

The effect of a.c. frequency on precipitation in Al-5.6 at % Zn

Y. ONODERA, K. HIRANO

Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan

The effects of alternating electric current on the formation of GP zones at 30° C from a supersaturated Al-5.6 at % Zn have been examined. The frequency of the applied current has been varied from 0 to 3000 Hz. A retarding effect has been observed for the frequencies 0, 25 and 100 Hz, while no appreciable effect has been observed for 200 and 3000 Hz. The results have been discussed on the basis of a current-assisted vacancy annihilation model in the presence of an alternating electric current.

1. Introduction

In connection with electromigration in metals and alloys, it is interesting to investigate the effect of the electric current stress on the precipitation reaction in alloys.

Erdmann-Jesnizer *et al.* [1] have shown that an alternating current of 1115 A cm⁻² at 50 Hz completely inhibits the precipitation of the solute carbon from a supersaturated Fe-0.04 wt % C alloy. Further, Koppenaal and Simcoe [2] have investigated the effect of the current stress on precipitation in an Al-4 wt % Cu and found that the precipitation rate at 80° C is accelerated by the d.c. stress (1000 to 3000 A cm⁻²), but retarded by the a.c. stress of 25 Hz, although its current density is fairly small (≈ 400 A cm⁻²) compared with the d.c. stress. On the other hand, no effect has been observed for an a.c. stress of 100 Hz (≈ 400 A cm⁻²). Following these observations, the authors have continued to investigate the phenomena from various aspects and also examined the reproducibility of the results. In previous studies by the present authors [3, 4], it was concluded that the acceleration by the d.c. stress of the precipitation process is due to the temperature increase caused by Joule heating, but the effect of the current *per se* is a retarding one. To explain this retarding effect, a mechanism has been proposed based upon the enhanced annihilation of the quenched-in excess vacancy by the flow of direct electric current. This mechanism is supported by the fact that the retardation of the formation of GP zones from supersaturated Al-5.6 at % Zn became more

marked as the concentration of the quenched-in excess vacancy increased [4]. Regarding the effect of the a.c. stress on precipitation, only a few experimental researches [1, 2] have been carried out and the mechanism involved is still unknown. In the present work, the effect of various a.c. frequencies on precipitation of the GP zones in an Al-5.6 at % Zn alloy has been investigated using a specimen of the same concentration as in [4], where the effect of the d.c. stress has been fully studied.

2. Experimental methods

Wires of an Al-5.6 at % Zn alloy, 0.4 mm in diameter and 5 cm in length, were prepared as described in [4]. The wire specimen was quenched into iced water after solution heat treatment at 450° C for 30 min. It was then aged under the influence of the a.c. current stress at 30 \pm 0.05° C in a large (50 l) water bath which was especially designed (Fig. 1) in order to eliminate the effect of Joule heating. The water was stirred by four mechanical stirrers and partly circulated at 200 cm sec⁻¹ in the immediate vicinity of the specimen by a water pump. Under these conditions, the temperature increase due to Joule heating was less than the experimental accuracy of the electrical resistance measurement at liquid nitrogen temperature, as described in a later section. The progress of the precipitation of the GP zones was followed by measuring the electrical resistance of the specimen at liquid nitrogen temperature. A reference wire was mounted on the same quartz

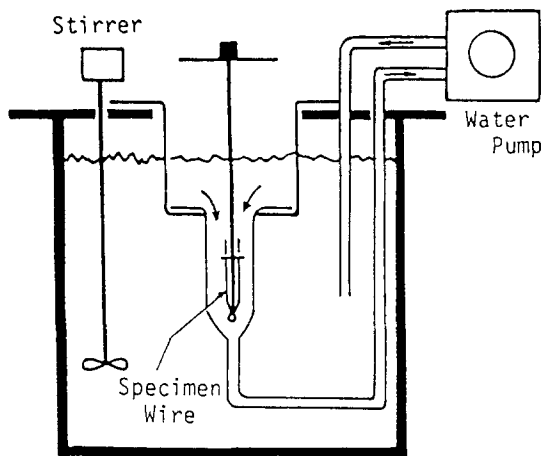


Figure 1 Schematic diagram of the water bath for ageing under the influence of current stress.

holder as the specimen wire. As a result, the reference was subjected to the same heat treatment as the specimen except that the specimen was stressed by the current. In order to examine the frequency dependence of the retarding effect, the fractional change $(\rho^J - \rho^0)/\rho^0$ was plotted against the current density J , where ρ^J is the specimen resistivity after ageing for 10 min at 30°C under the current stress, and ρ^0 is the reference resistivity after ageing for 10 min without the current stress (ordinary heat treatment). The slope of the straight line gives the retarding coefficient λ which was introduced in [4]. In the present work, the retarding coefficients were determined at five different frequencies including zero frequency.

After drawing specimens were initially stabilized for about one hour at 500°C in the single phase region in order to prevent recrystallization during such heat treatments as solution heat treatment, quenching and power ageing. This thermal cycle was repeated for each specimen used to determine a retarding coefficient λ at a given frequency.

3. Results

The experimental results for the determination of the retarding coefficients are shown in Figs. 2 to 6 for five different frequencies including zero frequency. For each experimental run, e.g., as shown in Fig. 2, the quenching temperature, ageing time and ageing temperature were fixed at 450°C , 10 min and 30°C , respectively. In the case of 0 and 25 Hz (Figs. 2 and 3), the retarding effect is clearly observed.

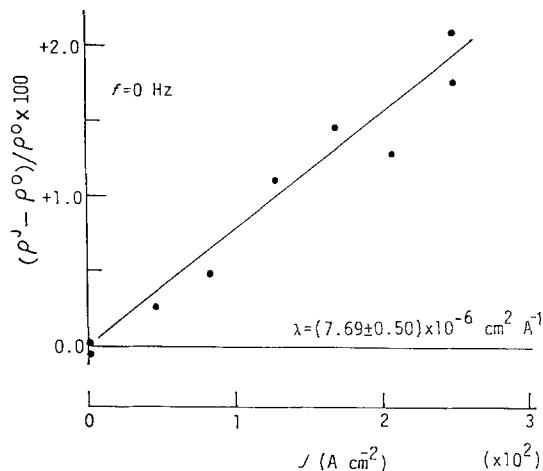


Figure 2 Effect of d.c. on the normalized fractional change in specimen resistivity.

The retarding coefficients for $f = 0$ and 25 Hz are $(7.7 \pm 0.5) \times 10^{-6} \text{ cm}^2 \text{ A}^{-1}$ and $(6.0 \pm 0.4) \times 10^{-6} \text{ cm}^2 \text{ A}^{-1}$, respectively. In Fig. 4, the experimental points are numbered in the order of measurement. Here the retarding effect is apparent at the initial stage of power ageing (1) and the value of $(\rho^J - \rho^0)/\rho^0$ increases in the sequence 3, 4, 5. However, it begins to decrease suddenly at 6 and finally approaches zero at 7, 8 and 9. At this frequency, λ is $(3.2 \pm 0.3) \times 10^{-6} \text{ cm}^2 \text{ A}^{-1}$ by using the values of the points 1 to 5. Although the retarding effect was not apparent at 200 Hz, as shown in Fig. 5, a small positive value of $\lambda = (0.2 \pm 0.4) \times 10^{-6} \text{ cm}^2 \text{ A}^{-1}$ was obtained from the statistical treatment of the experimental data. Fig. 6 shows the result for 3000 Hz; a negative

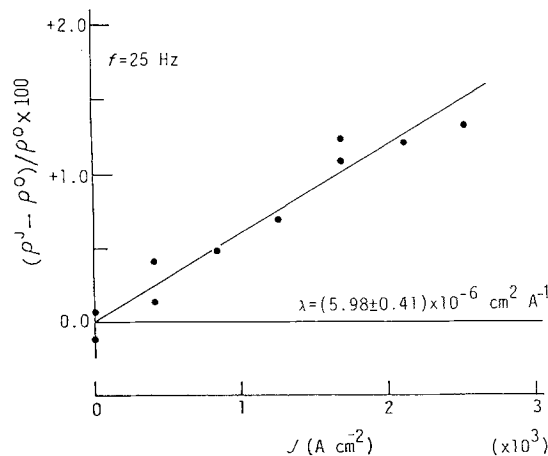


Figure 3 Effect of a.c. (25 Hz) on the normalized fractional change in specimen resistivity.

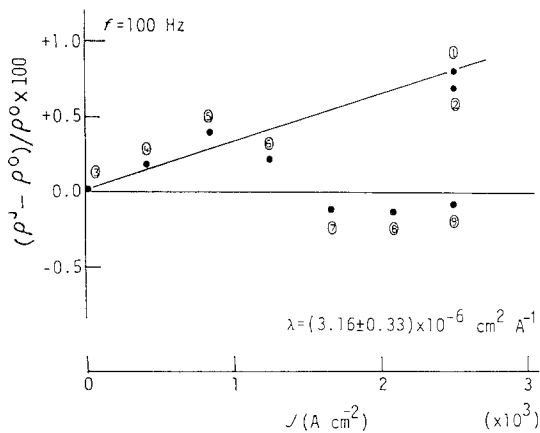


Figure 4 Effect of a.c. (100 Hz) on the normalized fractional change in specimen resistivity.

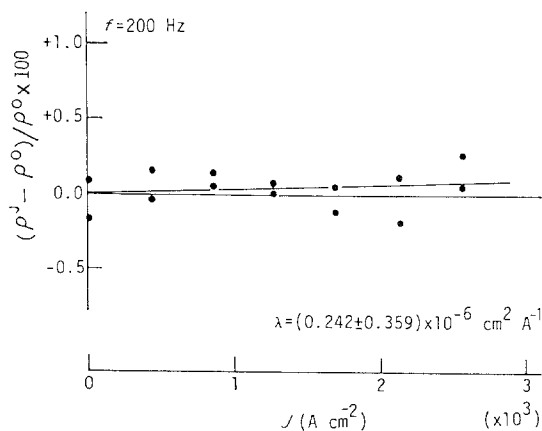


Figure 5 Effect of a.c. (200 Hz) on the normalized fractional change in specimen resistivity.

retarding coefficient was obtained, tentatively given as $(-1.2 \pm 0.3) \times 10^{-6} \text{ cm}^2 \text{ A}^{-1}$.

In Fig. 7, the three values of λ obtained above are plotted as a function of ωt , where ω is the angular frequency of the applied current and t the ageing time (600 sec).

4. Discussion

Let us examine the present experimental results with the model of the current-assisted vacancy annihilation proposed in our previous papers [3, 4], where the following three assumptions for the precipitation kinetics in the Al-5.6 at % Zn alloy were made:

1. The rate of the resistivity change in the specimen at liquid nitrogen temperature is proportional to the change in the solute concentration c in the matrix ($d\rho/dt \propto dc/dt$).

2. The precipitation rate of the solute from the matrix is proportional to the quenched-in excess vacancy concentration N_v ($dc/dt \propto N_v$).

3. The quenched-in excess vacancies are annihilated at sinks according to the first-order reaction ($dN_v/dt \propto N_v$).

With Assumptions 2 and 3 the overall expression for the precipitation kinetics is given by

$$-d\rho/dt = KN_v, \quad (1)$$

where K is the positive constant for a given ageing temperature.

Equation 1 corresponds to Equation 4 in [3] and is rewritten in the presence of a sinusoidal external electric field of angular frequency ω and amplitude E_0 , $E = E_0 e^{i\omega t}$ as follows;

$$-d\rho^J/dt = KN_v^J(\omega, t), \quad (2)$$

where the superscript J denotes the quantity under the influence of the current stress. As given by Equation 6 in [3], the rate of decrease in the quenched-in excess vacancy concentration can be expressed by

$$-dN_v^J(\omega, t)/dt = \gamma^J(\omega, t)N_v^J(\omega, t), \quad (3)$$

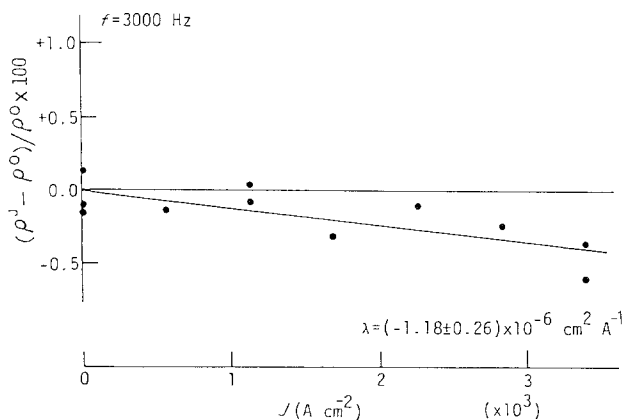


Figure 6 Effect of a.c. (3000 Hz) on the normalized fractional change in specimen resistivity.

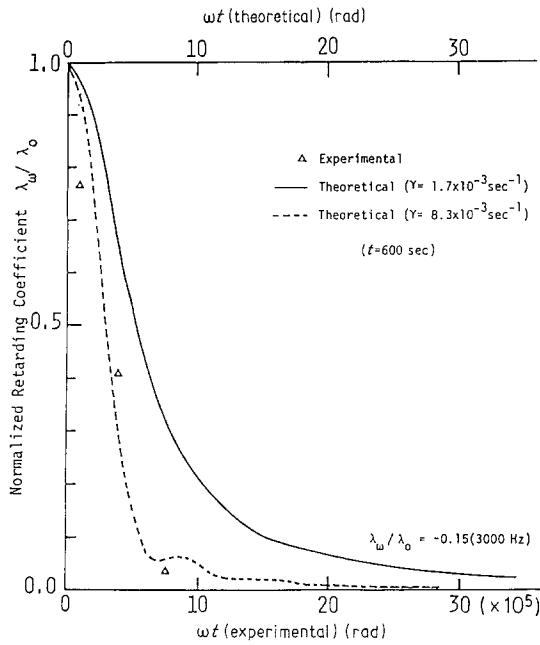


Figure 7 Theoretical and experimental curves of the normalized retarding coefficient plotted against applied current frequency.

where $\gamma^J(\omega, t)$ is the rare constant for the annihilation of the quenched-in excess vacancy concentration under the influence of the alternating electric field. As shown in the Appendix, the solution of Equation 3 is given by

$$N_v^J(\omega, t) = N_v(0)e^{-\gamma t}(1 - \delta\gamma t \sin \omega t / \omega t), \quad (4)$$

where $N_v(0)$ is the initial excess vacancy concentration ($t = 0$) and γ is the rate constant in the absence of the current stress ($E \propto J = 0$). The quantity δ is related to the external electric field strength E_0 by the relation $\delta = D_v |eZ^*| E_0 / (\gamma dkT)$, where D_v is the diffusion coefficient of the excess vacancies, d the mean distance between sinks, and e, k, T have their usual meanings. From Equations 2 and 4, we have

$$-d\rho^J/dt = KN_v(0)e^{-\gamma t}(1 - \delta\gamma t \sin \omega t / \omega t). \quad (5)$$

Integrating Equation 5 under the initial condition $\rho^J = \rho(0)$, we obtain

$$\rho(0) - \rho^J = KN_v(0) \left\{ \frac{1}{\gamma} (e^{-\gamma t} - 1) - \frac{\delta\gamma}{(\gamma^2 + \omega^2)} \times \left[1 - e^{-\gamma t} \left(\frac{\gamma}{\omega} \sin \omega t + \cos \omega t \right) \right] \right\}. \quad (6)$$

The solution for ordinary precipitation under the usual heat treatment in the furnace is obtained by putting $\delta = 0$ in Equation 6 as

$$\rho(0) - \rho^0 = \frac{KN_v(0)}{\gamma} (e^{-\gamma t} - 1). \quad (7)$$

Then, from Equations 6 and 7 we have

$$\rho^J - \rho^0 = \frac{KN_v(0)\delta\gamma}{(\gamma^2 + \omega^2)} \times \left[1 - e^{-\gamma t} \left(\frac{\gamma}{\omega} \sin \omega t + \cos \omega t \right) \right]. \quad (8)$$

If ωt tends to zero, Equation 8 becomes

$$\rho^J - \rho^0 = \frac{KN_v(0)\delta}{\gamma} (1 - e^{-\gamma t} - \gamma t e^{-\gamma t}). \quad (9)$$

Equation 9 is in reasonable agreement with Equation 10 in [3] where the case $\omega = 0$ (d.c.) was considered.

As defined in [4], the retarding coefficient λ is given by $(\rho^J - \rho^0)/(\rho^0 J)$. Then, according to Equations 8 and 9 the ratio of the frequency dependent retarding coefficient λ_ω to the retarding coefficient λ_0 at $\omega = 0$ can be expressed as

$$\frac{\lambda_\omega}{\lambda_0} = \frac{\gamma^2}{(1 - e^{-\gamma t} - \gamma t e^{-\gamma t})} \times \left[1 - e^{-\gamma t} \left(\frac{\gamma}{\omega} \sin \omega t + \cos \omega t \right) \right]. \quad (10)$$

We can easily estimate the value of λ_ω/λ_0 as a function of the current frequency by substituting γ and t for appropriate numerical values. In Fig. 7, the solid curves show the theoretical results calculated from Equation 10 for the ageing time $t = 600$ sec and the rate constant $\gamma = 8.3 \times 10^{-3}$ and $1.7 \times 10^{-3} \text{ sec}^{-1}$. The value of $\gamma = 8.3 \times 10^{-3} \text{ sec}^{-1}$ is estimated so as to fit the time dependence of the retarding coefficient given in Fig. 6 in [4], while $\gamma = 1.7 \times 10^{-3} \text{ sec}^{-1}$ is determined from the precipitation rate at 30°C by assuming that the reaction proceeds as a first-order one until 600 sec after quenching. In the same figure the experimental values of λ_ω/λ_0 are also presented for 25, 100, 200 Hz ($\omega t = 9.4 \times 10^4, 3.8 \times 10^5, 7.5 \times 10^5$). Here let us term the range of ωt corresponding to the change in λ_ω/λ_0 from 0.77 to 0.05 as the "threshold frequency range". The theoretical values of the threshold frequency range is 3 to 30 and 2 to 10 for $\gamma = 1.7 \times 10^{-3}$ and $8.3 \times 10^{-3} \text{ sec}^{-1}$,

respectively. On the other hand, the experimental value of the threshold frequency is $(1 \text{ to } 8) \times 10^5$.

The present experimental results for the retarding effect agrees qualitatively with the theory with respect to the fact that the retarding effect decreases abruptly with increasing frequency in a specific range of ωt , at most between 1 and 10. However, there exists a large discrepancy of the order of 10^5 between the theoretical and the experimental threshold frequency range. This inconsistency may be partly due to the implicit assumption that the mean sink distance d for the excess vacancy is independent of the frequency of the applied current which was employed in the derivation of Equation 10. Furthermore, there are some problems related to the assumptions made in [3]: (i) the same proportional constant in such rate equations as $d\rho^J/dt = KN_v^J$, $d\rho^0/dt = KN_v^0$ was used; (ii) the possibility of the space dependence of the excess vacancy concentration and of the specimen temperature caused by the current stress were neglected.

Finally we refer to the result for 3000 Hz shown in Fig. 6. The negative retarding coefficient cannot be explained in terms of Joule heating because the region of heat evolution caused by the current stress moves to the surface of the specimen wire with increasing current frequency and thus favours greatest heat dissipation.

5. Conclusions

The experimental results by Koppenaal and Simcoe [2] have been confirmed qualitatively by the present work. However, the frequency dependence of the retarding coefficient observed in the present work remains unexplained quantitatively on the basis of the model of the current-assisted vacancy annihilation proposed in our previous work.

Appendix

The rate constant $\gamma^J(\omega, t)$ in Equation 3 of Section 4 can be expressed as

$$\gamma^J(\omega, t) = \gamma \left(1 + \frac{D_v |eZ^*| E_0 e^{i\omega t}}{\gamma dkT} \right). \quad (\text{A1})$$

Integrating Equation 3 and putting $D_v |eZ^*| E_0 / (\gamma dkT) = \delta$,

$$- \int_0^t \frac{dN_v^J(\omega, t)}{N_v^J(\omega, t)} = \int_0^t \gamma (1 + \delta e^{i\omega t}) dt. \quad (\text{A2})$$

Then, we find

$$N_v^J(\omega, t) = N_v(0) \times \exp \left[-\gamma t \left(1 - \frac{\delta}{i\omega t} + \frac{\delta}{i\omega t} e^{i\omega t} \right) \right], \quad (\text{A3})$$

where $N_v(0)$ is the initial excess vacancy concentration.

Approximating the exponential term of the right-hand side of Equation A3 to the first order of δ , we have

$$\begin{aligned} & \left[\exp \left(1 - \frac{\delta}{i\omega t} + \frac{\delta}{i\omega t} e^{i\omega t} \right) \right]^{-\gamma t} \\ &= e^{-\gamma t} \left(1 - \frac{\delta}{i\omega t} + \frac{\delta}{i\omega t} e^{-i\omega t} \right)^{-\gamma t}. \end{aligned} \quad (\text{A4})$$

Again, the right-hand side of Equation A4 can be approximated to the first order of δ in the following way,

$$\begin{aligned} & e^{-\gamma t} \left(1 - \frac{\delta}{i\omega t} + \frac{\delta}{i\omega t} e^{-i\omega t} \right)^{-\gamma t} \\ &= e^{-\gamma t} \left[1 + \gamma t \left(\frac{\delta}{i\omega t} - \frac{\delta}{i\omega t} e^{i\omega t} \right) \right]. \end{aligned} \quad (\text{A5})$$

Then, Equation A3 can be written as

$$\begin{aligned} N_v^J(\omega, t) &= N_v(0) e^{-\gamma t} \\ &\times \left[1 + \gamma t \left(\frac{\delta}{i\omega t} - \frac{\delta}{i\omega t} e^{i\omega t} \right) \right]. \end{aligned} \quad (\text{A6})$$

The real part of Equation A6 is represented by

$$N_v^J(\omega, t) = N_v(0) e^{-\gamma t} \left(1 - \frac{\gamma}{\omega} \sin \omega t \right). \quad (\text{A7})$$

Equation A7 is the final expression for the time dependence of N_v^J in the presence of a sinusoidal external electric field of the angular frequency ω .

References

1. F. ERDMANN-JESNITZER, D. MROWKA and K. OUVRIER, *Arch. Eisenhüttenw.* **30** (1959) 31.
2. T. J. KOPPENAAAL and C. R. SIMCOE, *Trans. Met. Soc. AIME* **227** (1963) 615.
3. Y. ONODERA and K. HIRANO, *J. Mater. Sci.* **11** (1976) 809.
4. *Idem, ibid.* **12** (1977) 1109.

Received 10 November 1983
and accepted 24 January 1984