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ABSTRACT

A review is made of the stress corrosion cracking (SCC) problem, stressing the fact that the problem is still unsolved in spite of the great amount of work done. A comparison with sister disciplines, such as metallurgy, mechanics and electrochemistry shows that all of them are of very recent development, and contemporary to the SCC problem. All SCC theories have failed so far because too much was ignored at the time of their proposal. Considering that very little is known at present of what happens at the bottom of the crack at an atomic level, the chances of having a good SCC theory are still very dim. Finally, a decomposition of the process in rate-controlling steps is suggested. And a technique is described for the study of those cases where anodic dissolution is the rate-controlling step.

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* Based on the plenary lecture given at the 7th International Congress on Metallic Corrosion, Rio de Janeiro, 1978.

Development of the stress corrosion cracking problem

The preparation of this paper led to the conclusion that talking about stress corrosion cracking is a very difficult task. It seems that there is no other field in Corrosion Science where so many papers have been published. But at the same time, there is no other field in Corrosion Science, with perhaps the only exception of Corrosion Fatigue, where our ignorance is so deep. The stress corrosion cracking problem has been with us for over one hundred years. And yet, the input of problems from the field to the laboratory has so far been overwhelmingly higher than the output of solutions. This trend has not changed yet. New and unpredicted problems arise whenever a new advance in technology is introduced. The aim of the present paper is to analyse why we have not yet arrived at a reasonable stress corrosion cracking theory that could guide us in the prediction of stress corrosion cracking problems.

In a very elementary way the stress corrosion cracking process can be depicted as shown in Figure 1. Most metals, either by design or as the result of the manufacturing technique, are exposed to various stresses. The same metals can be used in relatively mild corrosive environments, without any serious corrosion problem. But, very often, the simultaneous action of stress *plus* corrosion leads to a cracking process, with cracks that propagate at a rate of a few millimeters per year to several millimeters per hour.

One of the oldest forms of cracking is that of caustic embrittlement, observed in steam boilers. A typical example of cracks in a riveted drum boiler was shown by Acock *et al* (1). Another very old form of stress corrosion cracking is the "season cracking" of brass. Numerous examples of cracking in small arm cartridge cases could be found in the General Discussion on Failure of Metals of 1921 (2) and in the Symposium on Stress Corrosion Cracking of 1944 (3).

A classic in the stress-corrosion-cracking literature was described by Johnson (4). It refers to the unexpected stress corrosion cracking failures of titanium alloy pressure vessels, containing nitrogen tetroxide. They were detected in January 1965, during the development of the Apollo Program, threatening to jeopardize it. Intensive research showed that minor amounts of nitric oxide in the nitrogen tetroxide were necessary to inhibit stress corrosion cracking of the titanium alloy.

Many other important examples of stress corrosion cracking failures are found in the literature. In a recent monograph Brown (5) shows the impressive picture of a bridge that collapsed as the result of stress corrosion cracking. This accident happened in 1967, and caused the death of 46 persons. Leak (6) surveyed failure cases in military aircrafts, most of them due to stress corrosion cracking, and leading to personal accidents and/or, to serious economic loss. Many more examples could be quoted from the literature. Let us see how the stress corrosion cracking problem developed through the years. Figure 2.

According to Keating (7) the cracking of boilers, often associated with explosions, began in the early days of the industrial boiler. Between 1865 and 1870, 288 boiler explosions were reported in England. They had similar experiences in America and Germany. Many of those failures were thought to be due to defects, either in the materials or in the design, but it is now believed that some of them were due to stress corrosion cracking.

The first evidence that a metal with internal stresses would crack in the presence of certain aggressive environments was reported by Roberts-Austen (8) in 1886. This author used ferric chloride solution to detect internal stresses in 13-carat gold. The stress corrosion cracking of brass, or "season cracking", was first seriously taken into account during the Boer War (9). Logan (10) reported that the first detailed description of brass "season cracking" was published by Sperry in 1906.

Stress corrosion cracking of aluminum alloys was first reported by Rosenhain and Archbutt (11) in 1919. Since then stress corrosion cracking of aluminum alloys has been a problem in modern technology. Speidel (12) reported that failures due to stress corrosion cracking of aluminum were observed during the construction of the Zeppelin in Germany, sixty years ago, and more recently they were also found in the Saturn rocket and in the lunar module during the NASA Apollo program.

The first case of transgranular stress corrosion cracking of austenitic stainless steel was observed in 1937, as reported by Ellis (13). More recently, we have witnessed such an avalanche of new cases of stress corrosion cracking that the exact dates have become irrelevant. The feeling is now that every metal or alloy can, under certain circumstances, suffer stress corrosion cracking.

Stress corrosion cracking theories

Numerous theories have been proposed to explain the stress corrosion cracking process. Some authors (7,14) suggested that stress corrosion cracking propagation was a combination of steps which included plastic deformation, brittle fracture and localized corrosion. Others (15) suggested that new solid faces were formed at the bottom of the crack, leading to fast localized dissolution. There were theories (16-20) that suggested that hydrogen was responsible for the crack propagation process, either by hydride formation or by hydrogen-induced metal decohesion. Some authors (21,22) supported the theory of a mechanism of a surface energy reduction by ion adsoption on the metal surface. Finally, the existence of a yield assisted anodic dissolution was also suggested (23-25). This dissolution was due either to the formation of new active sites at the bottom of the crack, or to a film breakdown process.

We are not going to analyse, in the present paper, the validity of each of these theories, a subject that has been the matter of long discussions in many conferences. What is clear at present is that none of these theories has been totally satisfactory, since they did not allow us to predict new cases of stress corrosion cracking. In order to find out why those stress corrosion cracking theories were not satisfactory, let us take one of them, and check it with our present knowledge. To avoid discussions, it had to be either a theory that was completely discredited, or one whose authors would not feel hurt by the present reviewer's comments. The stress corrosion theory chosen was the amorphous cement theory proposed by Rosenhain and Archbutt (11) in 1919, Figure 3. According to this theory, the "season cracking" of metals was due to a viscous or visco-elastic movement of the amorphous metal present in the intercrystalline boundaries. It was accepted that corrosion could accelerate the process, but it was believed at the time that in the absence of corrosion the cracking process could still happen.

In April 1921 a joint discussion was held by the Faraday Society, the Institution of Mechanical Engineers, the Iron and Steel Institute, the Institute of Metals and other important Societies (2). The title of the discussion was "The Failure of Metals Under Internal and Prolonged Stress". Rosenhain was in charge of the Introductory Lecture. He strongly defended the amorphous cement theory, and concluded that "at this time this theory appears to be overwhelmingly strong as compared to any other explanation". The mechanical engineers present at the meeting wanted to know how to stop "season cracking". But to their disappointment, most of the discussion was about the thickness of the amorphous layer. Was it two atoms thick, or was it several atoms thick?

The above story was brought up here because even today we very frequently get involved in long discussions about subjects that are later found to be irrelevant. We have to admit, though, that this and later theories, whether right or wrong,were of great help in planning new experiments to go deeper into the stress corrosion cracking problem. Nevertheless, looking back to all these developments we find two constants in the history of stress corrosion cracking. The first one is that the supporters of the various theories were always convinced that, with the exception of a few minor points, their theories explained at full length the stress corrosion cracking problem. The second constant is that the stress corrosion cracking problem has remained unsolved, and that we keep receiving from the field more and more cases of stress corrosion cracking failures. This picture has perhaps changed a little in the present days in the sense that now we are not at all sure about any of the theories.

Developments in related disciplines

If we look at the amorphous cement theory in the context of the other related disciplines, like metallurgy, electrochemistry, etc., we find that it was impossible at the time to have any good stress corrosion cracking theory. To center most of the argument on a property of the grain boundaries, as Rosenhain and Archbutt did, was correct. All the stress corrosion cracking cases known at the time were intergranular, Figure 4. It was only in 1937 that the first example of transgranular stress corrosion cracking was found. On the other hand, the idea of an amorphous cement is not a surprising one, because in 1919 Beilby's theories of amorphous or vitreous conditions produced in metals by straining or by polishing, were very popular (11).

Stress corrosion cracking is the result of a very close interrelation of disciplines like mechanics, metallurgy and electrochemistry. Let us see what degree of development had been attained in those fields at that time, Figure 5. The dislocation theory was developed between 1929 and 1934 (26, 27) and dislocation multiplication mechanisms, like the Frank-Read source, were only reported in 1950 (27). The relation between dislocation stacking fault energies and stress corrosion cracking, in particular for transgranular stress corrosion cracking, appeared only in 1962 (28-30). Incidentally the first papers on this subject seemed to prove that stress corrosion cracking was due only to stacking fault energies and dislocation pile-ups. It was found later (31) that, while this was a necessary condition, it was not a sufficient one, some other important parameters had to be considered.

Stress corrosion cracking is a process of fracture in the presence of an aggressive environment. Let us see how much was known at the time about fracture in the absence of the corrosive environment. If we examine the development of fracture mechanics (32), we see that by 1953-56 there was still great confusion in this field. At that time serious mechanical failures were taking place, like the "Comet" aircraft fractures, heavy-section fractures of large-steam-turbine components, gastransmission-pipe fractures, over a mile long, welded-ship fractures, etc. Fracture mechanics, as we know it now, was developed in the sixties. And, even now, the description of the problem is macroscopic. There is no information on what happens at the bottom of the crack at an atomic level. The use of fracture mechanics in stress corrosion cracking is very recent. The use of pre-cracked specimens in the study of stress corrosion cracking was introduced by Brown and Beachem (33) only in 1965.

From the above we conclude that many branches of mechanics and metallurgy, which are relevant to stress corrosion cracking, have developed only very recently. Something similar has happened in the field of Corrosion Science. Galvanostatic techniques were known at the beginning of the Century (34). About 1920 galvanostatic curves were used in the study of corrosion processes. In 1932 Hoar and Evans (35) explained for the first time the wet corrosion of iron by the use of polarization curves. In 1938 Wagner and Traud (36) introduced the principle of superposition of polarization curves. But it was only in 1942 that the first electronic potentiostat was described by Hickling (37) and it took about ten years to introduce the electronic potentiostat in corrosion studies (38). The use of electronic potentiostats in the study of stress corrosion cracking was of great importance. For example, caustic embrittlements of mild steel appeared in boilers around 1865. But it was only in 1967, one hundred years later, that with the use of potentiostats and slow straining techniques, Humphries and Parkins (39) obtained for the first time in the laboratory reproducible stress corrosion cracking of mild steel in caustic solutions.

The first information about the solution chemistry inside the stress corrosion cracks was published by Brown and coworkers (40) in 1969. The use of Ellipsometry, Auger analysis, ESCA, and other surface analysis techniques is very recent, and some of them are only at the beginning of their development.

Let alone the amorphous cement theory, we see now that many of the later theories had little chance of success. Too much was ignored at the time.

There is no way to predict how many new discoveries will be made in the field in the near future. But at least we know the level we have to reach before we have a clear picture of stress corrosion cracking. Electrochemical reaction mechanisms are described at an atomic level. To understand the interrelation between electrochemistry, metallurgy, and mechanics, we also have to know how each of these variables acts at an atomic level. Unfortunately very little is known about what happens at the bottom of a crack at an atomic level, Figure 6. And this is the level we have to reach before we understand the stress corrosion cracking process. The composition of the solution within a crack is known to be different from that of the bulk solutions (40,41). We know that outside the crack there are oxide films. Ellipsometry tells us about the thickness of those films. Tribo-ellipsometry (42) could even tell us about the rate of change of that thickness. But as far as the composition of the films, we are only beginning to learn something about it through Auger, ESCA, and other techniques. As for the nature of the films inside the cracks, it is all a matter of guessing. In some systems, that are very important from the stress corrosion cracking point of view, such as high temperature water, we do not even know what happens in the absence of stresses. The high temperature water electrochemistry is still at the beginning of its development. It is to be hoped that with the introduction of all these new and sophisticated techniques we will be able to advance quite a lot in the near future.

Crack propagation rate determining steps

One serious limitation found by this reviewer in the current stress corrosion cracking theories is that they are based on single step mechanisms. Some theories will support that stress corrosion cracking occurs as the result of anodic dissolution on the crack front (23-25, 43-45). Others will assume that hydrogen is of paramount importance in the stress corrosion cracking process (16-20). But in general all these theories are exclusive. No allowance is made for the coexistence of several steps in the crack propagation process.

Nevertheless, experience has shown that slight changes in the experimental conditions could lead to substantial changes in the morphology of the cracks or in the crack propagation rate. Mattsson (46) studied the effect of pH on the stress corrosion cracking morphology in brass exposed to ammoniacal solutions. Going from pH 4, up to pH 11, he reported that the cracks would change not only in their propagation rate, but would also change from transgranular to intergranular and back to transgranular again. Speidel (12) reported that aluminum, as many other metals, would show a stress-intensity dependent crack propagation rate. But in all these cases the crack propagation rate does not change monotonously. Two clear regions are found, Figure 7. The first one is stress-intensity dependent, while the second one is independent of stress intensity. The obvious conclusion is that, while at low stress intensity values the crack propagation rate is determined by a stress dependent step, at high stress intensity values the crack propagation rate is governed by a stress independent process.

Stress corrosion cracking being a kind of heterogeneous electrochemical reaction, many steps should be involved in the process. One possible description of the stress corrosion crack propagation kinetics is given in Figure 8, this being a completely hypothetical case, where successive steps have been assumed. The lowest step will be the rate-determining step, as shown by the asterisk. The different steps could be, for example:

1) Propagation of an elastic wave in the crystal.
2) Rate of movement of dislocations.
3) Rate of rupture of the oxide film or the salt at the bottom of the crack.
4) Anodic dissolution rate of the metal at the bottom of the crack; or some hydrogen-induced metal-decohesion process; or liquid metal diffusion rate; or even an adsorption-controlled process.

5 and 6) Dissipation of the reaction products.

For example, if step 3 is function of the stress intensity value, the higher the stress intensity, the higher the rate of step 3. But when step 3 becomes faster than step 4, the latter will become the rate-determining step. In this case, if step 4 is a stress independent step, the crack propagation rate will become stress independent too.

This way of describing the crack propagation mechanism is very useful, because it allows us to make sure that we are talking about the same steps when comparing two different experiments. There are cases of stress corrosion cracking where there is no agreement between different authors about the rate-determining step. This happens for example in stress corrosion cracking of titanium (20,43) and of aluminum-magnesium-zinc (47,48) alloys. Some authors suggest that an anodic reaction is involved (43,47), while others (20,48) support an hydrogen-controlled mechanism. It could happen that, under certain circumstances both mechanisms are involved. Cases of parallel steps should also be considered.

The next step will be to look for experimental techniques that could be used to discern between different rate-determining steps, and to study how different variables will affect those steps.

Anodic dissolution as the rate determining step

So far anodic dissolution has been the only rate determining step studied in a quantitative way. To this purpose the potentiostatic straining metal technique was used. This technique has been quantitatively tested for several stress corrosion cracking systems. But although it seems to be very promising, this reviewer has found that it has not been paid enough attention in the literature.

It is important to make clear at this point that while the anodic dissolution is known to be the rate-determining step, it is not yet known how, at an atomic level, this anodic dissolution leads to the separation of both sides of the crack. There is a very good coincidence between the evaluated current densities and the measured crack propagation rates, but there is no explanation for the fracture surfaces observed with Scanning Electron Microscopy. In this respect, the knowledge of the crack structure, at an atomic level, will be of great help.

The technique is based on the straining wire experiments introduced by Hoar and co-workers (25, 49-53) in Cambridge, England. Wire samples are strained at a constant potential and constant strain rate. The strain rates used are in the range of 10 to 300% per minute. This is much faster than the well known slow-straining technique developed by Parkins and co-workers (39,54), where strain rates of the order of 10^{-6}% per minute were used, and much slower than those used by Staehle and co-workers (55) and by Diegle and Vermilyea (56) in the study of transient repassivation processes, where strain rates of 500 to 6000 % per second were used. When the wire is strained, slip steps are produced on the metal surface, eventually leading to the exposure of bare metal to the solution.

This technique was applied by Hoar and Galvele (50) to the study of mild steel in boiling calcium nitrate solutions. A black film was present on the surface of the wire. This film was broken by straining the wire. The exposure of fresh metal to the solution led to an increase in the current density, as shown in Figure 9. This current increase was the result of the high current density on the freshly exposed metal. The experiments were continued up to the rupture of the wires. This took a couple of seconds for the fastest strain rate, and about one minute for the slowest. The current increase was faster in the first case because the rate of exposure of the fresh metal was higher. Another way of plotting these results is in function of the elongation. In this case the values of current for equal amounts of fresh metal exposure are compared. This is shown in Figure 10. In this case all the points fall on the same line. This means that for the same amount of fresh metal exposed, the same current is obtained, no matter how long it takes to reach that elongation. This indicates that no repassivation takes place on the bare metal in straining experiments of up to one minute. Or, in other words, the system shows a very slow repassivation rate. This is a property of the stress corrosion cracking system, as pointed out by Scully (57). Once the elongation is known (50), the fraction of area of bare metal exposed can be calculated by making a few simple assumptions. Then, if the change in current due to elongation is known too, the current density on the bare metal can be calculated. Through slow straining experiments, Hoar and Galvele measured the crack propagation rate, and calculated the current density required for the cracks to propagate by anodic dissolution alone. Table I shows the values found. A very good correlation was observed between both values. This showed that the crack propagation rate was determined by the anodic dissolution process. It is interesting to note that even in alkaline nitrate solutions stress corrosion cracking of mild steel was possible, provided that the electrode potential was high enough. This fact was unknown before this research, and it was predicted by the straining experiments.

If the current density on the fresh metal is known, by Faraday's law the crack propagation rate can be calculated. Another example of very good correlation between the values calculated by straining experiments, and those measured metallographically, Figure 11, was found by Hoar and Jones (52), for mild steel in caustic solutions.

Galvele, Wexler and Gardiazábal (58) used this technique to study the stress corrosion cracking of AISI 304 austenitic stainless steel in HCl solutions at room temperature. Incidentally, these authors proved in their work that there was a film formation process on the metal under these conditions. Earlier papers mentioned this system as an example of stress corrosion cracking of unfilmed metal. The conclusions of this work have been recently confirmed by Smialowska and Lukomski (59) using ellipsometric techniques.

From the straining experiments, Galvele et al (58) calculated the crack propagation rates, Figure 12. In agreement with previous publications, there was no stress corrosion cracking at low potentials. Nevertheless, there seemed to be a disagreement at high potentials, where no stress corrosion cracking was found. But the straining experiments indicated a monotonous increase in the crack propagation rate. The answer to this apparent contradiction was found by introducing a new parameter, which was also obtained during the straining experiments. The current density on the bare metal gave the crack propagation rate, which increased with the potential. But the current density on the static metal also increased with the potential. Eventually, at high potentials, both current densities became very close. There is general agreement (60) that for a crack to develop and to remain in existence the tip must progress more rapidly than the dissolving surface by a factor greater than 10x. Then the ratio of the bare-metal current to the static-metal current has to be higher than 10. This ratio of currents is an important parameter that gives a measure of the corrosion morphology. As shown in Figure 15, when the ratio is high, sharp cracks should be expected, while, when the ratio is low, trenches will be formed. Eventually, when the ratio is one, smooth generalized dissolution will take place on the stressed metal. These morphologies, predicted from short straining experiments, were actually found in stress corrosion cracking experiments (58).

This technique has been successfully applied in the following cases: AISI 304 in NaCl plus H_2SO_4 solutions at room temperature (61), AISI 304 in boiling 20N NaOH solutions (62), Incoloy 800 in boiling 17.5N NaOH solutions (62), and Inconel 600 in boiling 17.5N NaOH solutions (62). In all these cases the crack propagation rates and crack morphologies predicted by short term experiments were in coincidence with those found by conventional stress corrosion cracking experiments.

Conclusions

It is concluded that the unpredictability of stress corrosion cracking failures is mainly due to the absence of a good theory on stress corrosion cracking. Due to the fact that we ignore what happens at the bottom of the crack, at an atomic level, the chances of having at present a good theory on stress corrosion cracking are dim.

The importance of finding the rate-controlling steps in the crack propagation process is pointed out. For those cases where the rate determining step is anodic dissolution, a technique is described. From a theoretical point of view,this technique allows the detection of anodic dissolution rate-determining steps, and from an applied point of view, it provides a way for quick evaluation of stress corrosion cracking susceptibility. In the experiments with boiling NaOH solutions (62), for example, the conventional stress corrosion tests required about one year's work. By the straining experiments, on the other hand, the same information was obtained after only one week's work.

Finally, this reviewer would like to conclude by stressing the need we have of a more "academic" type of research. The trend in the last few years has been to support preferentially the so called "relevant" research. In this way the best we can get is just recipes for temporary relief of the stress corrosion cracking problems. But we urgently need more information about what happens at the bottom of the cracks, and more information about the rate-determining steps. Only then, we will have the necessary information to develop a sound theory of stress corrosion cracking, and we will be able to predict new cases of stress corrosion cracking. Only then, we will be able to avoid new unpredicted service failures.

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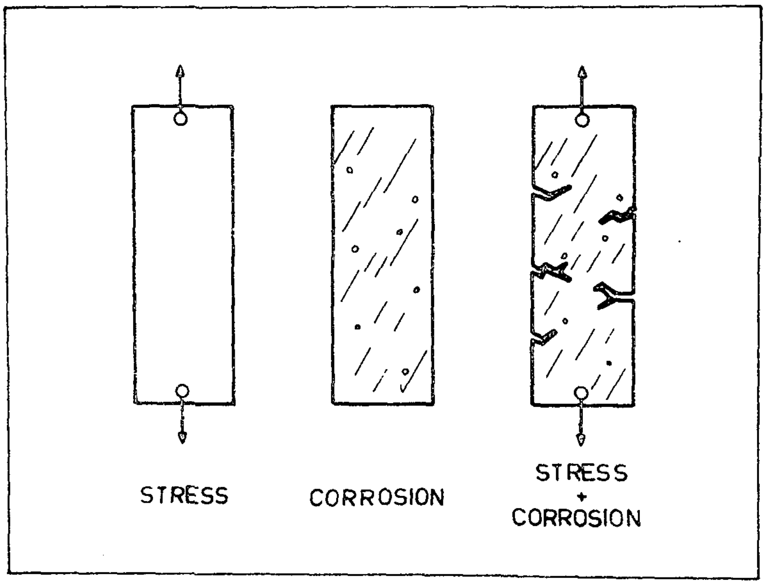
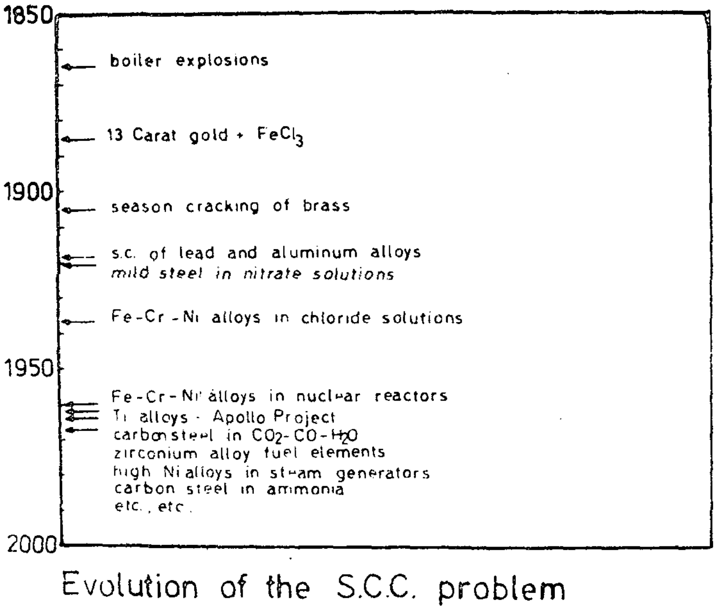


FIGURE 1: The simultaneous action of stress plus corrosion, very often leads to the stress corrosion cracking process.



Evolution of the S.C.C. problem

FIGURE 2: Historical evolution of the stress corrosion cracking problem.

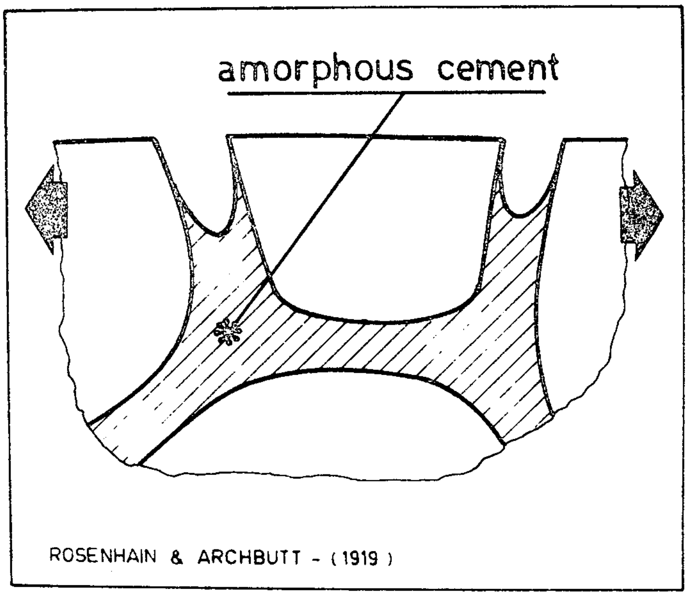


FIGURE 3: Amorphous cement theory of stress corrosion cracking proposed by Rosenhain and Archbutt (11).

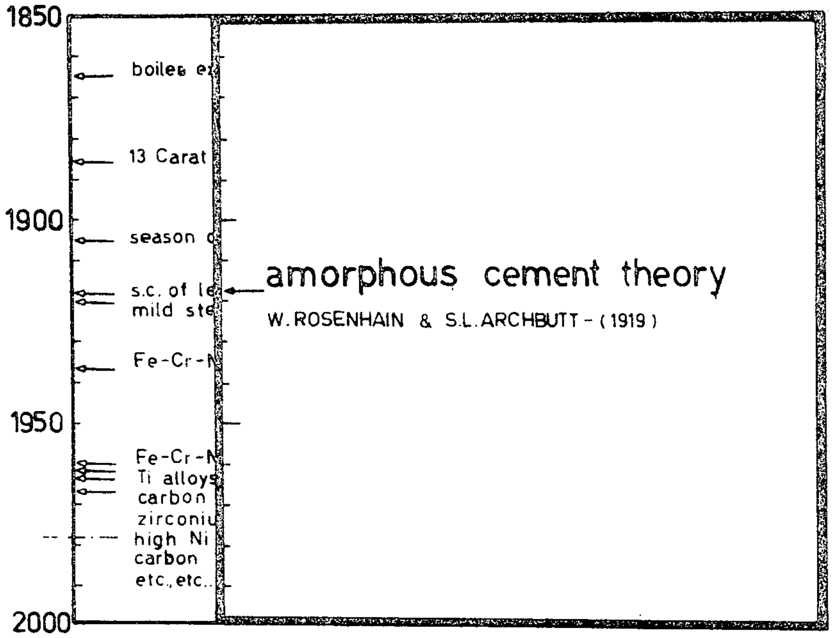


FIGURE 4: Location of the amorphous cement theory in the historical evolution of stress corrosion cracking.

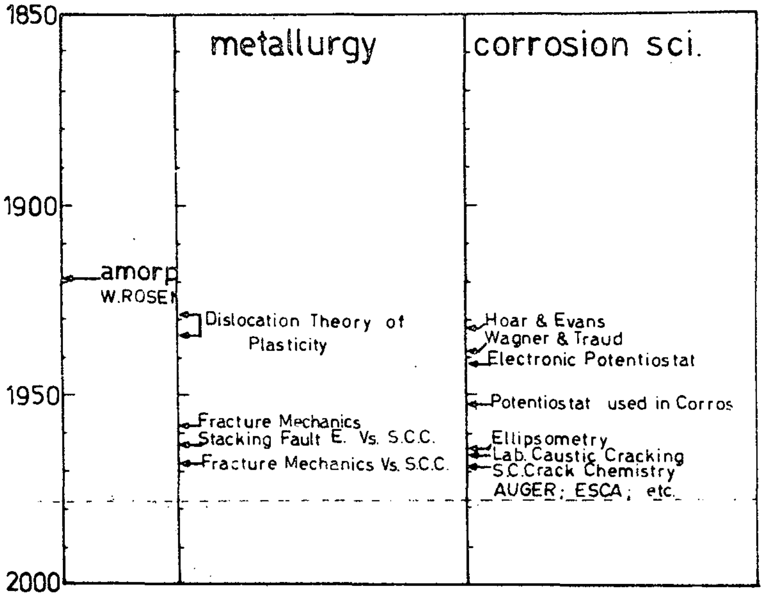


FIGURE 5: Compared historical evolution of metallurgy and corrosion science.

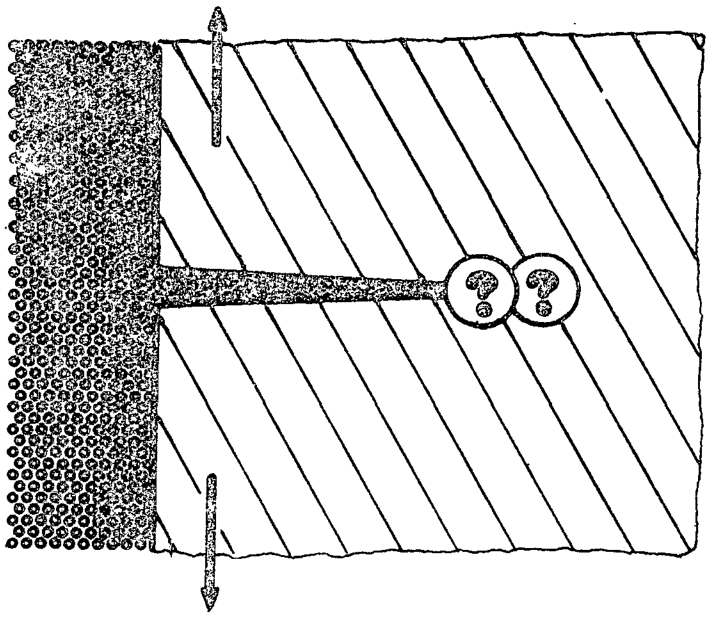


FIGURE 6: One of the main difficulties in the development of stress corrosion cracking theories is the ignorance of what happens at the bottom of the crack, at an atomic level. This ignorance is found both on the metal side and on the solution side.

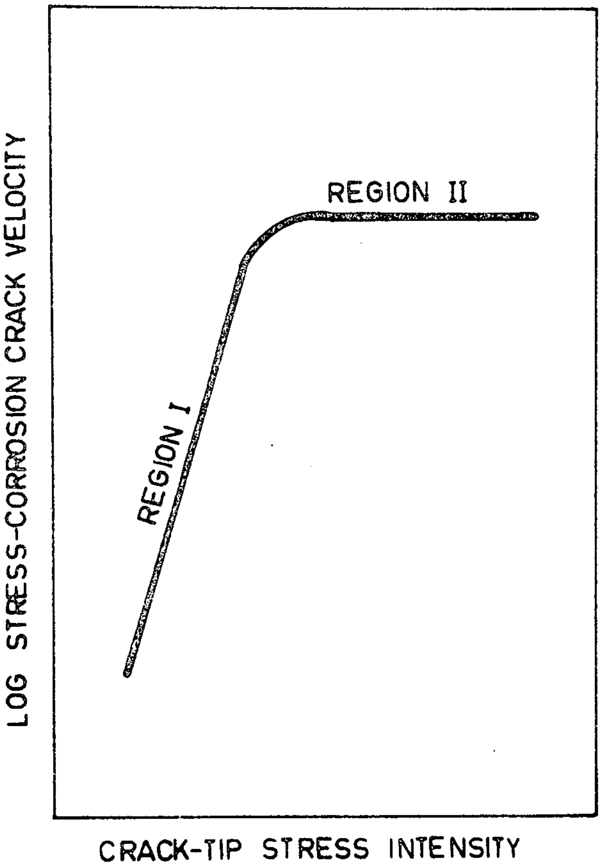


FIGURE 7: When studying the effect of crack-tip stress intensity on the stress-corrosion crack velocity two distinct regions are found.

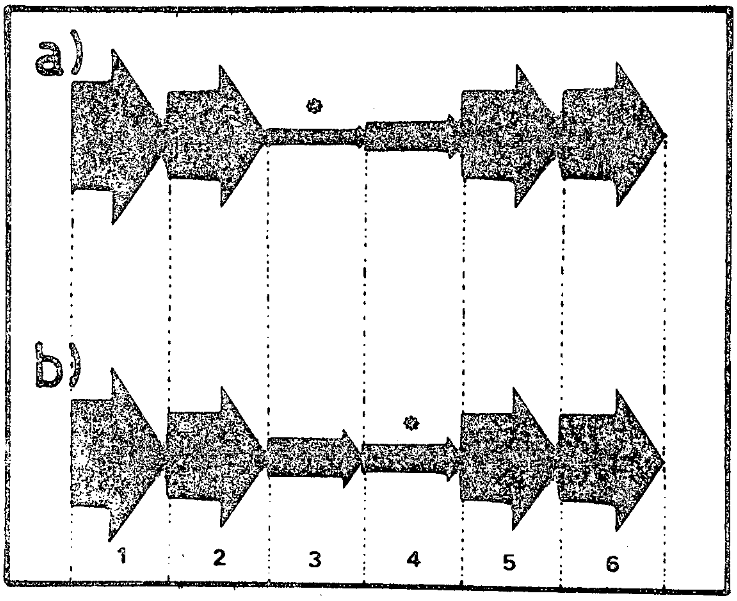


FIGURE 8: Multy-step description of the stress corrosion cracking process.

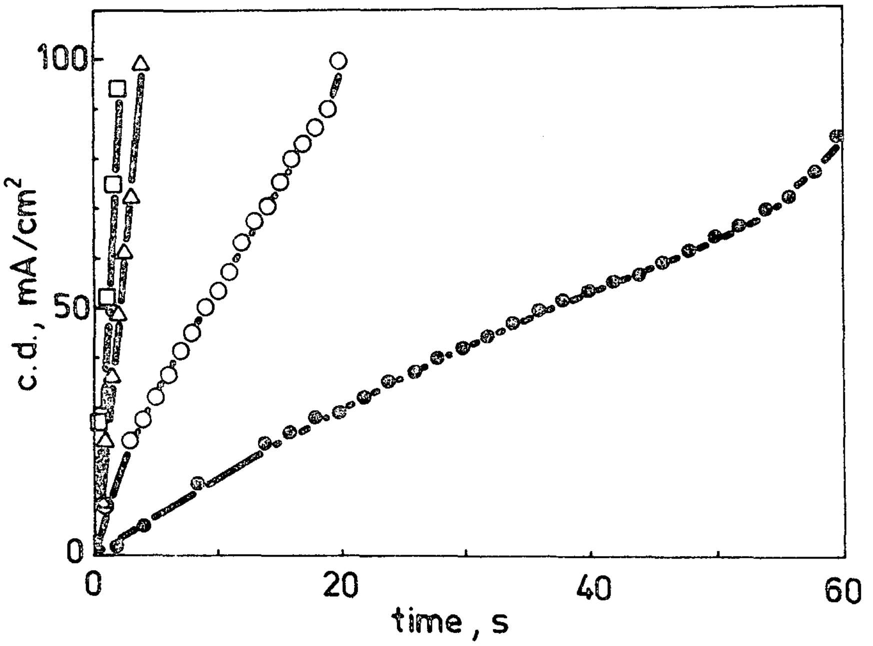


FIGURE 9: Potentiostatic current-density/time curves for mild steel straining at different strain rates in hot calcium nitrate solution. 4N $Ca(NO_3)_2$, pH 3.7, 102°C, e_H - 0.10V. Strain rate: □ 307%/min; △ 154%/min; ○ 31%/min; ● 8%/min. Hoar and Galvele (50).

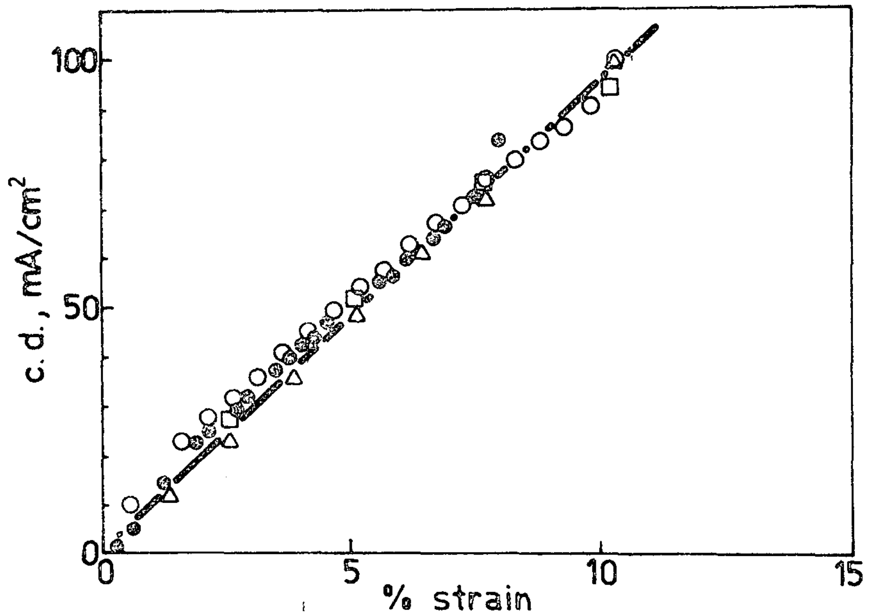


FIGURE 10: Variation of current density with % strain (data from Fig. 9). Strain rate: □ 307%/min; △ 154%/min; ○ 31%/min; ● 8%/min.

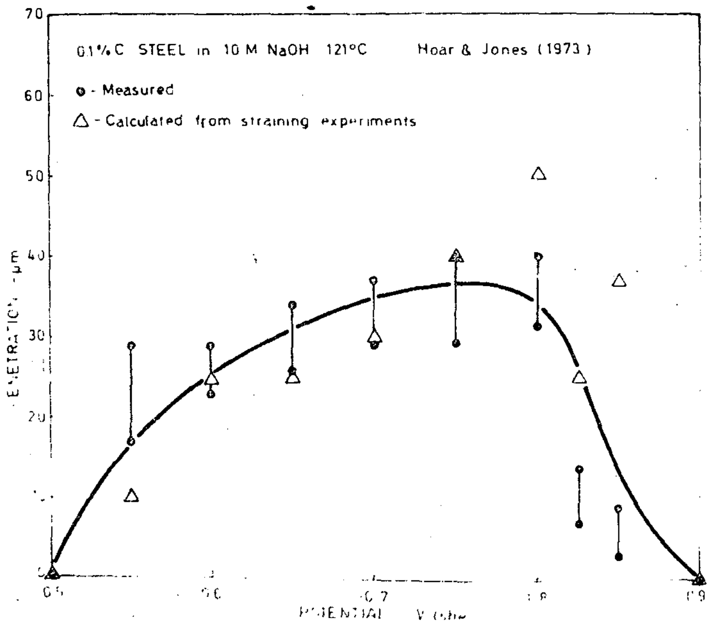


FIGURE 11: Crack penetration values calculated from straining experiments and measured metallographically, for mild steel in 10 M NaOH solution at 121°C. Hoar and Jones (52).

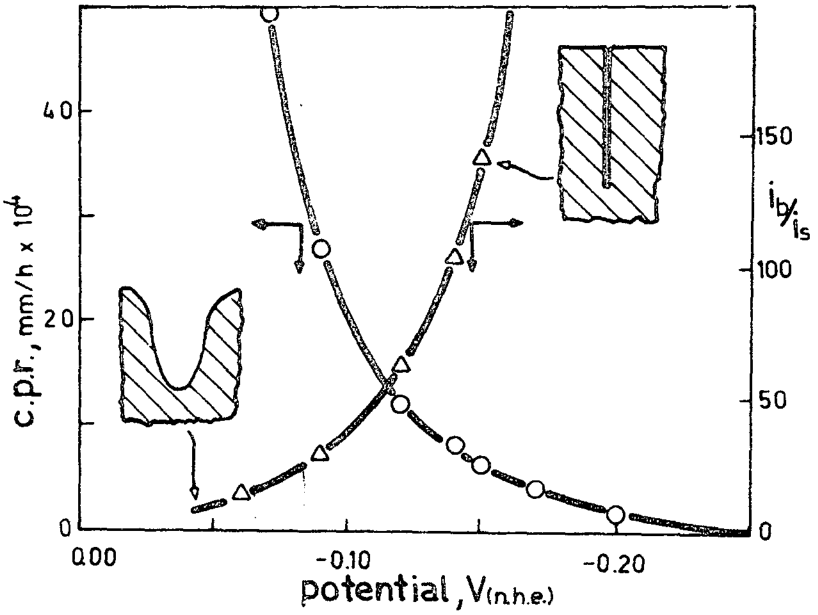


FIGURE 12: Crack penetration rates and crack morphologies calculated from straining experiments. AISI 304 stainless steel in 1 N HCl solution at room temperature. Galvele, Wexler and Gardiazábal (58).

TABLE I

CURRENT DENSITY AT NEW EXPOSED METAL IN FISSURES IN THE OXIDE FILM PRODUCED BY FAST STRAINING, COMPARED WITH THE CURRENT DENSITY REQUIRED TO ADVANCE CRACKS IN THE METAL AT MICROSCOPICALLY MEASURED RATE. (After Hoar and Galvele (50))

Solution	Potential $V_{(NHE)}$	pH	C.D. measured A/cm^2	C.D. required A/cm^2
4N $Ca(NO_3)_2$	-0.10	3.7	2.01	2.08
4N $NaNO_3$	-0.14	4.8	1.48	1.21
4N $NaNO_3$	-0.18	4.8	0.80	0.69
4N $NaNO_3$	-0.22	4.8	0.26	0.16
4N $NaNO_3$+NaOH	-0.14	10.3	1.32	0.73