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KINETICS OF GROWTH OF SPHERICAL GP ZONES: EXPERIMENTAL VERIFICATION OF THE VACANCY PUMP MODEL*

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The experimental verification of the "vacancy pump model" by X-ray small angle scattering is attempted on the Al–10% Zn and Al–10% Zn–0.1% Mg alloys. For the binary alloy the calculation of diffusion coefficients for the vacancy–zinc complexes and their initial number per unit volume gives values that cannot be explained by the existent data of activation energies. Without discussing the mechanism of the cyclic pump, a revision of the hypothesis that leads to the quantitative formulation of the model is suggested. For the ternary alloy, the possibility of a diffusion mechanism similar to that proposed for the binary alloy is admitted.

CINETIQUE DE CROISSANCE DES ZONES DE GUINIER–PRESTON SPHERIQUES: VERIFICATION EXPERIMENTALE DU MODELE DE LA POMPE A LACUNES

La vérification expérimentale des prévisions du modele de la "pompe des lacunes" par diffusion aux petits angles de rayons X été essayé sur des alliages Al–10% Zn et Al–10% Zn–0.1% Mg. Pour l'alliage binaire, le calcul des coefficients de diffusion des complexes lacunes–Zinc ainsi que leur nombre initial par unité de volume conduit à des valeurs qui ne peuvent pas être justifiées par les données existantes des énergies d'activation. Sans mettre en cause le mécanisme de pompage cyclique, la révision des hypothèses faites pour arriver a la formulation quantitative du modèle est suggérée. Pour l'alliage ternaire on admet la possibilite d'un mechanisme de diffusion analogue à celui proposé pour l'alliage binaire.

DIE WACHSTUMSKINETIK KUGELFÖRMIGER GP-ZONEN: EXPERIMENTELLER NACHWEIS DES LEERSTELLENPUMPENS

Der experimentelle Nachweis des als Modell vorgeschlagenen "Leerstellenpumpens" wird an den Al–10% Zn- und Al–10% Zn–0,1% Mg-Legierungen versucht. Die für die binäre Legierung berechneten Diffusionskoeffizienten für Leerstellen-Zink-Komplexe und ihre Ausgangskonzentration können durch bisherige Werte der Aktivierungsenergie nicht erklärt werden. Ohne das zyklische Pumpen zu diskutieren wird eine Revision der Voraussetzung, die zur quantitativen Formulierung des Modells führt, vorgeschlagen. Für ternäre Legierungen wird ein ähnlicher Diffusionsmechanismus für möglich gehalten, wie er für binäre Legierungen vorgeschlagen wurde.

1. INTRODUCTION

It is well known that the quenched-in vacancies play a very important role in the kinetics of formation of GP zones.[1–3] However, the mechanism by which these vacancies move has not been clarified.

The "vacancy pump model" proposed by Girifalco and Herman (GH),[4] based on a diffusion process involving solute atom–vacancy complexes, explains GP zones growth by taking into account two important experimental facts: (a) the number of quenched-in vacancies is always several orders of magnitude less than the number of solute atoms finally clustered in the zones; (b) the GP zones growth continues for periods of time much longer than the vacancy mean life time in a pure metal. This model has been developed for spherical GP zones, each one being considered independent of the others. Assuming that equilibrium exists between the complexes and the dissociated free solute atoms and vacancies, the following growth law is predicted

$$R\dot{R} = \alpha \exp(-\beta R t) \qquad (1)$$

where R is the zone radius. $\dot{R}$ is the time derivative, and

$$\alpha = vD_c N_c^0 \text{ (a)} \qquad \beta = 3D_c/L^3 \text{ (b)} \qquad (2)$$

In these expressions v is the solute atom volume, D_c the diffusion coefficient for complexes, and N_c^0 is the number of complexes per unit volume immediately after quenching; L is half the mean distance between zones in the alloy.

The development of the vacancy pump model involves some assumptions about the alloy structure during GP zone growth. Girifalco and Herman[4] have proposed their model for the early formation stages, when there are supposed to be very few zones, separated by a mean distance much greater than their radius. Based on this assumption, GH[4] have considered this distance as being constant during the aging process, a simplification which enabled them to further the mathematical treatment of the model.

Now, these assumptions are not in agreement with the latest interpretations obtained by the X-ray Small Angle Scattering (SAS) method, which has provided the greatest part of the information so far available about the GP zones structure. Recently Bonfiglioli and Guinier[5] have interpreted their results on Al–Zn alloys by assuming that some zones grow at the expense of others from the very beginning of the segregation. In these first stages there are more zones and they are closer together than later in the process. The

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zone radius, on the other hand, is not negligible with respect to the mean separation of the zones, which varies during aging time in a similar way to the zone radius.

However, taking into account the uncertainties in the interpretation of X-ray data, the aforementioned facts cannot be considered to invalidate the pump model. And, on the other hand, X-ray SAS is the most direct method for the experimental determination of zone radius as a function of aging time, i.e. verification of the predicted growth law. We attempt to do this verification, and for this purpose we have chosen the Al–10% Zn alloy. It has a simple structure, and can be retained by quench in an homogeneous state, a fact which enables us to observe the early stages of the GP zones growth process.[5] Simultaneously, and as a comparison, we propose to study also the Al–10% Zn–0.1% Mg system. It presents similar structure to the binary alloy, but there are appreciable changes in the kinetics.[6] For both alloys there are available resistometric results[2][7][8] which would allow an interesting comparison with X-ray data.

2. EXPERIMENTAL PART

The alloys were prepared in the way already described.[6] Impurities of Fe, Ca and Cu have been looked for by conventional chemical methods without being detected. The specimens, 0.1 mm thick foils, have been finally homogenized at 300°C and quenched into a mixture of solid CO_2 and chloroform at −65°C, and immediately transferred and stored in liquid nitrogen.

The SAS measurements were carried out using a system described elsewhere[9,10] in which the specimen can be put in place and removed under liquid nitrogen, without being heated at any moment. The specimen temperature during the experiments was always kept at about −150°C. The scattering curves were measured immediately after quench ($t = 0$) and then after successive aging treatments in a thermostated ethyl alcohol bath. Three different aging temperatures were chosen, −50, −20 and 20°C (±1°C). From the experimental curves the zones radii have been calculated by the well known method of Guinier.[11]

3. RESULTS

The experimental results are summarized in Table 1, while the variation of GP zones radii with aging time, at different temperatures, is shown in Fig. 1. From these curves $\dot{R}$ has been calculated graphically, and the graphs of Fig. 2 were constructed.

It is important to note that in the early stages the experimental error is very great. Not considering the systematic errors proper in the method of measuring zones radii[11] the most important uncertainties

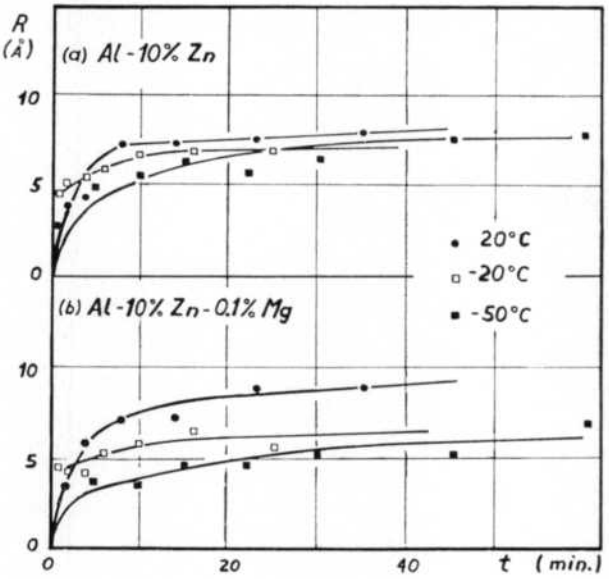

FIG. 1.

TABLE 1

Alloy	T(°C)		R(Å) vs. t(min)								
Al–10% Zn	−50	t	0	5	10	15	22	30	45	60	90
		R	0	5.0	5.6	6.4	5.7	6.6	7.7	7.9	7.3
	−20	t	0	1	2	4	6	10	16	25	—
		R	0	4.7	5.2	5.5	5.9	6.8	7.0	7.0	—
	20	t	0	1	2	4	8	14	23	35	—
		R	0	3.0	4.0	4.4	7.4	7.4	7.6	8.0	—
Al–10% Zn–0.1% Mg	−50	t	0	5	10	15	22	30	45	60	90
		R	0	3.8	3.6	4.7	4.7	5.2	5.2	7.0	6.7
	−20	t	0	1	2	4	6	10	16	25	—
		R	0	4.6	4.4	4.3	5.4	5.9	6.6	5.7	—
	20	t	0	1	2	4	8	14	23	35	—
		R	0	0	3.6	5.9	7.2	7.4	8.9	8.9	—

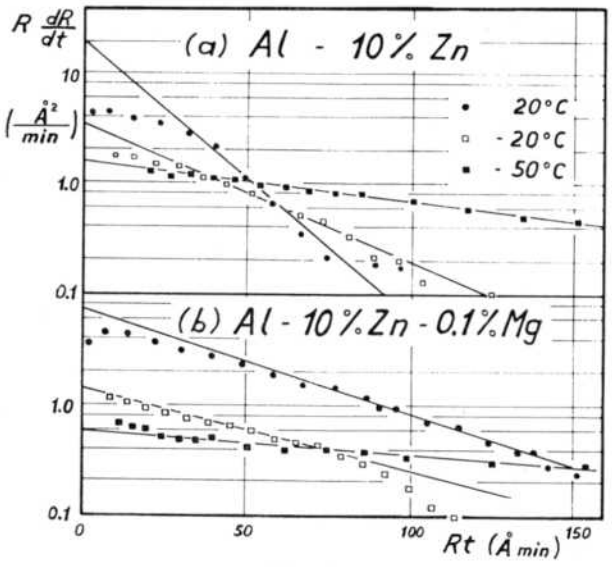

FIG. 2.

arise from the determination of the weak scattered intensities, and the error in the aging times. At the beginning of GP zones formation, the scattered intensity due to the zones is the same order of magnitude as the parasitic air scattering[5,6] and cannot be determined to better than 10 or 20%. Aging times can be measured within ± 1 sec; however, the specimen transfer from the liquid nitrogen storage to the thermostated bath takes some interval of time. Even if it is short it could be significant, mainly for the highest aging temperatures. It must also be taken into account that for heterogeneities smaller than 10 Å the SAS method is just at the limit of its possibilities. However, it is clear that the GP zones radii increase rapidly during the first minutes of aging, and reach a steady state after about 30 min.

Within experimental errors, it is also possible to say that in Fig. 2 straight lines are obtained when plotting the quantities stated by equation (1). Departures from straight lines are more remarkable for the binary alloy at 20°C. This is precisely the case in which the process is fastest, and consequently it is expected that the error in the determination of aging times is more important.

From the log $R\dot{R}$ vs. Rt plot, the slope β and the value at origin α have been calculated. The parameter β obtained using an integrated form of equation (1) given by Kahn and Girifalco[12] shows the error introduced in the graphical derivatives of the growth curves, Fig. 1, does not change the order of magnitude of β. The values of α and β directly obtained from Fig. 2 are summarized in Table 2.

4. INTERPRETATION OF RESULTS

The result which appears most directly from our experiments is that the form of the kinetic law for the

TABLE 2

Alloy	T(°C)	$\alpha \cdot 10^{18}$ cm^2 sec^{-1}	$\beta \cdot 10^{-4}$ (cm sec)$^{-1}$
Al–10% Zn	−50	2.6	1.3
	−20	5.6	4.7
	20	33.0	9.5
Al–10% Zn 0.1% Mg	−50	0.97	0.83
	−20	2.5	2.9
	20	12.00	3.6

alloys Al–10% Zn and Al–10% Zn–0.1% Mg is in agreement with the predicted by GH.[4] However, many phenomena could lead to variations of parameters similar to those observed in Fig. 1, and then fit the growth law.[1] It is only the analysis of the quantities α and β, and therefore the physical parameters D_c and N_c^0, which can give a reliable basis to test the validity of the pump model.

Qualitatively, the measured values of α and β vary with aging temperatures as predicted by equation (2). In Table 2 it can be seen that they increase systematically with temperature (for any given alloy and a fixed quenching temperature, N_c^0 has always the same value; assuming that there are no appreciable changes in L, the variation of α and β is due only to D_c which increases with aging temperature). It would have been interesting to do some experiments at fixed aging temperature, and vary the quenching temperature. But the range of possible quenching temperatures is actually limited: at high temperatures formation of vacancy clusters is expected; at lower quenching temperatures the measurements would not be accurate due to the slow rate of the process, and the weak scattered intensities. However, some observations, not detailed here,[13] were made on two Al–10% Zn specimens solution treated at 300 and 400°C, respectively, and quenched in water at 0°C. The subsequent aging at 20°C led to coincident values of β, while the parameter α corresponding to the quench from 400°C was about 30% higher than that corresponding to the quench from 300°C. This supplementary result is also in agreement with the predictions of equation (2a): the quenching temperature affects mainly the parameter N_c^0, which increases with this temperature.

For a more quantitative treatment, the numerical values of D_c and N_c^0 have to be calculated. We shall consider the simplest case of the binary alloy. In this case D_c can be calculated from the expression given by GH[4] and using 0.43 eV as the activation energy for complex diffusion (this is the value obtained by Panseri and Federighi[2] for the migration energy of Zn atoms towards GP zones). At the same time D_c can be calculated from the measured values of β using equation (2b). This was done assuming different values

TABLE 3

Aging temperature (°C)	D_c(cm² sec⁻¹) Calculated taking 0.43 eV as the value for the activation energy	D_c(cm² sec⁻¹) Calculated by formula (2b)
−50	10^{-12}	10^{-15}
−20	10^{-11}	10^{-14}
20	10^{-10}	10^{-14}

of L between 10 and 100 Å. It is not possible to take as a fixed value for L any of the figures given by Bonfiglioli and Guinier.[5] The structure model proposed by these authors is in contradiction with the simplified model assumed by GH. The comparison between the values of D_c obtained from our measurements using equation 2b with $L = 100$ Å, and the values calculated from the activation energy data, is shown in Table 3 for the three aging temperatures used in our experiments. It must be remarked that the value of L used is very large, considering the experimental data available (in fact L is always $\approx 3R$). Even in this particularly favourable case, the experimental values of D_c obtained using the kinetic law of GH,[4] are several orders of magnitude higher than the calculated using the activation energy data. Recently Girifalco, Herman and Kahn[14] have proposed $D_c \approx 10^{-14}$ cm²/sec, a value which is in agreement with our results. However, this would mean an activation energy for complex diffusion of about 0.70 eV. To the authors knowledge there is no experimental evidence of such a high value. Compared with the migration energy for vacancies in pure aluminium[15] a simple vacancy mechanism would in this case be energetically more favourable than the proposed mechanism.

Panseri and Federighi[2] and Perry[8] have measured independently the formation energies of vacancies in an Al–10 % Zn alloy, and have obtained the same value: 0.70 eV. Therefore, the vacancy atomic fraction C_v at the quenching temperature (300°C) is about 10^{-6}. This is the maximum possible value for the initial atomic fraction of complexes $C_c^0 (C_c^0 = N_c^0/6 \times 10^{22})$. However, the values obtained from our experiments and for different values of L, are much higher than 10^{-6}. Without considering values clearly meaningless ($C_c^0 = 1, 0.1, \ldots$) and for the most favourable case $L = 100$ Å, one finds $C_c^0 = 10^{-4}$ (Girifalco, Herman and Kahn propose $C_c^0 = 5 \times 10^{-4}$). In this case the energy of formation of vacancies would be 0.40 eV. As for pure aluminium this energy is 0.76 eV (16), then it should be admitted that the binding energy between a vacancy and a Zn atom is 0.36 eV. However, the highest value for this energy, measured by Takamura[17] on very dilute alloys, is 0.19 eV.

It can be seen that the vacancy pump model as it was developed by GH[4] leads us to contradictions with activation energy as well as X-ray data. Nevertheless, the idea of a cyclic pump mechanism is not unbelievable. The arguments on which GH[4] based their scheme (long vacancy life in the alloy matrix, great number of solute atoms transported by each vacancy) are in agreement with experimental facts. Instead, the hypothesis made in order to get a convenient mathematical description seem to be over-simplifying, in particular as far as structure is concerned. Restricting ourselves only to the structure, we can say the experimental data available indicate the interzone distances are not so large as to let us consider each zone to be independent. As a matter of fact, there is always a considerable size and interzone distance distribution in the solid solution. On the other hand, in the early stages of aging GP zones are likely concentration fluctuations, not very marked (as the weak scattered intensities observed show). Then, they cannot be considered as regions separated by sharp interfaces from the matrix as GH[4] did.

Taking all these facts into account it would be very difficult to develop an analytic expression suitable for experimental verification. The present approximation of the vacancy pump model can be considered as a very important step towards further developments. A positive fact is that the quantities α and β vary with aging and quenching temperature in the way predicted by equation (2). There seem to be a direct relationship between α and β and the physical quantities D_c and N_c^0, although the actual equations relating them would no longer be given by equations (2a) and (2b).

As far as the ternary alloy Al–10 % Zn–0.1 % Mg is concerned, the law predicted by the vacancy pump model is as well satisfied in this case. The values of α and β are the same order of magnitude as in the previous case, although they are greater by a factor of about two. Recent X-ray measurements have shown that the total number of solute atoms transferred to the zones, as well as the length of the process, are even larger for this ternary alloy.[6] A cyclic pump mechanism such as the proposed by GH[4] could also be valid in this case. If the role of the Mg atoms is limited to trapping vacancies in order to release them afterwards, as Perry,[8] and Gerold and Gould[18] suggested, then the pumping would occur in a way similar to the binary alloy. If, on the contrary, the Mg atoms are active agents in the diffusion process, as Panseri and Federighi proposed, then a GH mechanism would be improbable. The existent data are more in agreement with the former ideas. However, our present measurements are not conclusive on this subject.

5. CONCLUSIONS

Although the X-ray Small Angle Scattering results are not accurate during the early stages of formation of GP zones in Al–Zn alloys, this method provides the most direct way of obtaining the GP zones radii growth law with aging time. without too many arbitrary assumptions. In spite of the experimental uncertainties, the values obtained for these parameters are in agreement with those predicted by the authors of the model. However, they cannot be justified, even in the most favourable case, by the existent activation energy data. The idea of a cyclic pump mechanism for the transfer of solute atoms from the matrix to the zones seems to be feasible. But the further treatment of this idea contains many assumptions which lead to an oversimplified image of the solid solution behavior.

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