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The effect of direct electric current on precipitation in a bulk Al-4 wt % Cu alloy

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The effect of the stress of direct electric current on precipitation in a quenched Al–4.15 wt % Cu alloy is investigated by measurement of the change in electrical resistance of a bulk specimen as a function of current density up to about 3000 A cm^{-2} at a given annealing time. A similar effect of d.c. stress is observed at 50, 75 and 100° C. For a lower current density, a constant or slightly increasing resistance is observed, while for a current density higher than a critical value, the resistance decreases with an increase in density. On the assumption that the temperature increase of a specimen due to the Joule heating is proportional to the square of the current density, it is concluded that there exists some effect of d.c. stress *per se* to prevent the precipitation reaction, aside from the effect of the temperature increase due to the Joule heating, and it is suggested that this retarding effect is related to the sweeping out of quenched-in excess vacancies into grain boundaries by electromigration.

1. Introduction

In 1959, Erdmann–Jesnitzer *et al.* [1] reported for the first time that a direct electric current (d.c.) passing through a quenched Fe–C alloy during ageing at 80.6° C accelerated the ageing reaction rate, and that an alternating current (a.c.) of 50 Hz completely inhibited the progress of the ageing reaction. In the case of a direct current, they attributed such an increased reaction rate to the enhancement of diffusion of dissolved carbon ions by the d.c. stress. However, no satisfactory explanation has been given for both the d.c. and the a.c. stress.

Qualitatively almost similar results were obtained on quench ageing in an Al–3.98 wt % Cu alloy by Koppenaal and Simcoe [2] (abbreviated as K–S). They concluded that a d.c. stress accelerated the precipitation reaction, an a.c. stress of 25 Hz reduced it by a factor of two, and that of 100 Hz did not produce any noticeable effect.

Independent of these investigations of bulk materials, there are several experimental studies of the effect of d.c. stress on precipitation in Al–Cu thin films [3–9]. The purpose was to explore ways of prolonging the lifetime of conductors used as interconnnectors in integrated circuits. Of these studies, the investigation by Shine and Herd [7] dealt with the effect of d.c. stress on precipitation in a quenched Al–Cu thin fim. They examined the effect of d.c. stress of high current densities of the order of 10^6 A cm^{-2} on isothermal precipitation reactions in an Al–4.5 wt % Cu thin film, and found that the d.c. stress prevented the precipitation reaction. The situation seems very different between thin films and bulk materials. At present, however, it is necessary to accumulate well established experimental results under various conditions, rather than to discuss details of the origin of the different behaviour between bulk materials and thin films on the basis of insufficient data. Hence, the main purpose of the present work is to confirm the accelerating effect of d.c. stress *per se* on the precipitation reaction of the GP(1) zone suggested by K–S. Especially in the case of bulk materials, the most important point is how to distinguish the contribution of the effect of d.c. stress *per se* and of the additional temperature increase caused by the Joule heating from an observed total effect of d.c. stress. For this purpose, the resistance change in bulk specimens of Al–4.15 wt % Cu with current density has been measured after power annealing at a given temperature for 10 min. This method allows clarification of Joule heating more easily than that employed by K–S, in which the effect of d.c. stress on isothermal annealing curves was examined.

2. Experimental procedures

The specimens of an Al–4.15 wt % Cu alloy were obtained in the form of ingot bars from Sumitomo Light Metal Corporation Ltd. The main impurities in the specimen were 0.003 wt % Fe and 0.002 wt % Si. The ingot bar was cold-swaged and drawn into wires of 0.04 and 0.02 cm diameter, which were used as specimens and potential lead wires, respectively. Two specimens were arranged on a quartz holder as illustrated in Fig. 1. These specimens were subjected to the same heat-treatments; one was stressed with d.c., and the other was used as a reference without d.c., during annealing. The same piece of the specimen wire was used as current leads to avoid any trouble associated with the concentration change at the contact parts between the specimen and the current leads. Two potential lead wires were attached to the specimen at a separation of about 5 cm by spot-welding. For homogenization, the specimen was heat-treated in air at 539° C for a few days. The specimen was quenched into iced water from 539° C and immediately immersed into liquid nitrogen. The total time required for this manipulation was less than 7 sec. A rapidly stirred silicone oil bath was used for power annealing after quenching. The temperature of the bath was controlled to within ±0.5° C. Current densities during power annealing were varied up to about 3000 A cm^{-2}. The electrical resistance of the specimen was measured, unless otherwise stated, at liquid nitrogen temperature throughout the present experiments by the usual d.c. potentiometric method.

Since it is very difficult to estimate actual temperatures of the specimen during power annealing in the present experiment, the temperature of the oil bath was regarded as actual temperatures of the specimen. However, there is a possibility that the temperature thus determined might not be accurate enough because of the Joule heating caused by d.c. stress. To make a rough examination of the temperature increase due to the Joule heating, a chromel-alumel thermocouple of 0.01 cm diameter was then spot-welded on to a specimen and its temperature was measured in the oil bath as a function of current density under experimental conditions which, as near as possible, were the same as those during actual power annealing.

3. Experimental results

An isochronal annealing curve of an Al–4.15 wt % Cu for 10 min without d.c. stress was measured in the temperature region 50 to 200° C to examine the general behaviour of the resistance change versus annealing temperatures. It must be noted that the ischronal curve in the present work has a different meaning from the ordinary one in the study of precipitation processes; in the present work, after annealing for precipitation had been carried out for 10 min at a temperature between 50 and 200° C, the specimen was heated again at 539° C for 30 min for homogenization, quenched into iced water and then subjected to the subsequent annealing at another temperature. This treatment was repeated. The result obtained in this way is shown in Fig. 2, where the arrows indicate the temperatures at which power annealing was made. No conclusive result could be obtained at 160° C owing to the large scattering of measured values of the specimen resistance after power annealing. The amount of the scattering is ±0.7%. At 200° C, the

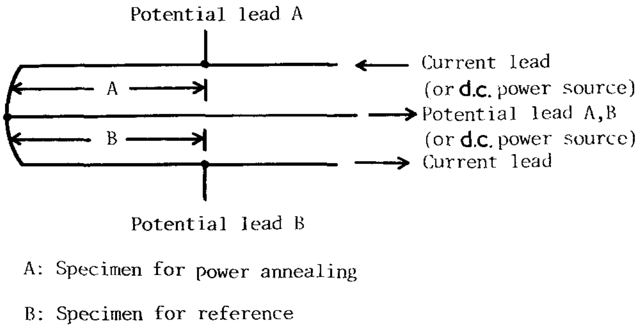

Figure 1 Schematic representation of the arrangement of a specimen for the measurement of electrical resistance.

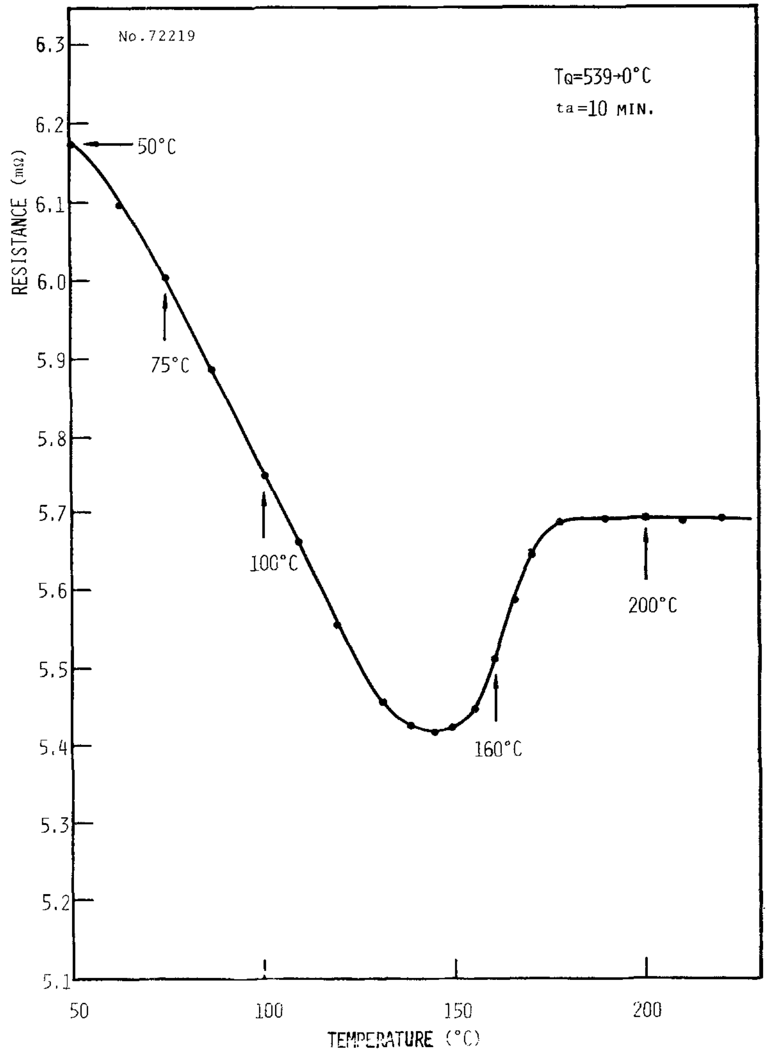

Figure 2 Isochronal annealing curve in an Al–4.15 wt%Cu alloy. Annealing time is 10 min for each annealing temperature.

effect of d.c. stress on the specimen resistance was not observed within experimental accuracy of 0.025%. Therefore, our representation will be restricted to the results of 50, 75 and 100° C. The results are shown in Figs. 3, 4 and 5. The fractional change in the resistance after power annealing $(R_J - R_0)/R_0$ is plotted as a function of current density, where R_J and R_0 are the resistances after annealing with and without d.c. stress, respectively. As shown in Fig. 3, the value of $(R_J - R_0)/R_0$ on lower currents have an almost constant or positively increasing trend with increasing current densities. After passing some critical value, they decrease and become negative with increasing current density. Practically the same tendency as at 50° C is observed at 75 and 100° C except that the constant or positively increasing trend for lower currents is not observed so clearly as at 50° C.

Fig. 6 shows a surface temperature increase, ΔT, measured directly using a thermocouple spot-welded on to a specimen, as a function of current density at various bath temperatures. In this figure, ΔT is plotted against the square of current density to confirm that this ΔT obeys the J^2 relationship. A linear relationship between ΔT and J^2 is obtained for all the bath temperatures of 72, 140 and 204° C. No difference in behaviour in the curves of ΔT versus J^2 was observed among the three bath temperatures. Therefore, it is very plausible that the Joule heating brings about a temperature

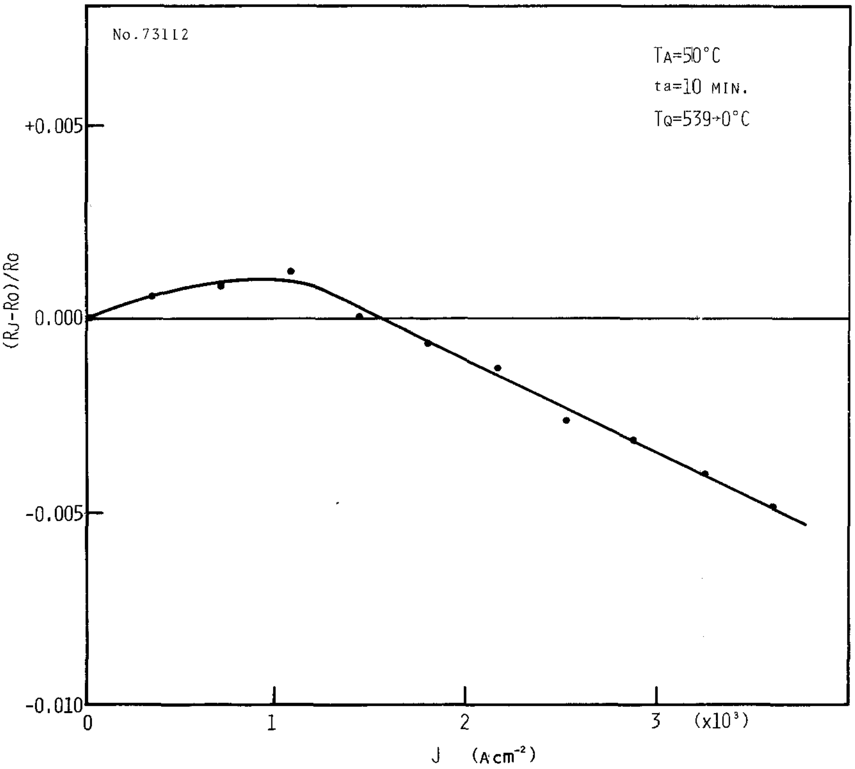

Figure 3 Fractional change in the resistance after power annealing at 50° C for 10 min as a function of current density.

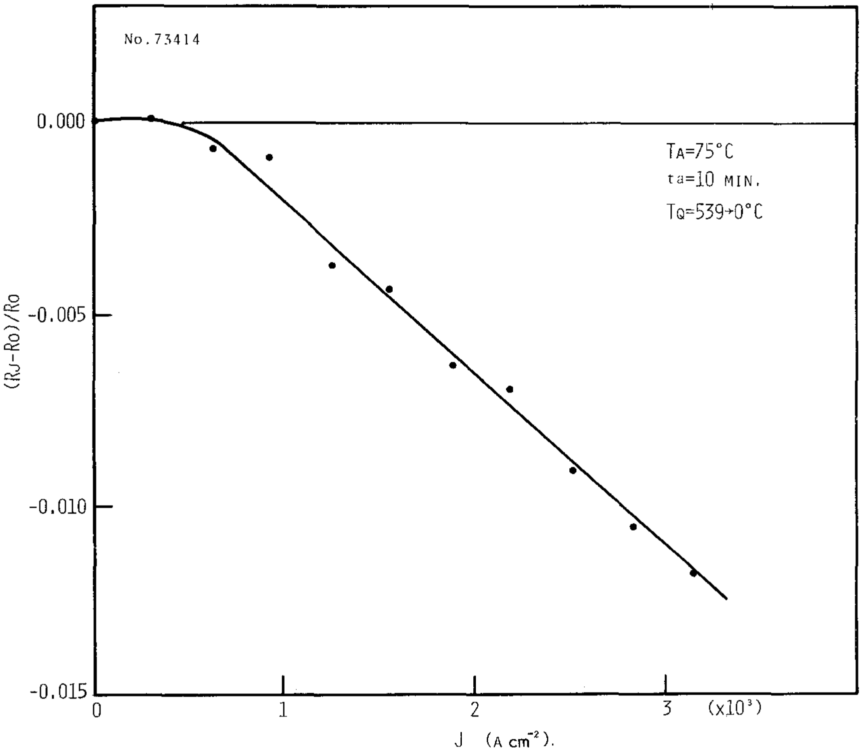

Figure 4 Fractional change in the resistance after power annealing at 75° C for 10 min as a function of current density.

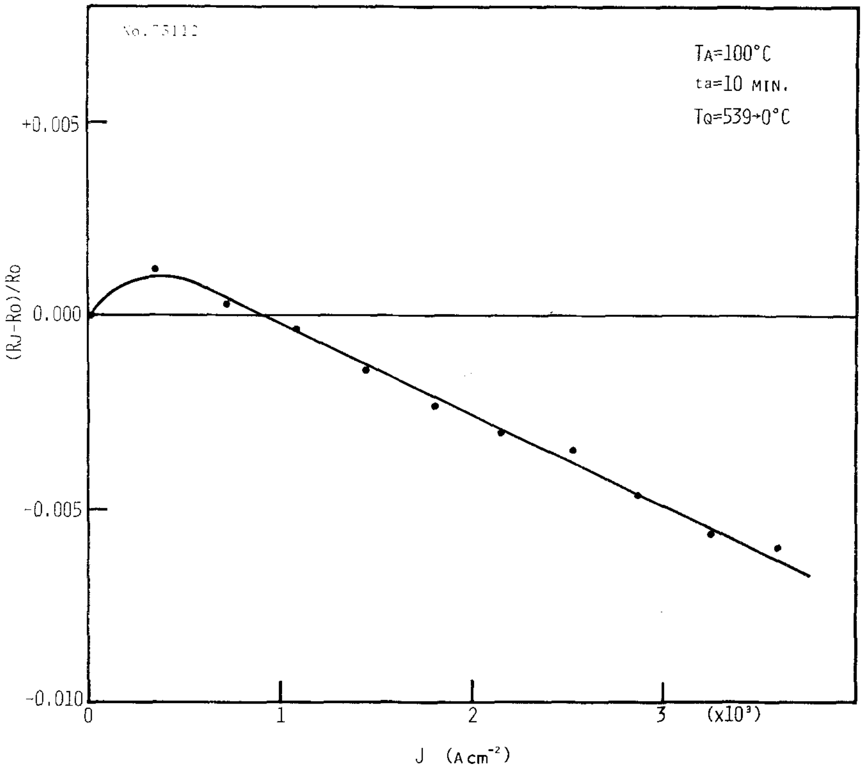

Figure 5 Fractional change in the resistance after power annealing at 100° C for 10 min as a function of current density.

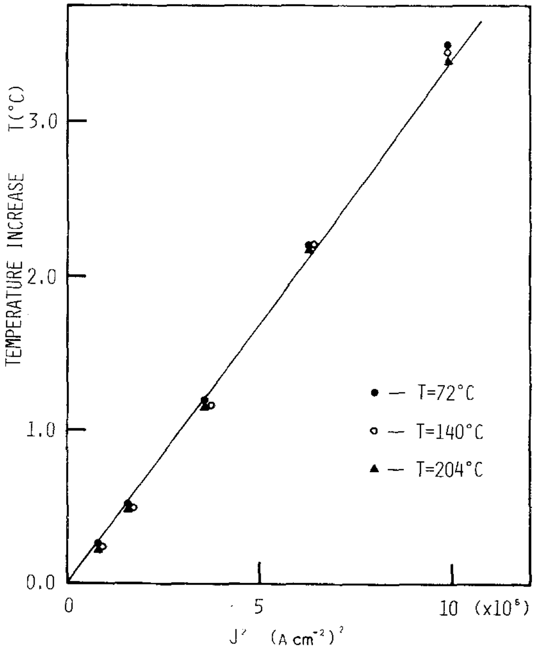

Figure 6 Surface temperature increase due to the Joule heating in a specimen as a function of current density at various bath temperatures.

increase in the specimen according to the relation $\Delta T \propto J^2$ at an arbitrary bath temperature employed in the present experiment.

Here let us estimate the difference between the temperature $T(R)$ on the surface and $T(0)$ in the centre of the wire specimen of radius R, electrical resistivity ρ, and of thermal conductivity κ, under the stress of a current density J, using the equation $T(0) - T(R) = \rho J^2 R^2/4\kappa$ [10]. Substituting 0.02 cm for R, 5×10^{-6} Ω.cm (at 100° C after quenching from 539 to 0° C) for ρ, 0.8 W cm^{-1}. deg^{-1} [11] for κ and 3×10^3 A cm^{-2} for J, we obtain $T(0) - T(R) \simeq 0.005°$ C. Thus the surface temperature can be identified as the bulk temperature of the specimen.

4. Discussion

The following three probable cases can be phenomenologically considered as the effect of d.c. stress on the precipitation reaction:

(1) it is due merely to the additional temperature increase in a specimen caused by Joule heating.

(2) it is due to a superposition of two different effects; the first is some retarding effect of d.c.

stress *per se* and the second, the temperature increase due to Joule heating.

(3) it is also due to a superposition of two different effects as in case 2; the first is some accelerating effect of d.c. stress *per se* and the second, the temperature increase due to Joule heating.

Since there is no evidence that in an Al–Cu alloy the atomic flux by electromigration shows a non-linear dependence on the electric current density J, it may be reasonable at this time to assume that the effect of d.c. stress *per se* is proportional to J as far as only the diffusion controlled precipitation reaction is taken into consideration. As a result, we expect that the $(R_J - R_0)/R_0$ versus J curve can have three features according to the following equations corresponding to the three cases described above in the temperature region from 50 to 140° C where the resistance in the isochronal annealing curve decreases approximately linearly with increasing annealing temperatures (Fig. 2);

$$(R_J - R_0)/R_0 = -\alpha J^2, \qquad (1)$$

$$(R_J - R_0)/R_0 = -\alpha J^2 + \beta J, \qquad (2)$$

$$(R_J - R_0)/R_0 = -\alpha J^2 - \beta J \qquad (3)$$

where α and β are positive constants. The three cases are schematically illustrated in Fig. 7. Of these three, case 2 appears to be consistent with the present experimental results for 50, 75 and 100° C. The J dependence of d.c. stress assumed above is tentative and more quantitive discussion based on a model will be given later.

Here let us briefly consider what factor determines the retarding effect of d.c. stress on the precipitation reaction. In connection with this, it should be noted that the change in the $(R_J - R_0)/R_0$ versus J curve, for example at 50° C, tends to diminish gradually by many repeated heat-treatments for homogenization, quenching and power annealing. In the resulting curve, there is no variation of the $(R_J - R_0)/R_0$ over a current range from 0 to 3000 A cm^{-2}, although this tendency was very small during one experimental run at a given annealing temperature. This fact strongly suggests that both effects of d.c. stress *per se* and of Joule heating are related to grain boundaries in the specimen, since the most noticeable structural change during the course of various heat-treatments may be grain growth. In the present experimental method, however, nondestructive measurement of the grain size was impossible at an arbitrary stage of heat-treatment, so that only the initial and final grain size were determined. The result shows that the inital mean grain size was 0.003 mm, and the final one, 1.06 mm. In the specimen after a series of the experiments had been performed, the "bamboo structure" was found. In addition, there is other indirect evidence which suggests local heating by d.c. stress at grain boundaries; local melting was observed in the specimen with the bamboo structure after about 20 sec when it had been stressed with a current density of 3000 A cm^{-2} at 539° C.

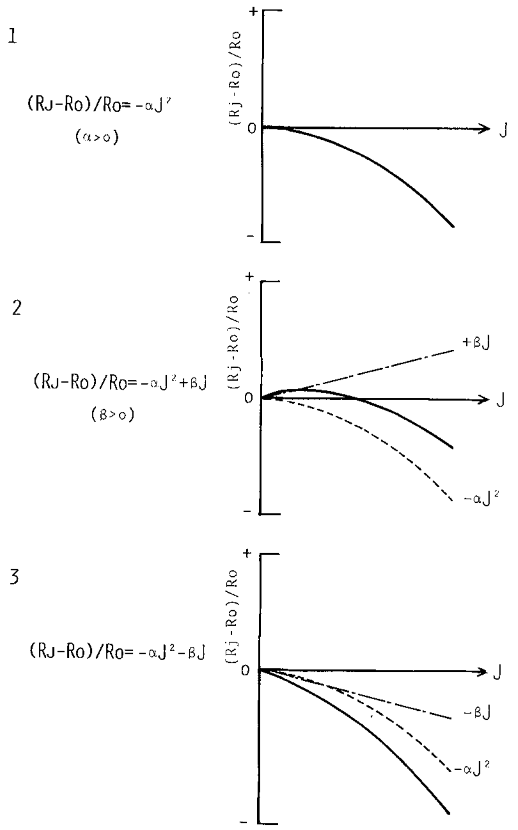

Figure 7 Schematic representation of the three possible behaviours of the $(R_J - R_0)/R_0$ versus J curve. Solid lines indicate the total effect.

Taking into account the results mentioned above, we therefore propose a model of "vacancy sweeping out" into grain boundaries by electromigration to interpret the retarding effect of d.c. stress *per se* on the precipitation reaction. Quenched-in excess vacancies are forced to migrate to permanent sinks, probably such as grain boundaries, by the applied electric current. Then, they annihilate there. The kinetic energy imparted by the applied current to metallic ions is so small compared with the vacancy formation energy, that the excess vacancies cannot be created again.

It is well known that the precipitation reaction mentioned here is that of the metastable GP(1) zone [12, 13] and that the reaction rate is governed by the concentration of the quenched-in vacancies as follows [14];

$$-\frac{d\rho^0}{dt} = KN_v^0 \tag{4}$$

$$-\frac{d\rho^J}{dt} = KN_v^J, \tag{4a}$$

where $d\rho/dt$ is the rate of the resistivity change during the progress of the precipitation reaction, N_v the quenched-in excess vacancy concentration, K is assumed to be constant for a given annealing temperature and positive for the stage where the resistivity decreases with the progress of the precipitation reaction. The superscripts 0 and J denote quantities during ordinary and power annealing, respectively. Furthermore, the disappearing rate of the excess vacancies at permanent sinks may be expressed as

$$-\frac{dN_v^0}{dt} = \gamma N_v^0, \tag{5}$$

$$-\frac{dN_v^J}{dt} = \gamma N_v^J + \frac{J_v}{d}, \tag{5a}$$

where γ is the constant, J_v the vacancy flux caused by electromigration and d the mean grain size along the direction parallel to the electric current flow.[†]

The second term of the right-hand side in Equation 5a expresses the numbers of excess vacancies disappearing at grain boundaries per unit volume and time, that is, the effect of "vacancy sweeping out". The vacancy flux is explicitly rewritten as $J_v = N_v^J D_v\ |eZ^*|\ \rho J/kT$, where D_v is the diffusion constant of the excess vacancy at temperature T, Z^* the effective charge number of the excess vacancy in electromigration, and ρ the electrical resistivity at T. The other symbols have the usual meanings. Equation 5a then becomes

$$-\frac{dN_v^J}{dt} = \gamma\left(1+\frac{D_v\,|eZ^*|\,\rho J}{\gamma dkT}\right)N_v^J = \gamma^J N_v^J. \tag{6}$$

$$\left[\gamma^J \equiv \gamma\left(1+\frac{D_v\,|eZ^*|\,\rho J}{\gamma dkT}\right)\right]$$

Equations 5 and 6 can be solved for N_v^0 and N_v^J under the initial condition $N_v^0 = N_v^J = N_v(0)$. The results are

$$N_v^0 = N_v(0)e^{-\gamma t}, \tag{7}$$

$$N_v^J = N_v(0)e^{-\gamma^J t}. \tag{7a}$$

Substituting Equations 7 and 7a into Equations 4 and 4a and solving for ρ^0 and ρ^J under initial condition $\rho^0 = \rho^J = \rho(0)$, we obtain

$$\rho^0 = \frac{KN_v(0)}{\gamma}(e^{-\gamma t} - 1) + \rho(0), \tag{8}$$

$$\rho^J = \frac{KN_v(0)}{\gamma^J}(e^{-\gamma^J t} - 1) + \rho(0). \tag{8a}$$

Using Equations 8 and 8a, we can easily verify the relation $\rho^J > \rho^0$ for an arbitrary t and J as fas as $\gamma^J > \gamma$. Thus, starting from a model situation we have confirmed that the retarding effect of d.c. stress certainly results in the relation $\rho^J > \rho^0$. Moreover, at the beginning of this section, we assumed the relation $(R_J - R_0)/R_0 = \beta J (\beta > 0)$ for the retarding effect of d.c. stress *per se*. This relation is also verified by using Equations 8 and 8a as follows: in the region where the applied electric current J is so weak that the thermal annihilation term of the excess vacancy γ is very large compared with the current-assisted annihilation $D_v\ |eZ^*|\ \rho J/dkT$ in Equation 6, Equation 8 can be approximated as

$$\rho^J = \frac{KN_v(0)}{\gamma}\left[(e^{-\gamma t} - 1) + \left(\frac{1}{\gamma} - \frac{e^{-\gamma t}}{\gamma} - te^{-\gamma t}\right)\frac{D_v\,|eZ^*|\,\rho J}{dkT}\right] + \rho(0). \tag{9}$$

From Equations 8 and 9 we have

$$\frac{\rho^J - \rho^0}{\rho^0}\left(= \frac{R_J - R_0}{R_0}\right) = \frac{KN_v(0)D_v\,|eZ^*|\,\rho}{\gamma\rho^0 dkT}\left(\frac{1}{\gamma} - \frac{e^{-\gamma t}}{\gamma} - te^{-\gamma t}\right)J. \tag{10}$$

The coefficient of J in Equation 10 which corresponds to β described above, is always positive for an arbitrary t and γ.

In the present experimental method, however, quantative examination of Equation 7 may be inappropriate because the mean grain size, d, may

[†] *d* may be considered to be the mean distance of permanent sinks (dislocations are also included) along the direction parallel to the current flow.

change gradually during many repeated heat-treatments at the homogenization temperature. It seems more suitable to examine the effect of d.c. stress on isothermal annealing curves where d will be able to remain constant throughout an experimental run, and an investigation is now in progress along this line.

Until now, it has tacitly been assumed that d.c. stress effects only the diffusion process of solute atoms, although it should be noted that the effect of d.c. stress on the nucleation stage of solute atoms might also be probable, including the recent theoretical proposition with respect to the void nucleation during electromigration by Suhl and Turner [15].

In conclusion, it becomes evident that in an Al–4.15 wt % Cu alloy the d.c. stress during quench annealing retards the precipitation reaction of the GP(1) zone in contrast to the conclusion obtained in an Al–3.98 wt % Cu alloy by Koppenaal and Simcoe [2], and that it is ascribed to the sweeping out of quenched-in excess vacancies into grain boundaries by electromigration.

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