pitting of pure Al in a 0.9M NaNO_3 plus 0.1M NaCl solution. The pitting potential is the same as for pure NaNO_3 solutions, but the pits are arrow-shaped and their interior is covered with a thick layer of corrosion products.

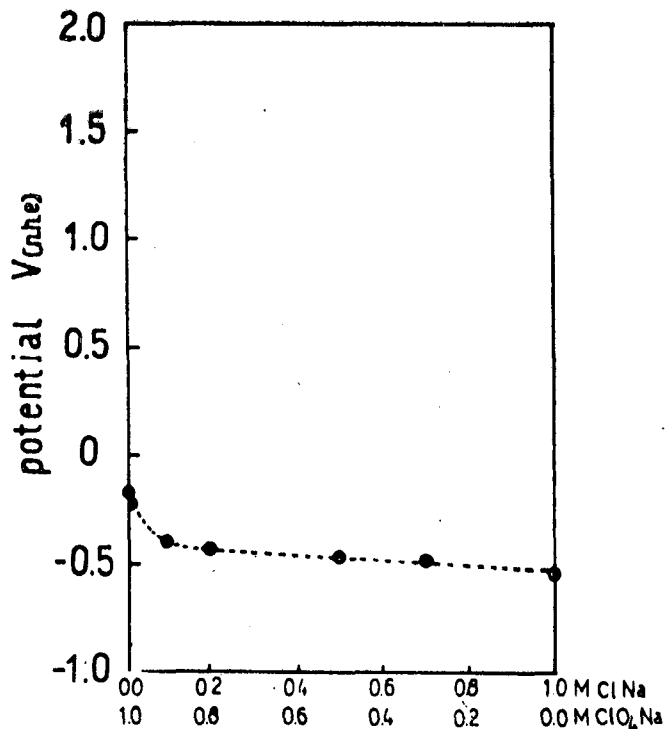


FIGURE 10 – Pitting potentials of Al 99.99% in neutral deaerated mixtures of NaCl plus NaClO₄ solutions at 25 C.

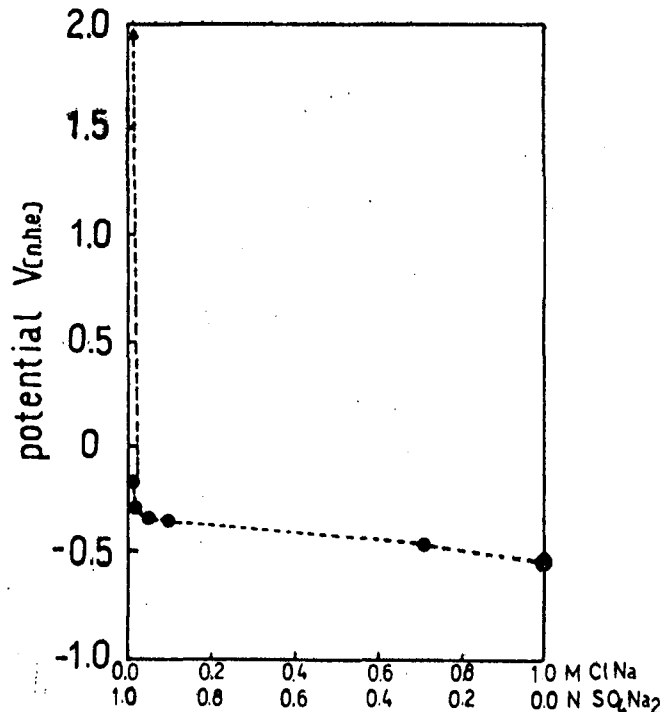


FIGURE 11 – Pitting potentials of Al 99.99% in neutral deaerated mixtures of NaCl plus Na₂SO₄ solutions at 25 C.

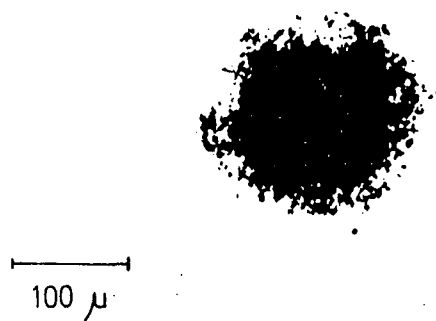


FIGURE 12 – Pitting of Al in a neutral deaerated 0.5M Na₂SO₄ plus 0.01M NaCl solution at 25 C. Pitting appears in the form of clusters of very small pits. The interior of the pits shows the same crystallographic etching found in pure NaCl solutions.

pitting is not exclusive for Al; it was also reported in stainless steels by Schwenk,¹⁰ and in Fe-Cr alloys by Szklarska-Smialowska *et al.*¹¹

Anodic Behavior of Al During Yielding

The study of the anodic behavior of yielding metals at constant potential was introduced by Hoar *et al.*¹²⁻¹⁷ as a technique for studying stress corrosion cracking mechanisms. By this method, oxide-free metal is continually

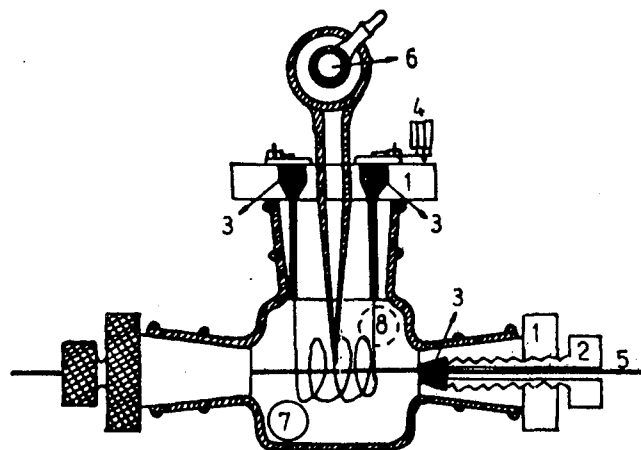


FIGURE 13 – Cell for the study of the anodic behavior of yielding wires under constant potential. Top view: 1–Teflon conical plug; 2–Perspex screw; 3–silicon rubber seals; 4–platinum counter electrode; 5–specimen; 6–reference electrode; 7–deaerated solution inlet; and 8–solution outlet.

exposed to the solution, and the current density (cd) observed is taken as measure of the SCC susceptibility of the metal in the given solution and electrode potential. This method could also be applied with profit to the study of those pitting cases where the role of the oxide film initially present on the metal is not clear. One of those cases is pitting of aluminum. While some authors report that the initial contamination of the oxide film is a decisive step in the pitting process,^{7,18} others state that such oxide film acts as an inert species in the pitting process.^{5,19}

In the present work, the yielding metal method was applied to study the behavior of Al in those solutions in which pitting is known to occur. Analar 99.9% Al wires, 0.6 mm diameter, and 1 mm diameter, 99.999% Al wires, 1 mm diameter, were used. The wires were previously annealed for 20 minutes at 400 C (752 F) in an argon atmosphere, and water quenched. Before the yielding experiments, the wires were electropolished in a solution of Buticellosolve-10% HClO₄ at 0 C and 25 V. Figure 13 shows the cell used for the yielding experiments. The solutions were prepared with analytical grade reagents and were deaerated with purified N₂. A saturated calomel reference electrode was used for the experiments in NaCl solutions, and a mercurous sulfate reference electrode in NaNO₃ solutions. All the potentials are reported in the normal hydrogen electrode (NHE) scale. The yielding experiments were made at constant potential, and the current changes were recorded during the experiments. The potential was kept constant with a Tacussel PRT 20-2X potentiostat. The straining of the wires was done with a motor-driven Hounsfield Tensometer, with constant rate of crosshead displacement giving initial strain rates of 1.6%/minute, 5%/minute, 21%/minute, and 90%/minute.

Yielding Experiments in Neutral 1M NaCl Solutions

Figures 14, 15, and 16 show the potentiostatic cd/time

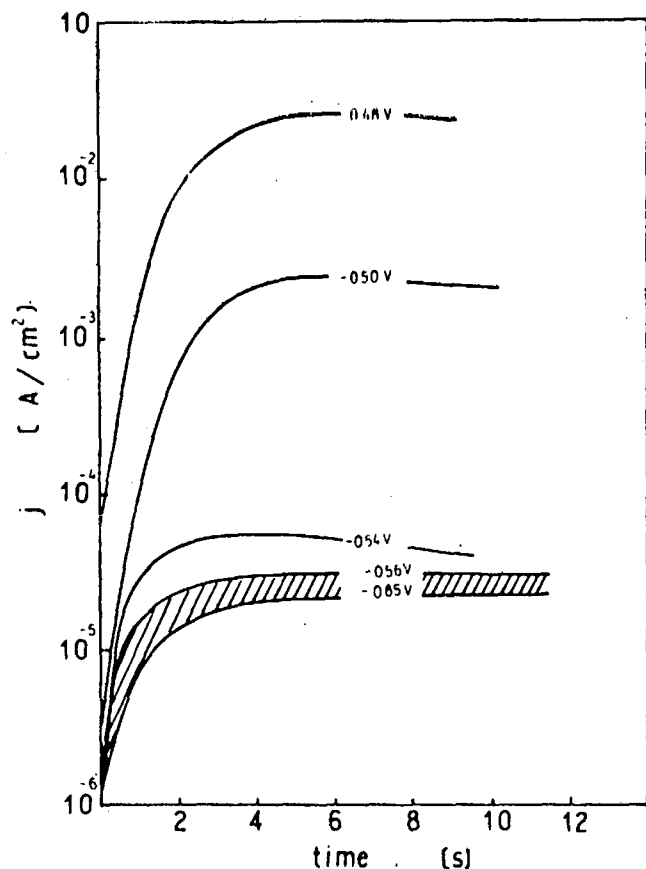


FIGURE 14 - Potentiostatic cd/time curves for Al 99.9% yielding in 1M deaerated NaCl solution at 25 C. Initial strain rate: 90%/min.

curves for straining Al 99.9% wires in neutral 1M deaerated NaCl solutions for three different strain rates. As soon as the plastic deformation started, the current showed a fast increase. After about 5% elongation, the cd leveled down and remained constant until the wires broke. Straining the wires at different potentials, it was observed that the maximum cd value remained constant for a wide range of potentials. But there was a certain "critical potential" value over which small increases in the potential were followed by a high increase in the maximum cd.

Interruption of the straining, at potentials below the "critical potential," showed that after a few seconds, the cd decayed to the low initial value. On the other hand, interruptions at potentials above that "critical potential" were also followed by a current decay, but the cd remained much higher than the one observed below the "critical potential."

The specimens strained below the "critical potential" did not show any visible corrosion, either under the light microscope or by scanning electron microscope. On the other hand, specimens strained in neutral NaCl solutions, at or above the "critical potential" showed an intensive pitting of the metal surface (Figure 17). The pitting density of the yielding Al was much greater than that observed on the static metal (Figure 2).

By plotting the maximum cd values in a potential-

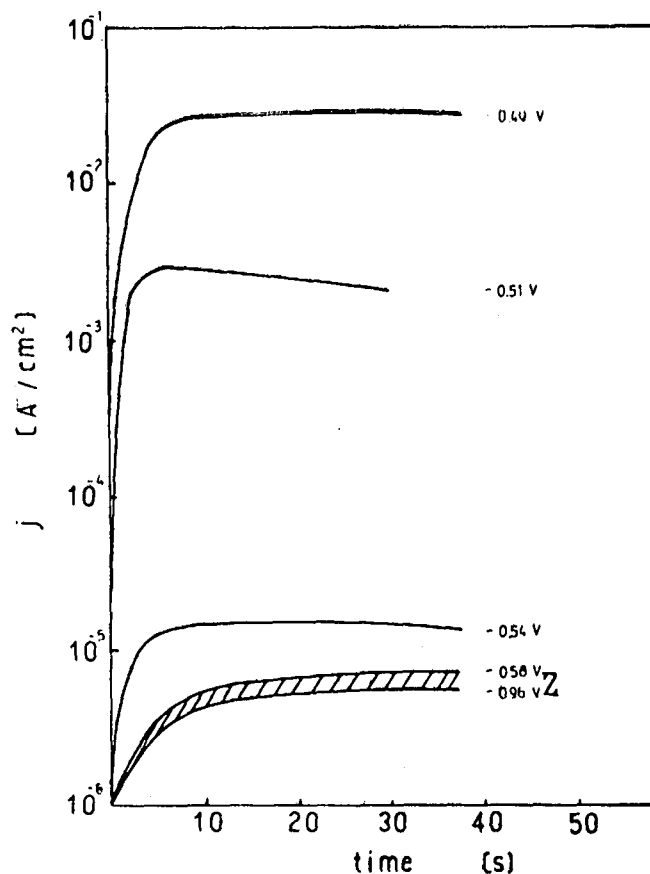


FIGURE 15 - Potentiostatic cd/time curves for Al 99.9% yielding in 1M deaerated NaCl solution at 25 C. Initial strain rate: 21%/min.

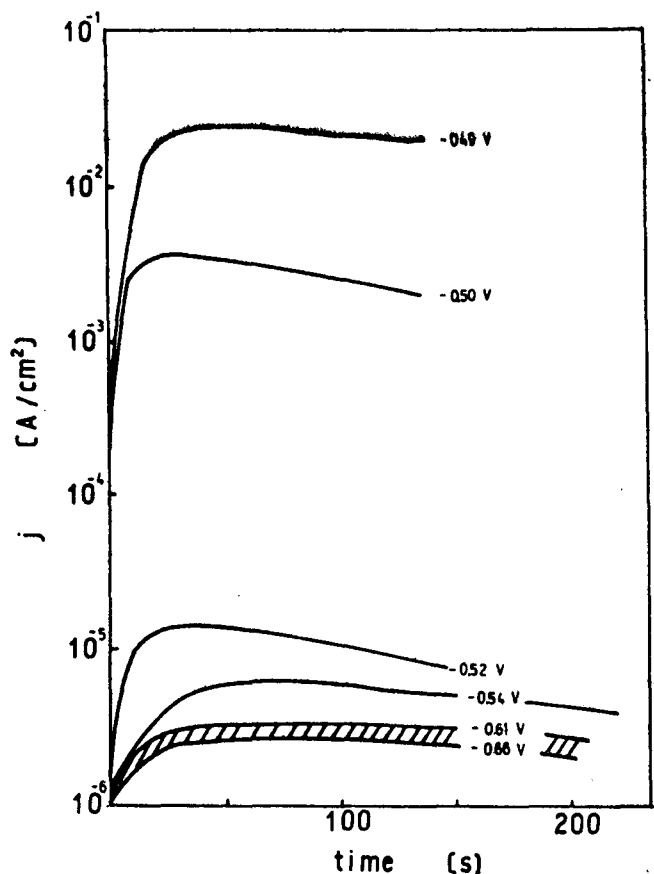


FIGURE 16 – Potentiostatic cd/time curves for Al 99.9% yielding in 1M deaerated NaCl solution at 25 C. Initial strain rate: 5%/min.

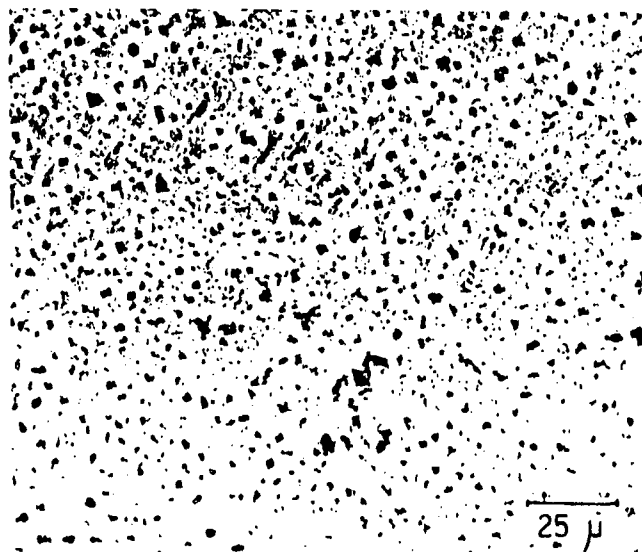


FIGURE 17 – SEM picture of Al 99.9% wire strained in 1M deaerated NaCl solution at -0.48 V (NHE). The surface of the wire appears heavily pitted.

current diagram, two different zones are observed (Figure 18). The potentiostatic polarization curve of Al is included in the same diagram as a reference. This polarization curve was determined on wires previously deformed to 5%

elongation in air. This deformation was applied to the specimens to compensate any effect that the strain might have on the polarization curve.

The results in Figure 18 identify the "critical potential" observed during yielding with the pitting potential of the static metal. Below the pitting potential, the maximum cd observed is a function of the strain rate and it is not affected by the electrode potential. The higher the strain rate, the higher the cd reached during the experiment. Above the pitting potential, the cd during straining is higher than that in the static metal and a higher pitting density is observed.

The results in Figure 18 can be interpreted as follows. Before yielding, the Al carries an oxide film of the order of 30 Å.¹⁸ During yielding, slip steps are formed on the surface of the metal. According to Thomas and Nutting,²⁰ the slip lines observed on Al are composed by several steps of the order of 600 Å each (Figure 19). The number of steps per line increases with the deformation of the metal.

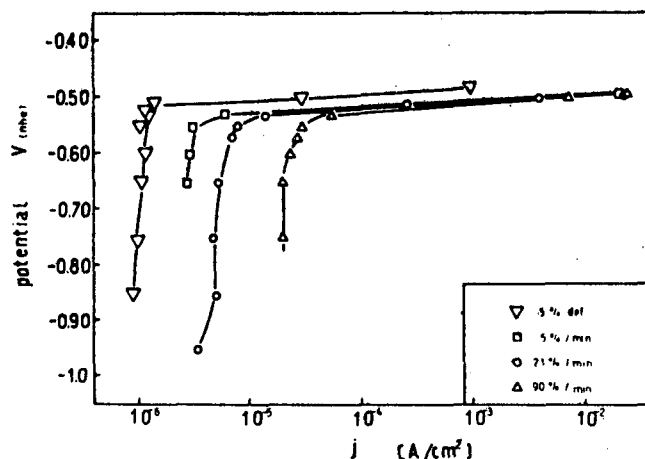


FIGURE 18 – Stationary cd for Al yielding in deaerated 1M NaCl solution at 25 C. Δ : 90%/min; $\circ$: 21%/min; $\square$: 5%/min; ∇ : Potentiostatic polarization curve for 5% deformed Al.

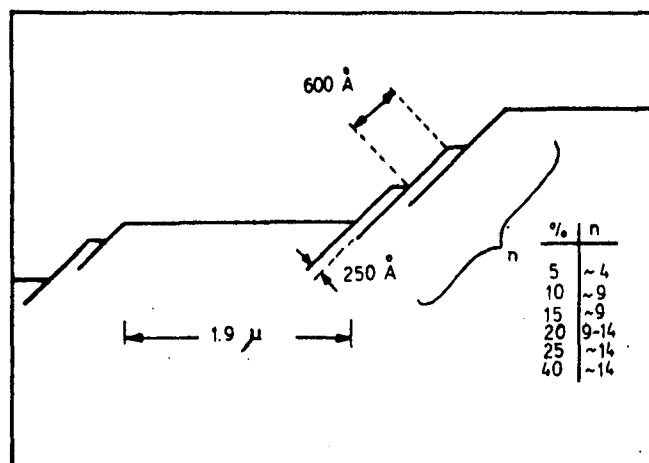


FIGURE 19 – Structure of slip bands in plastically deformed Al, according to Thomas and Nutting.²⁰

The aluminum oxide film being very fragile²¹ the formation of each step should be expected to expose to the solution an oxide-free metal surface. Since the rest of the surface of the metal is not disturbed, all the current increase observed during yielding below the pitting potential should concentrate on those steps. The value of the maximum cd observed during straining Al in neutral NaCl solutions, below the pitting potential, is similar to the one reported by Bubar and Vermilyea²¹ for straining Al in ammonium borate solutions. In the experiments of Bubar and Vermilyea, the only possible anodic reaction on the yielding Al was the reforming of the metal. The similarity in the cd values and the fact that no pitting is observed on specimens yielded below the pitting potential in a NaCl solution lead to the conclusion that if oxide-free Al is exposed to a neutral deaerated NaCl solution, below the pitting potential, the only anodic reaction occurring on the metal will be film formation.

The effect of strain rate on the cd at potentials below the pitting potential, is explained by the analysis made by Staehle and Murata²² on the effect of yielding over passive metals. It is based on the idea that if a constant strain rate is applied to a metal, the number of slip steps produced per unit of time will be constant. If repassivation is the only anodic reaction, each step will become inactive after a while. During yielding, a stationary state will be reached when the number of new steps produced at any time is equal to the number of steps repassivated during the same time. The cd measured under those conditions should be constant. Under conditions of constant repassivation rate, in the stationary state, the number of steps being repassivated will be proportional to the strain rate. The higher the strain rate, the higher the stationary cd.

At potentials higher than pitting potential, the cd for Al in NaCl solutions is much higher for the yielding metal than for the static metal. As mentioned above, the pitting density is also much higher in the yielding metal than in the static metal. This indicates that the rupture of the oxide film facilitates the nucleation of pits by increasing the number of nucleation sites.

Yielding in 1M NaNO₃ Solutions and in 4M pH 11.0 NaCl Solutions

Straining 99.999% Al in neutral 1M NaNO₃ solutions at potentials below the pitting potential gave results similar to those found in neutral NaCl solutions. The pitting potential in the solution was 1.7 V (NHE). Yielding experiments below this potential showed that the cd increased quickly up to a stationary value (Figure 20). Interruption of straining, at those potentials, was followed by a rapid current decay to the low initial cd value. Observation of the specimens with the light microscope or with the SEM did not reveal any pitting on the deformed specimens. By observation with the SEM, no difference between specimens strained in 1M NaNO₃ solutions, at potentials below the pitting potential, and specimens strained in air was observed (Figure 21).

When straining the metal in NaNO₃ solutions at potentials higher than the pitting potential, the cd never

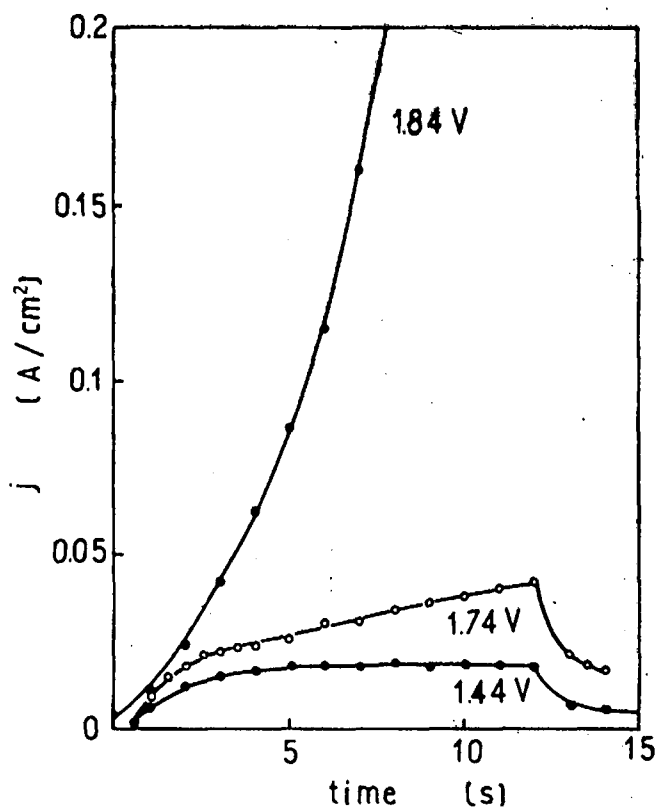


FIGURE 20 — Potentiostatic yielding of Al 99.999% in neutral 1M NaNO₃ solution. Effect of potential and of interruption of straining over the anodic behavior of the metal.

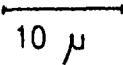


FIGURE 21 — SEM picture of Al 99.999% deformed 6% by elongation in air.

reached a constant value but kept increasing during all the experiment. Interruption of the straining, at potentials near the pitting potential, produced a small current decay. At higher potentials, the current kept increasing even after interruption of straining.

During yielding at potentials higher than the pitting

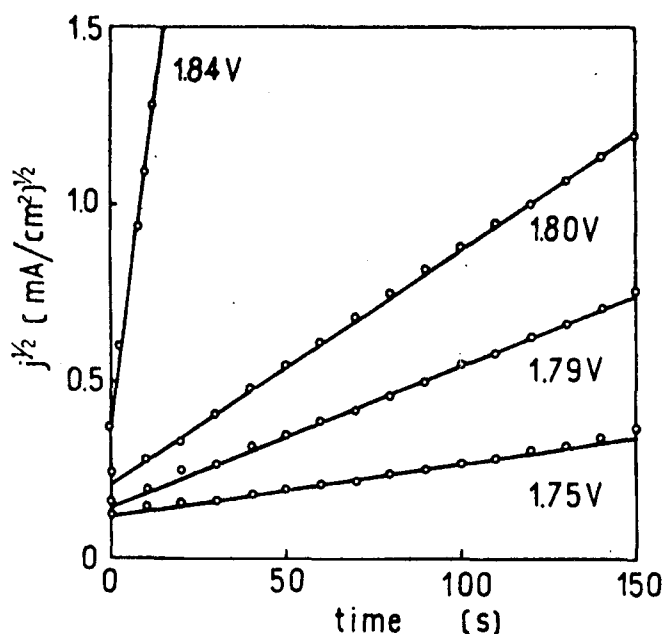


FIGURE 22 — Potentiostatic yielding of Al 99.999% in 1M NaNO_3 solution at potentials higher than the pitting potential.

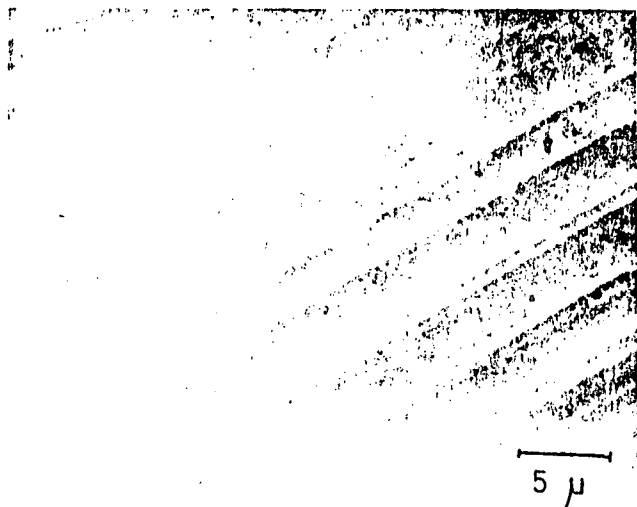


FIGURE 23 — SEM picture of Al 99.999% after yielding in 1M NaNO_3 solution at 1.8 V (NHE). Total elongation: 5%.

potential, the cd was found to follow a law of the type:

$$J = a \cdot t^b, \quad (1)$$

where J = current density, t = time, and a, b = constants.

In a range of potentials of about 100 mV over the pitting potential, potentiostatic yielding of Al in a de-aerated 1M NaNO_3 solution gave $b = 2$. A straight line is obtained when the square root of the cd is plotted as a function of time (Figure 22). The light microscope observation of the yielded specimens showed the presence of loose white corrosion products over the slip bands. No pitting was observed on these specimens. The fine structure of the

corroded slip bands could not be resolved with the SEM. Nevertheless, it was observed that on specimens strained above the pitting potential, the slip bands appeared heavily marked (Figure 23), while it was difficult to observe them on specimens deformed below the pitting potential.

When the potentiostatic yielding of Al in 1M NaNO_3 solutions was done at potentials over the range mentioned above, b was higher than 2 and pitting nucleation is observed on the yielded specimens.

Potentiostatic measurements made on static Al in a 1M NaNO_3 solution, at potentials higher than the pitting

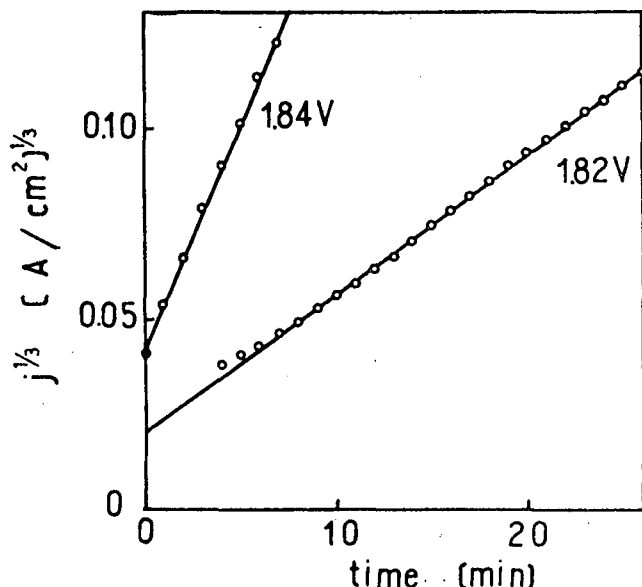


FIGURE 24 — cd/time curves for Al 99.999% polarized at constant potential in 1M NaNO_3 solution.

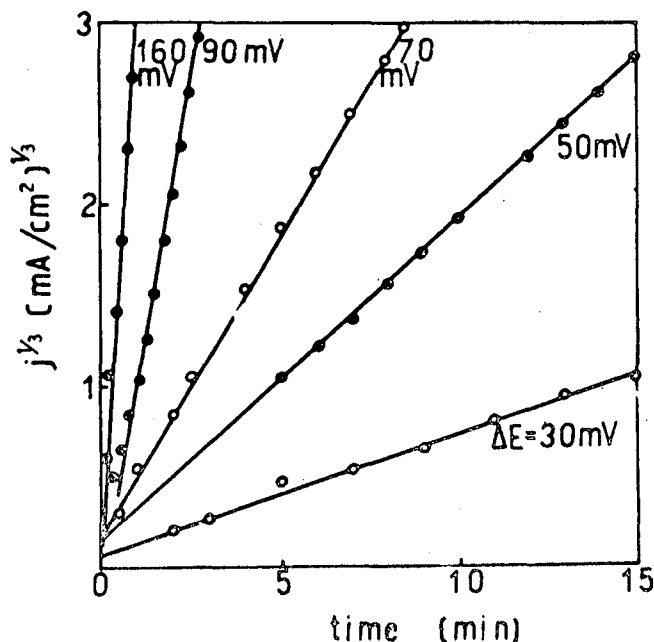


FIGURE 25 — cd/time curves for Al 99.99% polarized at constant potential in de-aerated 4M NaCl solution, pH 11.0, according to Kaesche.⁴

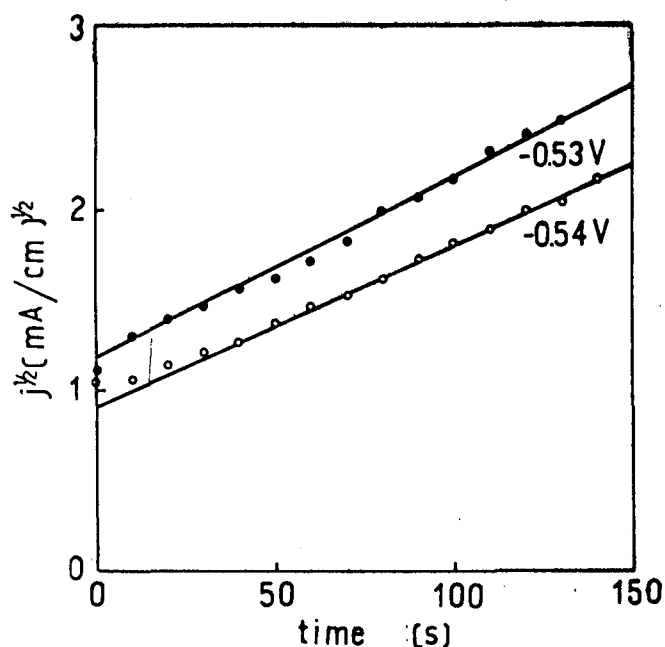


FIGURE 26 — Potentiostatic yielding of Al 99.999% in deaerated 4M NaCl solution, pH 11.0.

potential, gave a value of $b = 3$. The cube root of the cd gave a straight line with time (Figure 24). Under such conditions, hemispherical pits were formed on the specimens.

Kaesche⁴ reported that hemispherical pits are formed on Al in pH 11.0, deaerated, 4M NaCl solutions. By potentiostatic polarization of static Al, this author found a value of $b = 3$ (Figure 25). During the present work, for polarization lengths similar to those reported by Kaesche, the formation of hemispherical pits was confirmed. Potentiostatic yielding experiments with Al in this solution gave $b = 2$ (Figure 26) for potentials higher than the pitting potential. The range of potentials where the behavior $b = 2$ was found, was much smaller than in NaNO_3 solutions, about 20 mV. But, as with NaNO_3 solutions, no pitting was observed on specimens yielded under conditions giving $b = 2$. The SEM micrographs showed, as with nitrate solutions, that the slip bands in Al were heavily marked on specimens yielded above the pitting potential, while they were difficult to detect on specimens yielded below the pitting potential.

Discussion of the Potentiostatic Yielding Experiments

The cd/time curves found for potentiostatic yielding of Al in NaNO_3 solutions and in alkaline NaCl solutions, above the pitting potential, can be interpreted from the morphology of the pits.

Engell and Stolica^{2,3} showed that the relation:

$$J = a \cdot t^3 \quad (2)$$

is obtained during pitting of metals, but the following conditions are necessary:

1. The pits must grow in hemispherical shape.

2. The cd inside the pits must be constant.

3. The number of pits per unit area must increase in a linear function with time.

$$N = A \cdot t \quad (3)$$

Where N = number of pits per unit area, A = constant, and t = polarization time.

Engell and Stolica^{2,3} showed that Equation (2) is valid for the pitting of iron in sulfuric acid containing chloride ions. The same equation was found valid by Kaesche⁴ for pitting growth in Al in alkaline NaCl solutions. The conditions established by Engell and Stolica were fulfilled in pitting of Al in a NaNO_3 solution, where hemispherical pits were produced, and where the cd increased with time according to Equation (2).

The potentiostatic cd/time curves for yielding Al can be explained in a very similar manner. Following the arguments used by Engell and Stolica, it results that to get a relation:

$$J = a \cdot t^2 \quad (4)$$

the following conditions should be fulfilled:

- 1'. Pitting must grow in semicylindrical shape, with the axis lying parallel to the surface of the metal.

- 2'. The cd inside the pits must be constant.

- 3'. The number of semicylindrical pits, per unit area, must increase as a linear function with time.

All these conditions are fulfilled for potentiostatic yielding Al in NaNO_3 solutions and in alkaline NaCl solutions. The Condition 1' appears to be fulfilled because all the pitting is nucleated on the slip bands, and the semicylindrical pits appear as a natural modification of the hemispherical pits found on static metal. Condition 2' should be fulfilled on a yielding metal whenever Condition 2 is fulfilled on a static metal. As for Condition 3', it appears as a result of the experimental method, since as a constant strain rate is imposed to the wire, the number of steps formed per unit of time should be constant.

The potentiostatic yielding experiments so far described show that while under certain conditions the straining of the metal contributes to extend pitting, as with Al in neutral NaCl solutions, there are other conditions under which the straining of the metal produces nucleation of pitting only on slip lines.

Existence of a Pitting Potential in Al

The particular type of morphology of the pitting of Al in Cl^- solutions could lead to the belief that this is not a real case of pitting. Although this subject has already been discussed in a previous paper,¹ it seems convenient to insist on a few points.

Figure 27 shows a typical polarization curve of Al in NaCl solutions. It is observed that after a range of potentials at which the metal remains passive, there is a critical potential above which the current shows a very high increase. This curve was determined in steps of 10 mV, waiting at each potential until a constant current was

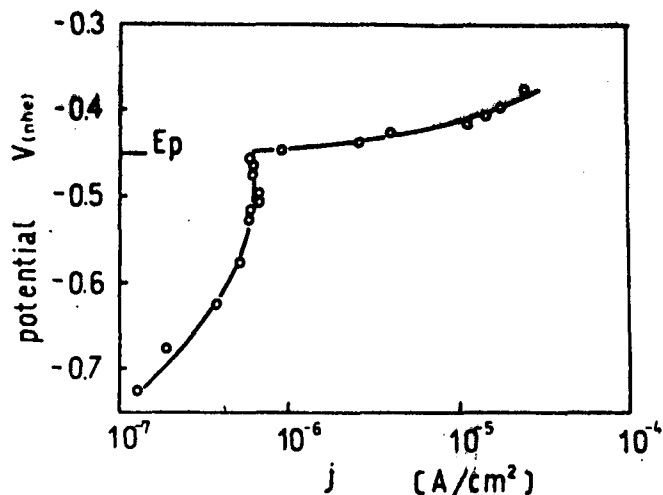


FIGURE 27 - Anodic polarization curve of 99.99% Al in deaerated 0.1M NaCl solution. Ep: potential at which pitting starts.

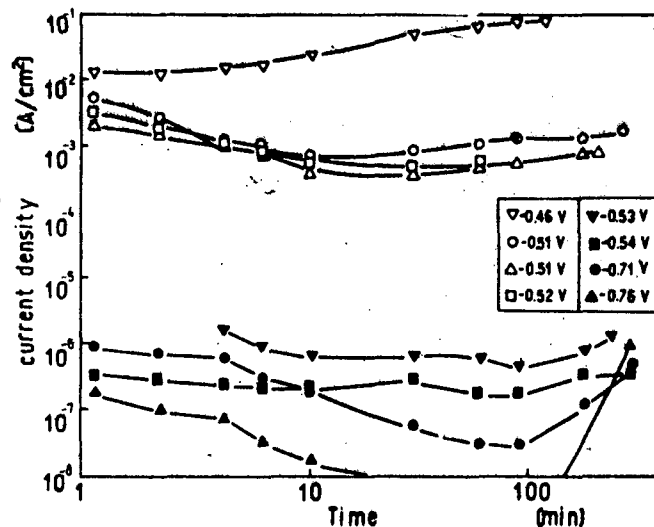


FIGURE 28 - Current-time curves for 99.99% Al in deaerated 1M NaCl solution at various potentials.

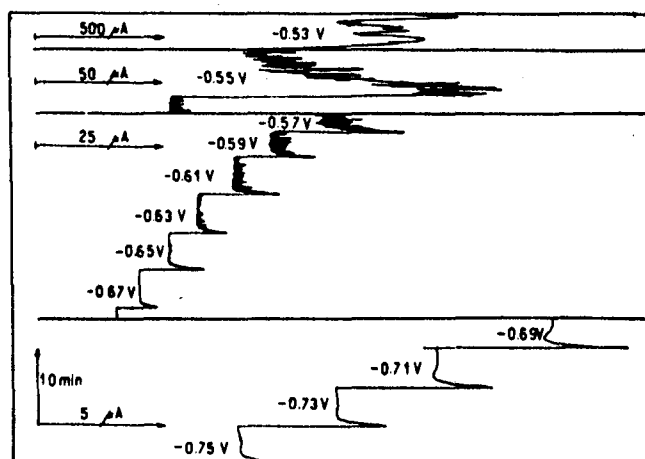


FIGURE 29 - Oscillation of the current during polarization under constant potential. Al 99.99% in deaerated 1M HCl solution.

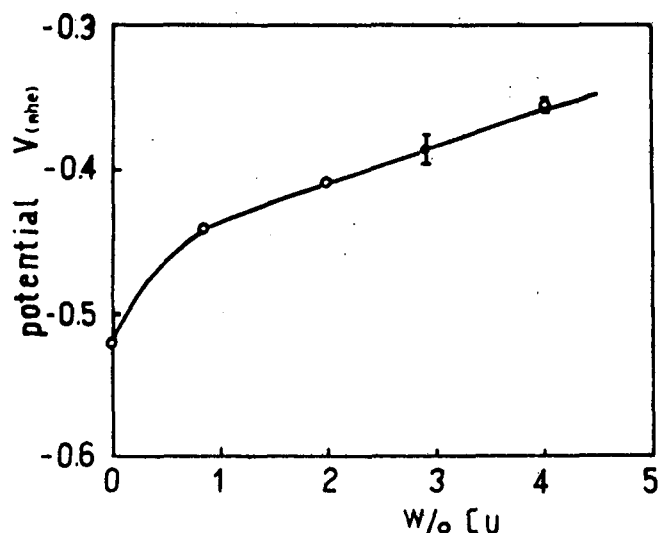


FIGURE 30 - Pitting potentials of splubilized Al-Cu alloys in deaerated 1M NaCl solution at 25 C.

attained. Since it could be argued that not enough time was allowed at each potential, and that the critical pitting potential could be much lower under other experimental conditions, a series of experiments was performed to study the effect of polarization time over the pitting potential. These experiments consisted in recording changes in the anodic cd for 5 hours when specimens of Al were held at various constant potentials in 1M deaerated NaCl solution (Figure 28). When the potential was maintained at different values up to -0.53 V (NHE), the cd remained below 1 $\mu\text{A}/\text{sq cm}$ after 5 hours and no pitting was observed. But with a potential only 10 mV higher than -0.53 V (NHE), the cd increased by more than three orders of magnitude and pitting commenced. These experiments showed that if there is an induction time for the pitting of Al, a change in potential of 10 mV should decrease the induction time by at least four orders of magnitude. Therefore, it can be con-

cluded that pitting of Al is related to a critical potential which does not depend on an induction period.

Nevertheless, Figures 27 and 28 give by no means a complete description of pitting of Al. During the polarization curve measurement, there are other phenomena which cannot be ignored. Although a stationary cd is attained after a short potentiostatic polarization, there are flicks of current clearly detectable.

Figure 29 shows the recording for a polarization curve for Al determined in 1M deaerated HCl solution. At low potentials, no flicks were detectable. As the potential was increased, the number of perturbations per unit of time increased, and finally at the pitting potential, the concentration of those flicks was so high that it produced an increase in the total cd measured. In neutral NaCl solutions, the perturbations observed were usually higher than those in acid solutions.

This behavior is not exclusive for Al. Similar oscillations were reported by Lotlikar and Davies²⁴ for high purity zinc, and by Szklarska-Smialowska *et al*²⁵ in stainless steels.

It was observed²⁶ that the current oscillations in Al in NaCl solutions were diminished or even suppressed if any surface-active agents were present in the solution.

Mechanism of Pitting of Al

Although as pointed out by Kolotyrkin²⁷ and by Hoar, Mears, and Rothwell suggested that at the pitting potential, *propagates*, it is not so easy to explain how it *starts*. Hoar, Mears, and Rothwell suggested that the pitting potential, the aggressive anion, adsorbed on the oxide film surface, begins to penetrate the film under the influence of the electrostatic field across the film/solution interface when the field reaches a critical value corresponding to the breakdown potential.

The yielding experiments reported above show that the oxide film does not interfere with the anodic reaction occurring at the pitting potential. Exposing an oxide-free metal at a potential below the pitting potential, the only anodic reactions observed are oxide formation and repassivation. This indicates that the pitting potential is not related to an electrostatic field across the oxide solution interface, and that pitting of Al is independent of any process of oxide film contamination. At or near the pitting potential, there must be some change in the metal/solution interface that conducts to a predominance of the dissolution reaction over the repassivation reaction. In those cases where information was available,²⁸ it was found that the pitting potentials were very close to the zero charge potentials (zcp), Table 1. An oxide-free metal exposed to a solution at potential below the zcp will be predominantly faced with positive ions and water molecules. Under such conditions, the reaction of the metal ions with the water molecules which gives an oxide film will predominate over the reaction of dissolution of the metal. Over the zcp, the oxide-free metal will be faced with an increasing number of negative ions. It is well known that the negative ions

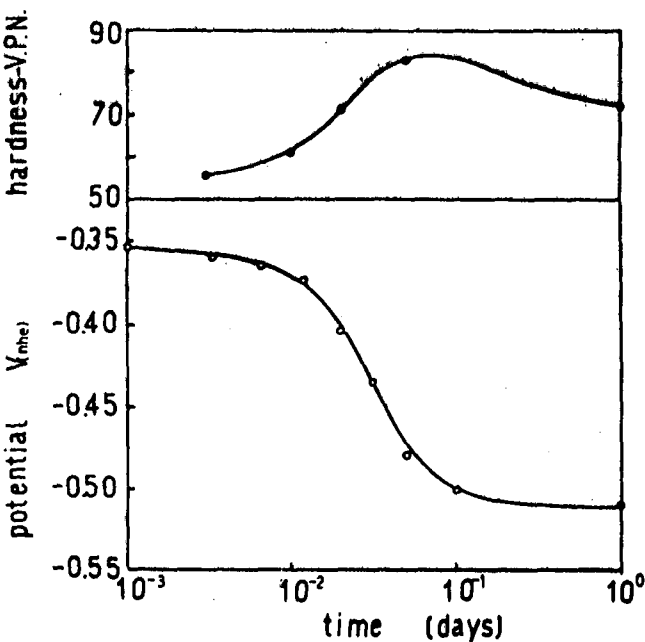


FIGURE 31 — Effect of aging time on pitting potentials and hardness of Al-4% Cu aged at 240 C. Deaerated 1M NaCl solution at 25 C.

accelerate the anodic dissolution of the metals.²⁹ Under those conditions, the process of metal dissolution will predominate over the process of metal passivation.

The zcp would be the potential at which a pit could *start*, but a higher potential would be necessary to create the conditions that *maintain* an active pit. In the case of Al, it is necessary to obtain a concentration of Cl⁻ ions high enough to maintain the corrosion products in solution inside the pit. If the electrolyte contains a high concentration of inactive ions, e.g., sulfate ions, (Figure 11), the Cl⁻ ions will not reach the pit by transport and the pit will become inactive by occlusion with corrosion products. In this case, oscillations in the current will be observed, but no stable pits will appear. If inside the pit, we have Al(NO₃)₃ solution, which tends to decompose precipitating Al

TABLE 1 — Zero Charge Potentials and Pitting Potentials (E_p)

Metal	zcp (V(NHE)) ²⁸	E _p (V(NHE))	Electrolyte	Ref.
Al	-0.52 (ClK 0.01M)	-0.40	NaCl 0.01 M	1
		-0.53	NaCl 1M	1
		-0.37	NaBr 1M	1
Fe	-0.33 - -0.40 (HCl 0.01M)	-0.35	NaCl 0.5M	57
Mg	-1.04 ⁽¹⁾	-1.2	NaBr 1M	27
		-1.45	NaCl 0.5M	27
Ni	+0.29 ⁽¹⁾	+0.28	NaCl 0.1M	50
Zn	-0.51 ⁽¹⁾	-0.78	NaCl 1M (pH 9.0)	58

(1) Values calculated with formula: E_{zcp} = W_e - 4.72, from Ref. 28. W_e values from Reference 59.



FIGURE 32 — Pitting nucleated along (111) planes. Al-4% Cu aged 15 minutes at 240 C. Deaerated 1M NaCl solution at 25 C.

hydroxides,³⁰ instead of having AlCl_3 solution which dissolves big amounts of Al hydroxides,³¹ the conditions for maintaining pitting will be complicated by the formation of solid products inside the pit. Higher pitting potentials should be expected to maintain the necessary transport of the aggressive nitrate ions through the amorphous alumina precipitate.

Those potentials for *maintaining pitting*, or pitting potentials, could be calculated from the transport data of the active species, the rates of the anodic and cathodic reactions, the rates of the chemical decomposition of the corrosion products, etc. An attempt to do such calculations was made by Kaesche⁴ for pitting of Al in alkaline NaCl solutions.

Pitting and Intergranular Corrosion of Al-Cu Alloys

In a recent paper,¹ it was shown that by alloying Al with Cu, the pitting potential of Al could be increased in more than 100 mV. In the same paper, a mechanism for intergranular corrosion of aged Al-4%Cu based on the difference in pitting potentials between the Cu-rich grain bodies and the Cu-depleted grain boundaries was proposed. Nevertheless, the existence of a depleted region in aged Al-4%Cu is open to discussion if the literature available on precipitation hardening³² is taken into consideration. In view of this discrepancy, further experiments with Al-Cu alloys were made.

The effect of Cu content on the pitting potential of Al-Cu in deaerated 1M NaCl solution was studied. Alloys of Al with 1, 2, 3, and 4 wt % Cu were prepared with Al 99.99% and Cu 99.999%. The cast material was reduced by rolling to a thickness of 1 mm, and coupons of 10 x 30 mm were cut from the cold rolled sheet. The coupons were solubilized for 2 hours at 530 C (986 F) and water quenched. A few specimens of Al-4% Cu were used in solubilized condition, and the others were aged for different periods of time at 240 C (464 F). This temperature was chosen because it made it possible to obtain overaged material in a reasonable aging time. For the polarization measurements, an electrical contact was made with a wire fastened to the specimen through a hole in it. The electrical contact wire, the edges of the specimen, and one of its faces were covered with an epoxy resin, leaving exposed a surface of about 1 sq cm. Before the polarization measurements, the specimens were electropolished in a 10% HClO_4 -buticellosolve mixture. Part of the aged specimens were used for hardness measurements. These specimens were electropolished as mentioned above, and the hardness was measured with a Durimet (Leitz, Wetzlar) microdurometer with a load of 1000 g.

The pitting potentials were measured at 25 C in a deaerated 1M NaCl solution by a galvanostatic method. A constant current of the order of 1 mA/sq cm was applied to the specimens and the potential changes were recorded. After a short polarization time, the potential reached a stationary value, and the pitting potential was measured after 3 hours of polarization. In each case, the pitting potential value was confirmed by increasing the polarization current and checking whether the same stationary

potential was obtained. The pitting potentials reported (Figure 30) are the mean values measured on at least 5 different specimens. The scattering in the pitting potentials was lower than ± 10 mV. It was observed that by alloying Al with Cu, a rapid increase in the pitting potential occurred for the first 1% of Cu, and for higher Cu concentrations, a linear relation was found between pitting potential and Cu content.

It is known that during the aging of Al-Cu, a sequence of complex transformations occur in the matrix of the alloy. Al-4% Cu was used to study the effect of aging on the pitting potential. The pitting potentials of the aged alloy were measured by the galvanostatic method. It was observed (Figure 31) that the pitting potential of the alloy was very sensitive to the heat treatment. As previously mentioned¹ the pitting potential of the overaged alloy was more than 100 mV lower than that of the solubilized alloy. The hardness measurements are included in Figure 31 for reference. The hardness curve obtained in the present experiments is coincident with the measurements reported by Hardy³³ for an Al-4.0% Cu alloy aged at 240 C.

It was found that the pitting potential decreased as soon as the hardness of the alloy started to increase. At 240 C, the only precipitate formed in Al-4% Cu is θ' phase.³⁴ Beck showed³⁵ that in Al-4% Cu aged at 240 C, the θ' phase precipitate was surrounded by a copper depleted region. This author could not detect by the oxide replica oxide method any precipitate after the aging time required for peak hardness. Nevertheless, Beck found that at peak hardness, the copper content of the matrix was only 0.5%. From Figure 30, we found that the pitting potential for an alloy of Al-0.5% Cu would be about -0.46 V (NHE). On the other hand, at peak hardness (Figure 31), the pitting potential found was -0.48 V (NHE). This showed a good agreement with the matrix concentration value reported by Beck.

Pitting in aged Al-4% Cu was distributed along very well defined lines (Figure 32). The orientation of these lines changed from grain to grain, showing that they were related with the crystallographic orientation of the grains. By X-ray diffraction it was found that these lines coincided with traces of planes (111). As it is known,³² the θ' phase precipitates along the planes (111).

The present results could be used to explain the variation of pitting potential with aging of the alloy found in Figure 31. As shown by Beck, the θ' phase is surrounded by a solute depleted zone. On the other hand, the Cu concentration reported by Beck for the matrix at peak hardness is coincident with the values expected from Figures 30 and 31. All these observations point to the conclusion that the changes in pitting potential found during aging of Al-4% Cu were due to the solute depletion of the matrix produced by precipitation. To support this conclusion even further pitting does not follow any more the θ' phase precipitates, but nucleates at random¹ when all the matrix has its minimum Cu content, as it is the case in the overaged condition.

At potentials below the pitting potentials reported in Figure 31, no pitting of the type shown in Figure 32 was

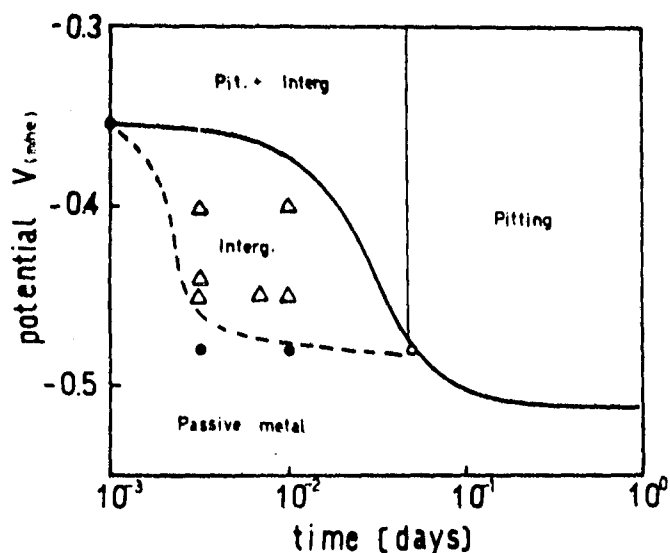


FIGURE 33 — Regions for intergranular corrosion and pitting for Al-4% Cu aged at 240 C. Deaerated 1M NaCl solutions at 25 C.

detected any more. But there was still a range of potentials where intergranular corrosion occurred. A series of experiments was performed to determine the range of potentials and heat treatments that originated intergranular corrosion. The aged Al-4% Cu specimens were exposed in the NaCl solution for about 20 hours at constant potential. Afterwards, the specimens were deformed by bending and observed under the microscope to detect any intergranular corrosion. As reported in a previous paper,¹ intergranular corrosion in aged Al-Cu alloy occurs only above certain potentials. Exposure to NaCl solution below that potential does not produce intergranular corrosion. Nor does intergranular corrosion occur in solubilized or in overaged conditions. It is known that during aging precipitation starts at the grain boundaries and develops there at a higher rate than in the matrix of the alloys.^{3,6} As shown by Galvele and De Micheli¹ in order to have intergranular corrosion, a difference in the pitting potentials of the grain boundaries and the grain bodies is a necessary condition. In this way, a hypothetical pitting potential curve can be drawn for the grain boundaries (Figure 33) delimiting the regions for intergranular corrosion, passivity and pitting for Al-4% Cu in 1M NaCl solution.

All the results obtained in the present work point to the fact that there is a solute depleted zone along the grain boundaries, and that during intergranular corrosion, the attack localizes in that depleted zone. The confusion in the literature seems to arise from the way the theory of precipitation developed. At the time, the idea of a solute depleted zone was applied to intergranular corrosion,^{3,7} the precipitate free zone along the grain boundaries was assimilated to a solute depleted zone.^{3,6,3,8} Later it was found that the precipitate free zone was not due to solute depletion, but to vacancy depletion.^{3,2} This observation was extended by some authors to the process of intergranular corrosion^{3,9} assuming that there was not any solute depleted zone in the grain boundaries. Nevertheless,

no information is available supporting the idea that a depletion of vacancies could affect the electrochemical behavior of a metal. It seems more reasonable to conclude, as shown by Kelly and Nicholson^{3,2} for Al-4.4 Ag, that the precipitate free zone and the solute depleted zone are different zones, the latter being the smaller of the two.

Anodic Behavior During Yielding of Al-Cu

The anodic behavior of solubilized Al-4% Cu wires in deaerated 1M NaCl solutions during yielding was studied (Figure 34). The yielding experiments were made at different constant potentials with an initial strain rate of 90%/minute. As with pure Al, it was observed that the current increase to a stationary value, and that the stationary current varied with the potential. Here again it was observed that the influence of the potential on the maximum cd was lower below the pitting potential than above it.

As with Al, it is supposed that below the pitting potential, the current increase is due to repassivation, while above the pitting potential, it is due to pitting. Comparing the values in Figure 34 with those for pure Al (Figure 14), it is found that in a range of more than 100 mV while Al shows intense pitting during yielding, Al-Cu only shows the current increase due to repassivation. This range of potentials corresponds to the difference in the pitting potentials

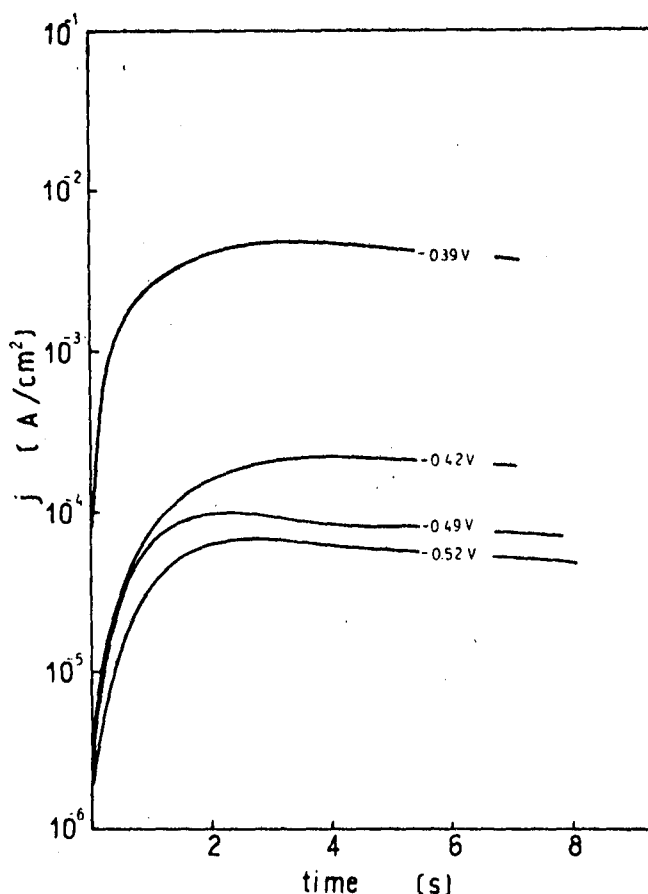


FIGURE 34 — Potentiostatic cd/time curves for yielding solubilized Al-4% Cu in 1M deaerated NaCl solution at 25 C. Initial strain rate: 90%/min.

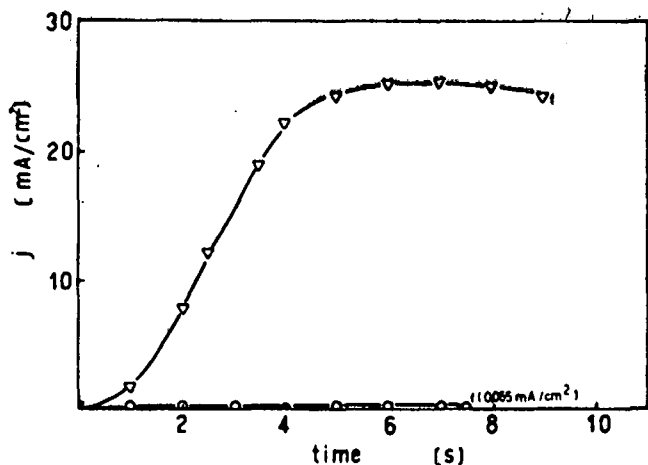


FIGURE 35 — Potentiostatic $cd/time$ curves for yielding in 1M deaerated NaCl solution at -0.49 V (NHE). Initial strain rate 90%/min. $\circ$: solubilized Al-4% Cu; ∇ : Al 99.9%.

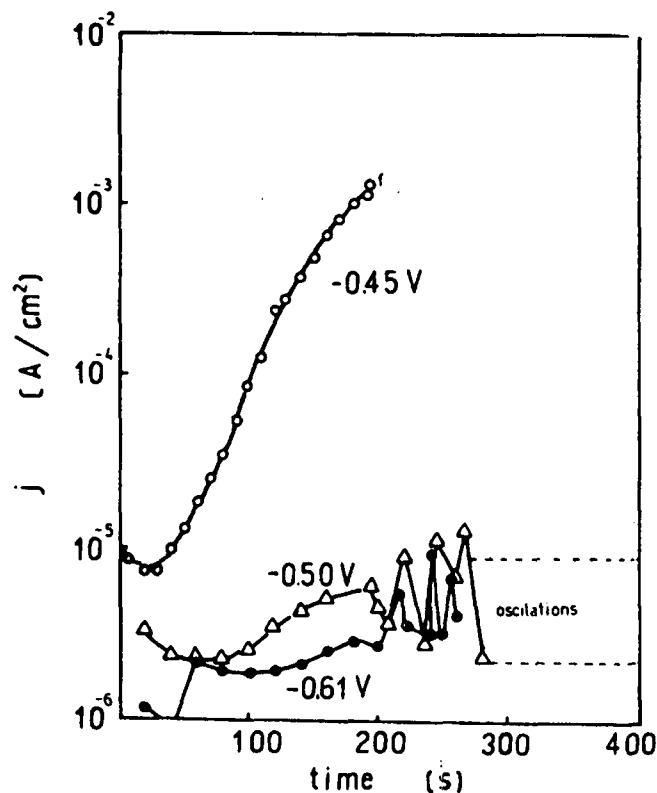


FIGURE 36 — Potentiostatic $cd/time$ curves for yielding in 1M deaerated NaCl solution. Al-4% Cu aged 3 hours at 210 C. Initial strain rate: 1.6%/min.

and Nutting.³⁸ As shown above, that precipitate-free zone is composed of a large vacancy-depleted zone and a much smaller solute-depleted zone. The electrochemical behavior of the vacancy-depleted zone can be assimilated to the behavior of the solubilized Al-4% Cu, while the behavior of the solute-depleted zone will be very similar to pure Al. From the experiments described above, the anodic behavior of aged Al-4% Cu during yielding in 1M NaCl solution can be predicted. It is evident from Figure 35 that yielding at constant potential will not give a homogeneous distribution of attack in the soft precipitate-free zone. If the aged material is deformed at a potential below the pitting potential of the solute-depleted zone, the only reaction on the metal surface will be repassivation of the metal. Above the pitting potential of the solute-depleted zone, the deformation will generate intense corrosion of this zone, while the vacancy depleted region will still show a process of repassivation. This localized corrosion will generate intergranular fissures propagating by mechanically intensified pitting of a narrow front along the grain boundaries, i.e., stress corrosion cracking. Such behavior can be checked by measuring the elongation of aged Al-4% Cu wires in 1M deaerated NaCl solution at constant potential (Figure 37). It is found that if the potential is increased above the pitting potential of the solute depleted zone, there is a very high decrease in the ductility of the metal. On the other hand, if the metal is yielded at a potential below the pitting potential, the elongations found are the same as obtained in air. The pitting potential of the solute depleted zone is estimated from the measurements of solute depletion published by Beck,³⁵ and the pitting potentials for different compositions of Al-Cu alloys given in Figure 30. In all the yielding experiments of aged Al-4% Cu, even in air, the fracture of the wires appeared to be intergranular. The oscillation of current observed during straining at low potential (Figure 36) are attributed to the exposure of big

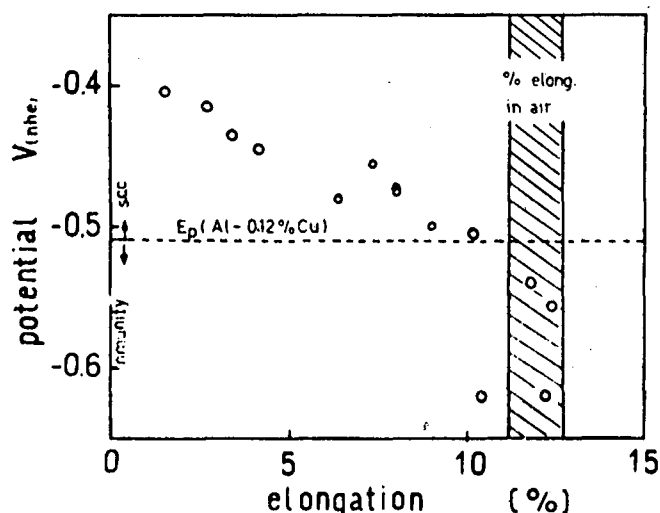


FIGURE 37 — Effect of potential on ductility of aged Al-4% Cu, during potentiostatic yielding in 1M deaerated NaCl solution. Aging: 3 hours at 210 C. Initial strain rate: 1.6%/min.

of both materials. Yielding both metals at an intermediate potential (Figure 35), it is observed that the current increase for Al is almost three orders of magnitude higher than that for Al-Cu.

Yielding experiments were also performed with wires of aged Al-4% Cu (Figure 36). The deformation of the aged material is not homogeneous. Most of the deformation occurs in the precipitate-free zone along the grain boundaries, as shown with electron microscope studies by Thomas

oxide-free metal areas produced by mechanical tearing along the grain boundaries. At higher potentials, the mechanical tearing is quickly overtaken by anodic dissolution along the grain boundaries. With a sufficiently low strain rate, all fissure propagation would be due to anodic dissolution.

SCC of Al-Cu Alloys

Mears, Brown, and Dix³⁷ suggested that SCC occurs along localized paths. The function of stress would be to open the crevices produced by corrosion. In the particular case of Al-Cu, the localized path is the solute depleted zone along the grain boundaries. According to the authors, the corrosion of this zone would be due to a difference in potentials between the grain boundaries and the grain bodies. Logan,⁴⁰ on the other hand, proposed a film-rupture mechanism by which SCC propagates due to rupture of the protective film and electrochemical dissolution of the unprotected metal. For SCC of Al-Cu, Colner and Francis⁴¹ proposed a combination of both mechanisms. According to these authors, the deformation localized along the grain boundaries will rupture the protective oxide film, fresh metal being thus exposed. There will be a constant tendency to refilm this naked metal. If the strain rate is slow, the metal will have time to repassivate, but with a high strain rate, the refilming will not be completed and the crack will propagate.

The results of the present work show that Logan's mechanism does not apply to Al and Al-Cu alloys. The plastic deformation could rupture the oxide film, but at potentials lower than the pitting potential, the metal will repassivate as shown in Figure 18. The strain rate is not important either, since a high strain rate will increase the number of slip steps undergoing repassivation, but will not change the type of anodic reaction.

The mechanism proposed by Mears, Brown, and Dix is quite in agreement with the results of the present work. Nevertheless, a few modifications should be made. As shown by Galvele and De Micheli,¹ the existence of a depleted zone is a necessary but not a sufficient condition to produce localized corrosion. The presence in the media of anions capable of breaking the passivity of the alloy is also necessary. And the metal must be at a potential higher than the pitting potential of the depleted zone; otherwise the alloy will remain passive.

As for the effect of heat treatment on SCC susceptibility, when aging over peak hardness, Figure 31 the pitting potential of the grain bodies decreases very quickly. When the pitting potential of the grains is equal to the pitting potential of the boundaries corrosion will not concentrate any more on the grain boundaries, but it will spread all over the metal surface. Under such conditions, the metal will not be susceptible to SCC.

Stress, in the particular case of SCC of Al-Cu alloys in neutral NaCl solutions, will open the fissures and accelerate the anodic process at the pitting potential.

SCC of Other Al Alloys

Since many age-hardenable Al alloys are susceptible to

TABLE 2 — Pitting Potentials of Phases Present In Aged Aluminum Alloys

Alloy	Phase	E_p (VNHE)	Ref.
Al-4% Cu	Al-Cu	-0.39	1
	Al ₂ Cu	-0.40	
	Al	-0.52	
Al-Mg	Al	-0.52	42
	Al-Mg	-0.60	
	Mg ₂ Al ₃	-0.87	
Al-Mg-Si	Al-Mg-Si	-0.50	42
	Al	-0.52	
	Mg ₂ Si	-1.35	

intergranular stress corrosion cracking, it would be interesting to see if the mechanism proposed for Al-Cu could be also extended to other Al alloys. Table 2 shows the pitting potentials in deaerated NaCl solutions for the phases present in aged Al-Cu alloys measured by Galvele and De Micheli,¹ and for Al-Mg and Al-Mg-Si, measured by Batrakov.⁴² In Al-Cu alloys, the stresses will deform the soft zone along the grain boundaries where the depleted zone is present. If the potential is higher than the pitting potential of the depleted zone, corrosion will concentrate along the grain boundaries producing fissures and the alloy will stress corrode. In the Al-Mg alloy the solute depleted zone has the highest pitting potential and the other two phases will corrode first. The lowest pitting potential corresponds to the hard intermetallic phase. In this alloy, the only possible SCC mechanism would be one of electrochemical dissolution of the intermetallic phase and simultaneous rupture of the Al rich zone by mechanical tearing. A mechanism like this is precisely what was proposed by Beck and Sperry⁴³ for SCC of Al-Mg. Similarly for Al-Mg-Si, SCC will occur only by dissolution of the intermetallic phase. And as it is known, this alloy is susceptible to SCC only under certain heat treatments where a continuous layer of the Mg₂Si is formed along the grain boundaries.

The comparison of these three Al alloys shows the complexity of the SCC processes. The observations made on the mechanism of SCC of one alloy allow no extrapolation to other alloys without a careful study.

Relation Between Pitting and SCC

The relation found between pitting and stress corrosion cracking of Al-Cu alloys raises the question of how frequently both processes are related.

There are cases of stress corrosion where a good correlation between the conditions for pitting and those for SCC is found. One example of this is the SCC of Ti alloys in methanol plus HCl solutions.⁴⁴ In other cases, on the other hand, the literature is confusing as in the case of SCC of stainless steels in MgCl₂. Staehle *et al.*⁴⁵ found that the corrosion potential for stainless steel in boiling MgCl₂ corresponds to a passivity breakdown. Smialowski and

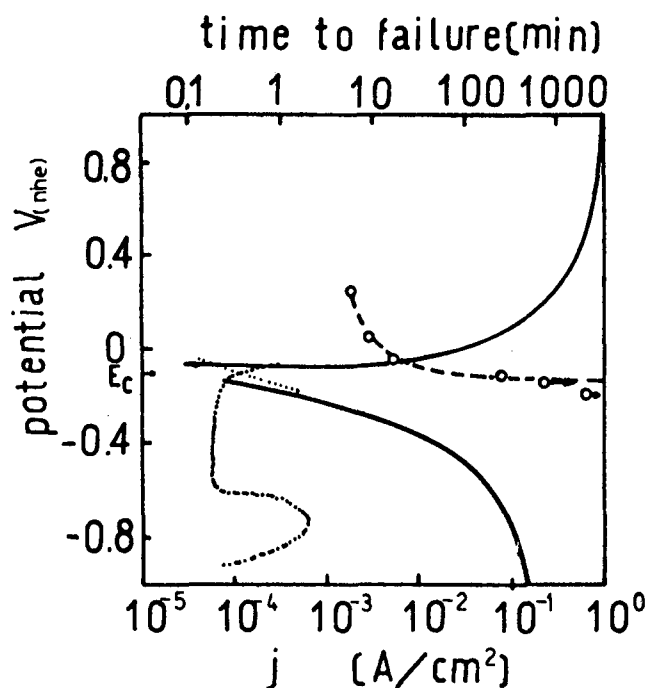


FIGURE 38 — Potentiostatic polarization curve and the effect of potential on time to failure for Type 302 steel in 35 w/o MgCl_2 solution at 125 C, from Smialowski *et al.*⁴⁶ Dotted line: actual anodic curve from Staehle *et al.*⁴⁵

Rychik, on the other hand, found that the time to failure reached a maximum at that critical potential (Figure 38). This figure was redrawn from the results of both papers.^{45,46} These results indicate that to get SCC of stainless steel in MgCl_2 , it is necessary to reach the conditions for pitting. Nevertheless, Uhlig and Cook⁴⁷ discard any relation between pitting and SCC of stainless steel in MgCl_2 , and Graf and Springe⁴⁸ consider that pitting and SCC are related but competing processes; when one process occurs the other cannot occur.

In spite of these affirmations, most of the results published point to the conclusion that in both cases the same anodic process is taking place. It is found that Ni increases the critical potential for SCC⁴⁹ and also the critical potential for pitting.⁵⁰ Nitrates inhibit SCC of stainless steels⁴⁷ but they also inhibit pitting.⁵¹ Molybdenum seems to be an exception since it is deleterious for stainless steel in boiling MgCl_2 ⁴⁵ but inhibits pitting at room temperature.⁵⁰ Nevertheless, Streicher⁵² found that Mo is deleterious even for pitting at temperatures higher than 50 C (122 F).

The yielding experiments with Al showed that depending on the experimental conditions, it is possible to nucleate pitting on the slip lines or to have it all over the metal. In NaNO_3 and alkaline 4M NaCl when the potential is slightly higher than the pitting potential, pitting nucleates on the slip lines, but at higher potentials, generalized pitting is observed. This could explain the competing behavior of pitting and SCC found by Graf and Springe.⁴⁸ There should be a range of potentials where pitting nucleates at slip lines, giving the conditions for initiation of SCC, while

above these potentials, pitting generalizes. According to this, the mechanism of initiation of SCC proposed by Smith and Staehle⁵³ should be modified stating that in the slip steps under the conditions for SCC, the repassivation process is replaced by a pitting process.

The way pitting could conduce to SCC in different systems could be:

1. By dissolving a localized path as in Al-Cu.
2. By localization on slip lines as it seems to occur in stainless steels.
3. By production inside the metal of a local zone with an acid electrolyte, similar to that found in SCC cracks.^{54,55}

The criterion of correlation between pitting and SCC

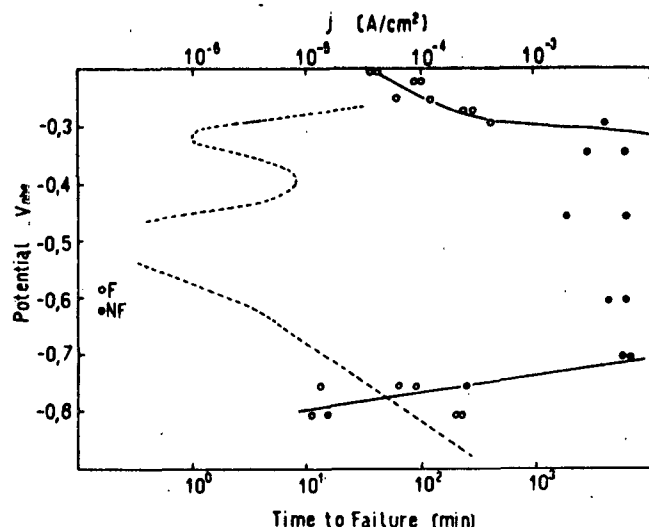


FIGURE 39 — Potentiostatic polarization curve and time to failure for AISI 4340 steel in 0.5M NaCl solution at 25 C, from Galvele and Semino.⁵⁷

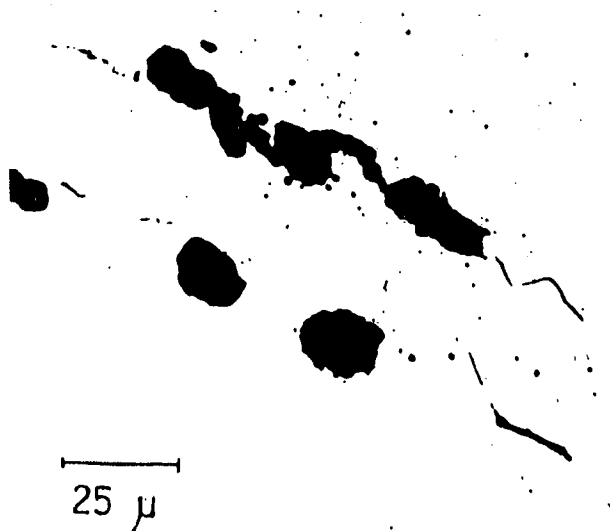


FIGURE 40 — Fissures initiating at pits. AISI 4340 steel in deaerated 0.5M NaCl solution at 25 C, $E = -0.24$ V (NHE), from Galvele and Semino.⁵⁷

has a practical implication. It gives the electrochemical conditions under which a metal should be tested for SCC susceptibility. In our laboratory,^{5,6} Zircaloy 2 was found to be susceptible to SCC in NaCl solutions if exposed at a potential near the pitting potential. It was also observed^{5,7} that in NaCl solutions, the AISI 4340 steel has a pitting potential equal to high purity iron, and that the 4340 steel has short time to fracture at the pitting potential while no fracture is observed at a potential slightly lower (Figure 39). In this case, pitting acts perhaps, according to Figure 40, by creation of a local acid solution; the conditions are set to initiate hydrogen embrittlement of the steel.

Potential/Molar Fraction Diagrams

Hoar⁶ in 1966 proposed the use of "potential/(anion/water)" diagrams for the display of experimental data available for passivity, anodic brightening, pitting, etc. Such diagrams have the advantage of showing in one single figure, the effect of the electrode potential and the electrolyte composition on the anodic behavior of a metal. A few of these diagrams are being determined in our laboratory. The determination of the diagrams has not been completed yet and we are only reporting the experimental technique used and part of the results obtained. A discussion of the results and their relation with previous work by other authors will be the subject of a separate paper.⁶⁰ It should be stressed that there is some difficulty in drawing such diagrams because while the definitions of good brightening, passivity, or etching are clear, there are wide transition zones where the denomination becomes subjective and exposed to discussion.

Experimental Method

The determination of the diagrams was done in two steps. In a first series of experiments, the polarization curve for each concentration was determined. The polarization curve was used to find out the potential ranges for the different form of anodic dissolution. A second series of experiments was performed to determine the morphology

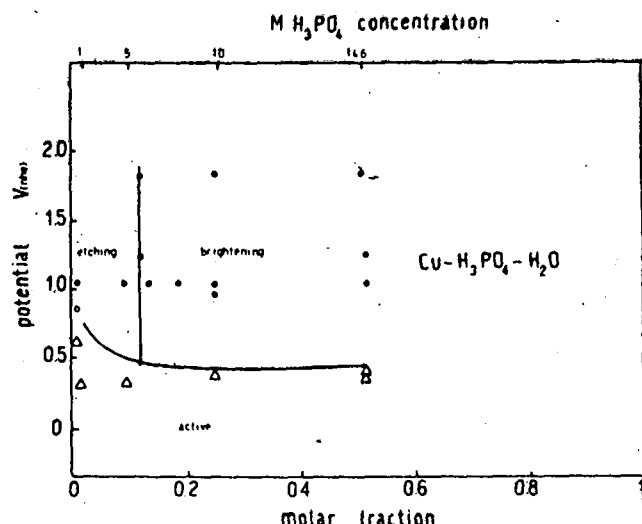


FIGURE 42 — Potential/molar fraction diagram for Cu- $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ at 25 C.

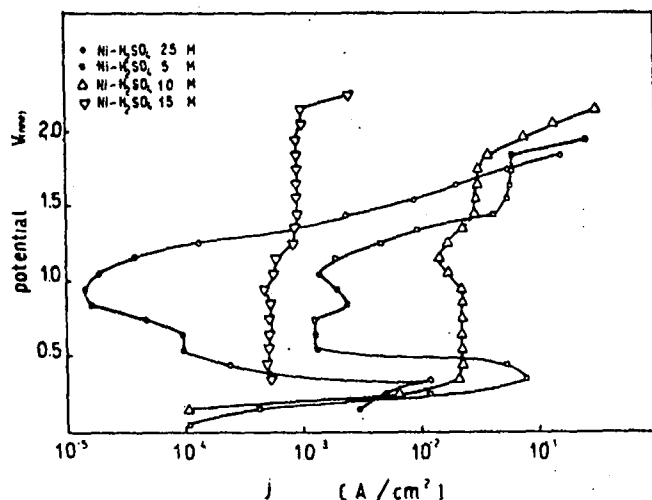


FIGURE 43 — Potentiostatic polarization curves for Ni in deaerated H_2SO_4 solutions at 25 C.

of the anodic attack. In these experiments, the specimens were exposed at constant potential for different lengths of time. The exposure time varied from a couple of hours to various days. The exposure at constant potential lasted until the amount of metal equivalent to a penetration of 10 microns was dissolved. The potentiostatically corroded specimens were metallographically observed to find out the type of attack, and this information was used to draw the potential/concentrations diagrams.

Results

Cu- $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$: Potentiostatic polarization curves were determined in deaerated 1M, 5M, 10M, and 14.6M H_3PO_4 solutions (Figure 41). It was observed that the limiting current increased with the acid concentration. The potential-molar fraction diagram is very simple (Figure 42), showing only active, etching, and brightening regions.

Ni- $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$: The potentiostatic polarization curves

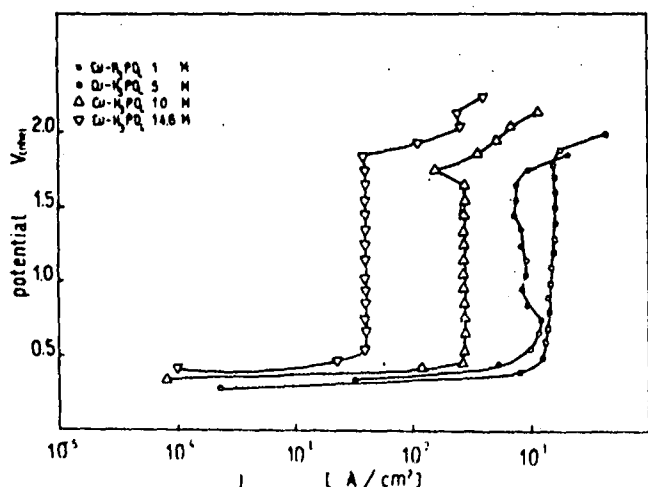


FIGURE 41 — Potentiostatic polarization curves for pure Cu in deaerated H_3PO_4 solutions at 25 C.

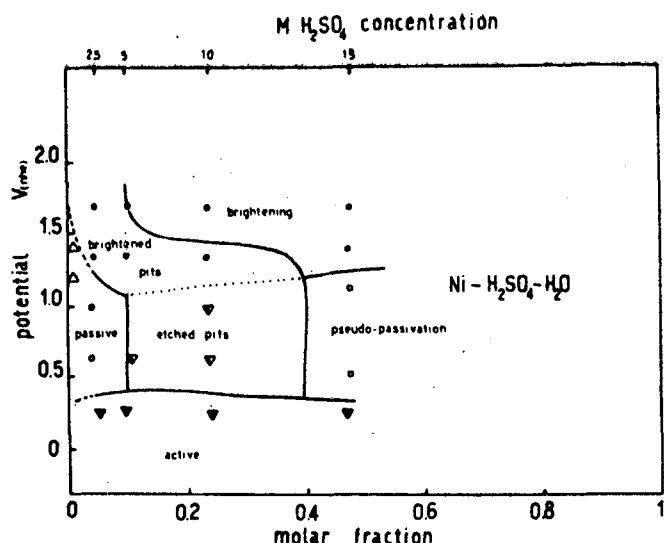


FIGURE 44 — Potential/molar fraction diagram for Ni- $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ at 25 C.

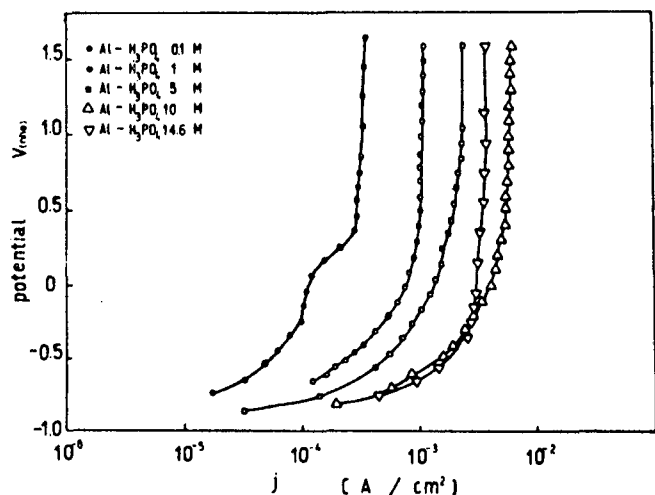


FIGURE 45 — Potentiostatic polarization curves for Al in deaerated H_3PO_4 solutions at 25 C.

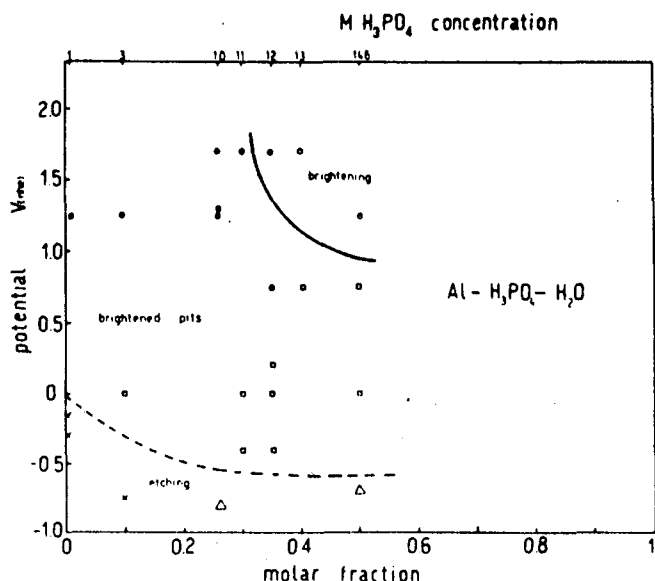


FIGURE 46 — Potential/molar fraction diagram for Al- $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ at 25 C.

(Figure 43) are similar to those reported by Gilli *et al.*⁶¹ The potential-concentration diagram (Figure 44) is more complex, since there are regions of passivity, pseudo-passivity, and two different forms of pitting. In this case, the morphology of the pits changed with the electrode potential.

Al- $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$: Figure 45 shows the potentiostatic polarization curves for this system. The diagram obtained (Figure 46) is very simple, showing only etching, brightened pits, and brightening.

Conclusions

From the results reported in this paper, the following conclusions can be drawn:

1. Brightened hemispherical pits are not a general rule in pitting of metals.
2. Exposing bare aluminum to an "aggressive" solution such as NaCl solutions or NaNO_3 solutions does not lead to pitting if the electrode potential of the metal is lower than the pitting potential.
3. Potentiostatic yielding experiments with Al show that the oxide film acts as an inert species in the pitting process.
4. Yielding of Al at the pitting potential can accelerate pitting nucleation as in neutral NaCl solutions, or can lead to pitting nucleation on slip steps as in NaNO_3 solutions and in alkaline NaCl solutions.
5. It is suggested that the experimental pitting potential is the potential for *maintaining* pitting. The potentiostatic yielding experiments and the effect of surface-active agents on the current oscillations indicate that the *initiation* potential for pitting should be related with the zero charge potential of the metal.
6. In contradiction with recent literature on aging mechanisms of Al alloys, evidence is given of the existence of a solute depleted zone along the grain boundaries of aged Al-Cu alloys.
7. The pitting potential of Al-4% Cu depends on the heat treatment, and shows an important drop when the alloy comes close to peak hardness.
8. Potentiostatic yielding experiments with Al-4% Cu show that SCC susceptibility of the alloy begins when the metal reaches the pitting potential of the depleted zone.
9. A mechanism of SCC based on an anodic dissolution of a depleted zone is applicable to Al-Cu alloys, but cannot be extended to other Al alloys, such as Al-Mg or Al-Mg-Si.
10. There is good correlation between pitting and SCC. Three mechanisms are suggested by which pitting could lead to the initiation of SCC.

(1) By dissolution of a localized path, SCC occurring only at potentials higher than the pitting potential of such path.

(2) By nucleation of pitting on slip steps during mechanical deformation of the metal. SCC will occur in the range of potentials where pitting nucleates only on slip steps. As soon as pitting nucleation starts on other parts of the metal surface, the susceptibility to SCC disappears.

(3) By producing a heterogeneity in the electrolyte in contact with the metal. In the cases of hydrogen

embrittlement, by creating a zone with an acidic solution capable of hydrogen evolution.

11. The criterion of pitting related with SCC leads to a practical method for determination of the electrochemical conditions which conduct to SCC susceptibility of an alloy.

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DISCUSSION

J. Postlethwaite, University of Saskatchewan:

Could it be the case that critical potentials for the breakdown of passivity have a different meaning when applied for the transition metals and their alloys, and to the nontransition metals such as aluminum which form different types of passive films. Aluminum pits below the breakdown potential (as characterized by a rapid rise in current density during polarization) whereas the transition metals do not suffer chloride pitting below their breakdown potentials, which it would appear are "true" breakdown potentials which can be used as a basis of protection from chloride pitting.

Authors' Reply:

I think Postlethwaite's suggestion is a very interesting

one. Nevertheless, I am afraid that our present knowledge of pitting is not sufficient to make such a distinction between the behavior of transition metals and that of nontransition metals. As mentioned in our paper, oscillations similar to those found by us in aluminum were also observed on stainless steels. It is evident that further study is necessary in this area.

B. E. Wilde, U. S. Steel Corporation:

1. Regarding your comments that I do not think much of pitting potentials. The problem I have is that I do not think they are useful regarding the corrosion performance of stainless alloys in sea water. There is no question in my mind that pitting potentials accurately predict material resistance to pit-initiation, at least on stainless alloys.

2. The question of stress corrosion cracking in high strength steels at potentials noble to the pitting potential can be quite firmly attributed to hydrogen embrittlement. Data recently published by myself and Professor Troiano much longer ago, have confirmed the marked absorption of hydrogen into the steel as a direct result of pitting corrosion. The hydrogen absorption fluxes in this potential region (noble) is almost equal to that observed under cathodic conditions ($-1.1 V_{SCE}$) where everyone is prepared to attribute cracking to hydrogen embrittlement.

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Authors' Reply:

I must thank Wilde for his comments on hydrogen permeation in high strength steels. I am very glad to see that his measurements confirm the conclusions we came to and which are based on potentiostatic polarization measurements.

As for the pitting potentials, my intention was only to emphasize something that was clearly stated in Smialowska's paper on "The Analysis of Electrochemical Methods for the Determination of Characteristic Potentials of Pitting Corrosion", but which is frequently overlooked in the literature. It refers to how careful one has to be when measuring pitting potentials. To confirm the existence of a pitting potential for aluminum, Figure 28, we used exposures of 5 hours at each potential. A similar method was necessary to show the existence of such potential for iron in neutral sodium chloride solutions.^{5,7} And as for stainless steels it was found¹ that the method used to measure the pitting potentials could lead to errors of several hundreds of millivolts.

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