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Formation and Reversion of G-P Zones in Al-1.3 at. % Ag Alloy

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The kinetics of clustering and reversion of G-P zones in an Al-1.3 at. % Ag alloy have been investigated by resistivity measurements, with special attention to the initial parts of reversion. From an analysis of clustering kinetics, vacancy formation, solute migration and solute-vacancy binding energies have been deduced to be 0.70, 0.53 and 0.10 eV respectively.

The activation energy for reversion, which is identified as the activation energy for solute atom diffusion, is found to vary from 0.98 to 1.46 eV with increasing reversion time. This is attributed to variations in the vacancy concentration in equilibrium with small dislocation loops.

1. Introduction

In aluminium alloys containing copper or silver, the ageing process consists of an initial fast reaction followed by a slow reaction [1, 2]. During the fast reaction stage in Al–Cu alloys, the vacancy concentration is in excess and independent of the ageing temperature [3]. Further, when an Al–Cu alloy specimen is reverted from the fast-reaction stage, the activation energy for reversion is found to be approximately the same as the activation energy for the fast reaction [4]. On the contrary, the activation energy for reversion is found to vary with the reversion time, when the reversion is made from the range of the slow reaction. This has been attributed to the variation in the available vacancy concentration during reversion [5].

In a recent communication [6] we provided evidence for the existence of the slow reaction in Al–1.3 at. % Ag alloy, quenched from 580° C and aged at low temperatures. Among the different mechanisms suggested to explain the slow reaction, the one based on vacancy cluster formation is found to be the most probable one. According to this, the slow reaction is sustained for a long time by the vacancy concentration in equilibrium with the dislocation loops, formed by the condensation of vacancies. Hence, the difference in the activation energies for reversion, corresponding to the fast and the slow reaction stages, can be attributed partly to the difference in the vacancy concentrations during these different stages of ageing and partly to the form (free, bound or condensed) in which they are present. Thus, a determination of the activation energy for reversion during the later stages of ageing in Al–Ag alloys will throw light on the role of vacancy clusters during reversion. The purpose of the present investigation is two-fold: (i) to evaluate the vacancy formation, solute migration and solute-vacancy binding energies in an Al–1.3 at. % Ag alloy, and (ii) to study the kinetics and the operating mechanism of reversion.

2. Experimental Procedure

Details of the mode of specimen preparation have been given elsewhere [7, 8]. Analysis of the alloy showed that it contains 1.25 at. % Ag and the following impurities: Cu, 5 ppm; Fe, 5 ppm; and Si, 20 ppm. The specimen was made from a 2 m length of 0.8 mm diameter wire; about 50 cm on both ends were rolled flat and split into two so as to serve as current and potential leads; and the central portion wound into a helical coil on an insulating rod was used as the specimen. Resistivity changes were followed by the standard 4-probe potentiometric technique. The accuracy of measurement was 1 in 10^6 and reproducibility better than ± 0.01 %.

For isothermal ageing, the specimen was quenched into ice-water mixture and then immediately transferred to the ageing bath in the range −30 to 0° C. The resistivity increments were measured at the respective ageing temperatures.

For the reversion studies, the specimen was solution-treated at 580° C for 10 to 12 h and quenched into water at 0° C. It was purposely maintained at 0° C for 15 sec to facilitate the development of the maximum number of small dislocation loops [3, 9] and immediately transferred to a liquid air bath.

The specimen was aged for 250 min at 50° C before reversion; this was found to be sufficient to take the specimen to the slow reaction stage. Reversion was done by an interruption technique. In this technique, the specimen was reverted for a predetermined time (the minimum reversion time being 1 sec), then quickly dipped in benzene and finally transferred to a liquid air bath (−186° C) for measurements.

To make the effects of the dislocation loops and excess vacancies as conspicuous as possible, a reversion temperature range of 130 to 180° C was selected. The method of least squares was employed for all activation energy calculations.

3. Results and Analysis

3.1. Isothermal Ageing: Evaluation of Vacancy-Silver Binding Energy

The quenched-in resistivity measured at liquid air temperature was found to increase with increasing quenching temperature. This is due to quenched-in vacancy concentration and the attendant quench clustering. Quench clustering is so predominant in the Al–1.3 at. % Ag alloy (resistivity peak, representing a critical zone size in isothermal ageing, could be observed only for low quenching and ageing temperatures) that it is essential to eliminate the quench clustering effect from the quenched-in resistivity values in order to evaluate the vacancy formation energy. One way of doing this is to extrapolate the isothermal ageing curves to the resistivity value after reversion, R_{rev}, as done by Kimura, Kimura, and Hasiguti [10] and to determine the initial rates of ageing from such curves. The initial rates of clustering, as determined by this procedure, may be considered to be proportional to the concentration of quenched-in vacancies and could be used to evaluate the vacancy formation energy. The actual procedure consisted of quenching the sample from selected temperatures, and ageing at −25° C for about 30 min followed by reversion at 200° C for 6 min (sufficient for complete reversion) and finally quenching the specimen back to −25° C (the ageing temperature) for measuring the resistance after reversion, R_{rev}. R_{rev} was consistently found to be less than R_0, the first measurement that we could take after quenching. Fig. 1 gives the isothermal ageing curves extrapolated to R_{rev}. DeSorbo *et al* [11] showed that the rate of resistance change, $\mathrm{d}R/\mathrm{d}t$, follows the relation:

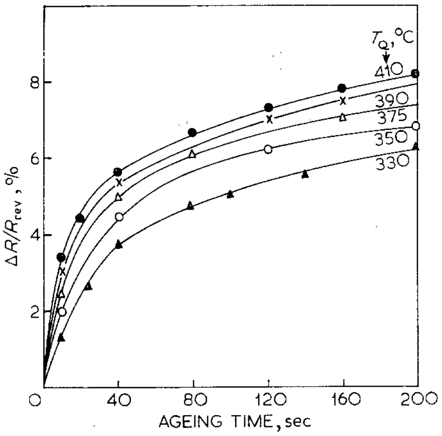

Figure 1 Effect of quenching temperature on isothermal ageing at −25° C.

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{1}{a + bt} \tag{1}$$

where t is the ageing time and a and b are constants. Perry [12] suggested:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{1}{a + bt + ct^2} \tag{2}$$

for explaining the results on Al–Zn system. However, in the present case, equation 1 was found to be valid. The values of the initial rate of resistance change, a^{-1}, were computed by using the increment ratio $(\Delta t/\Delta R)$ between successive measurements, as a measure of $(\mathrm{d}t/\mathrm{d}R)$ at the mean time, t, of each interval. Fig. 2 shows the variation of the initial rates with $(1/T_Q)$, where T_Q is the quenching temperature. The slope gave 0.70 ± 0.02 eV for the apparent vacancy formation energy, E_F', in this alloy.

The vacancy concentration (atom fraction) in the alloy at the quenching temperature, T_Q is given by:

$$c_V = A[1 - 12\,C_1 + 12\,C_1 \exp(E_B{}^{\text{v-Ag}}/kT_Q)] \exp(-E_F/kT_Q) \simeq A' \exp(-E_F'/kT_Q) \tag{3}$$

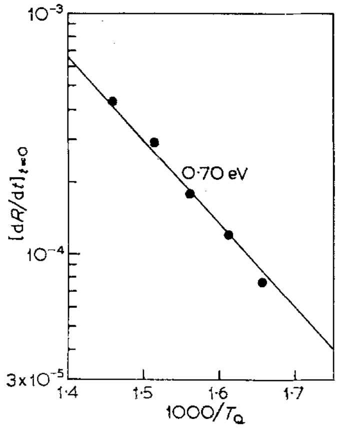

Figure 2 The variation of the initial rate of resistance change with quenching temperature. $T_A = -25°$ C.

Here C_1 represents the atom fraction of Ag in the alloy, E_B^{v-Ag} is the vacancy-silver binding energy, E_F and E_F' are the vacancy formation energies in the pure metal and the alloy respectively, k is the Boltzmann constant, and A and A' are also constants. By substituting $A = 1$ (tentatively assumed), $C_1 = 0.013$, $E_F = 0.76$ [13] for pure aluminium and different assumed values (0.05 to 0.2 eV) of E_B^{v-Ag}, the value of c_V from equation 3 was evaluated for different quenching temperatures. A plot of log c_V against $(1/T_Q)$ gives a straight line whose slope would give E_F', the apparent vacancy formation energy in the alloy. These formation energies are shown in fig. 3 as a function of the assumed v–Ag binding energy values. Since $E_F' = 0.70$ eV in Al–1.3 at. % Ag alloy, the value of E_B^{v-Ag} could be read from fig. 3 as 0.10 ± 0.02 eV. By a similar procedure, for an Al–0.64 at. % Ag alloy, we had earlier obtained the following values: $E_F' = 0.61$ eV and $E_B^{v-Ag} = 0.13$ eV [7].

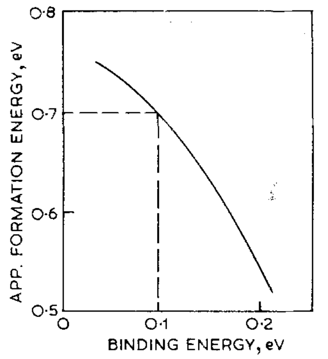

Figure 3 Plot showing the apparent formation energy (calculated) as a function of the assumed binding energy values.

3.2. Isothermal Ageing: Evaluation of Migration Energy

The isothermal ageing curves in the temperature range −30 to 0° C were obtained after quenching the specimen from 350° C into water at 0° C. The quenching temperature was kept low to avoid the effects of the slow reaction. The results are presented in fig. 4. To get the apparent migration energy of the solute, the following procedure was employed: the logarithm of times for fixed changes in resistivity, particularly in the initial stages of ageing, were plotted against the reciprocal of the ageing temperature and the activation energy determined from the slope. These were then plotted against the selected values of resistivity change (fig. 5) and extrapolated to zero resistivity change to give an apparent migration energy of 0.55 eV for silver.

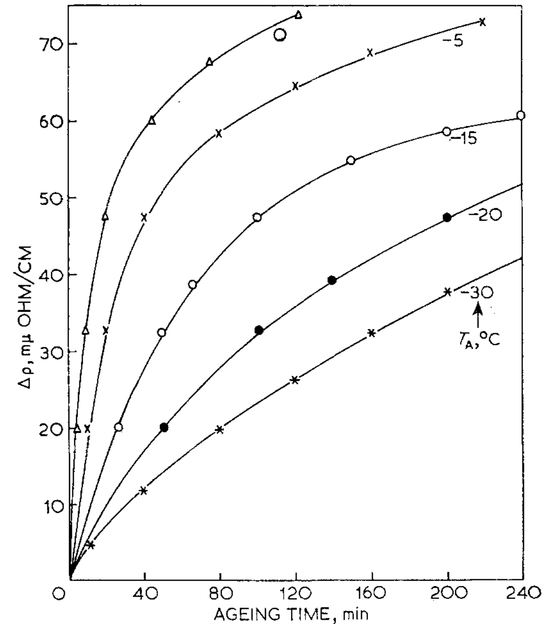

Figure 4 Isothermal ageing curves after quenching from 350° C. T_A is indicated on the curves.

This value was checked by the method suggested by Turnbull *et al* [1] wherein the resistivity isotherms were superimposed by multiplying with a suitable scaling factor, *f*. The variation of *f* with the ageing temperature is given by:

$$f = A \exp(-E_M{}^{Ag}/kT_A) \qquad (4)$$

where $E_M{}^{Ag}$ is the apparent migration energy for silver atom. The application of this method has been discussed in an ealier publication [7]. The Arrhenius plot (fig. 6) of the data gives 0.53 ± 0.02 eV for the silver atom migration energy in the alloy. A similar value is also obtained by using the initial rate of ageing. These values are slightly smaller than the value obtained by the first method, but are certainly more reliable. This value would correspond to the activation energy for the fast reaction.

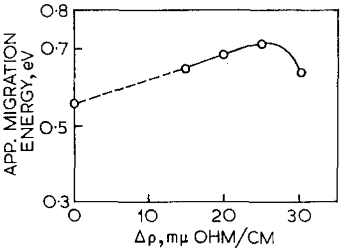

Figure 5 Plot showing the variation of apparent migration energy with the selected values of resistivity change. The curve is extrapolated to zero resistivity change to give an apparent migration energy of 0.55 eV.

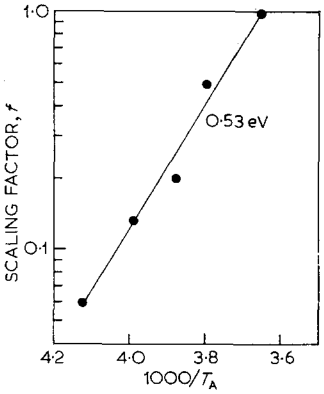

Figure 6 Migration energy calculated from the variation of "scaling factor" with the reciprocal of ageing temperature.

3.3. Evaluation of the Activation Energy for Reversion

For a specimen quenched from 580° C and aged up to the slow reaction stage (250 min at 50° C), the percentage change in resistance ($\Delta R/R_0\%$), as a function of reversion time at different temperatures (130 to 180° C) is plotted in fig. 7. Here R_0 is the resistance at reversion time, $t = 0$. For reversion temperatures above 180° C, the peak could not be detected due to the very rapid dissolution of G-P zones, while at lower temperatures, it may take longer to record the peak during reversion.

The activation energy for reversion was determined from the temperature dependence of the initial rates of resistance change. The initial rate of resistance for any given reversion temperature was obtained by plotting the reciprocal of resistance change (dt/dR), against the mean time, extrapolating this curve to $t = 0$ as shown in fig. 8 and taking the reciprocal of this value. From the plot (fig. 9) of log (initial rate) against $1/T_R$ where T_R is the reversion temperature, the activation energy for reversion is estimated to be 0.98 ± 0.04 eV at the beginning of reversion. The cross-cut method was also employed to evaluate the activation energy. The times to ($\Delta R/R_0\%$) = 0.5, are plotted against the reciprocal of the reversion temperature in fig. 10 to give an activation energy of 1.10 ± 0.03 eV. For higher values of ($\Delta R/R_0\%$), the activation energy was higher (1.46 ± 0.03 eV) and remained the same, irrespective of the value of $\Delta R/R_0\%$. Considering the initial rate method as a cross-cut method corresponding to $\Delta R/R_0\% = 0$, we find that the activation energy for reversion increases from 0.98 to 1.46 eV as $\Delta R/R_0\%$ changes from 0 to 1 and remains constant thereafter. An activation energy of 0.49 eV is obtained by the initial rate method, when a specimen was reverted from the fast reaction stage and is comparable with the migration energy of silver atom during the fast reaction stage (section 3.2).

3.4. Effect of Pre-Ageing Time on Reversion

In fig. 11 is given the change in resistivity during ageing at 25° C after quenching from 350 and 580° C. When $T_Q = 350°$ C, the resistivity decreases through the peak and remains constant after about 100 min, while the changes persist over a longer time (more than 300 min) when quenched from 580° C. A similar behaviour has been observed by X-ray work in Al–Zn system [14]; the zones grow gradually to a constant size when the specimen is quenched from low temperatures, while the zones keep growing slowly but steadily for a longer time if the specimen is quenched from a higher temperature.

The isothermal resistivity curves obtained during reversion at 175° C, of specimens quenched from 580° C and pre-aged at room temperature for 100, 1000, 3200 and 10000 min are displayed

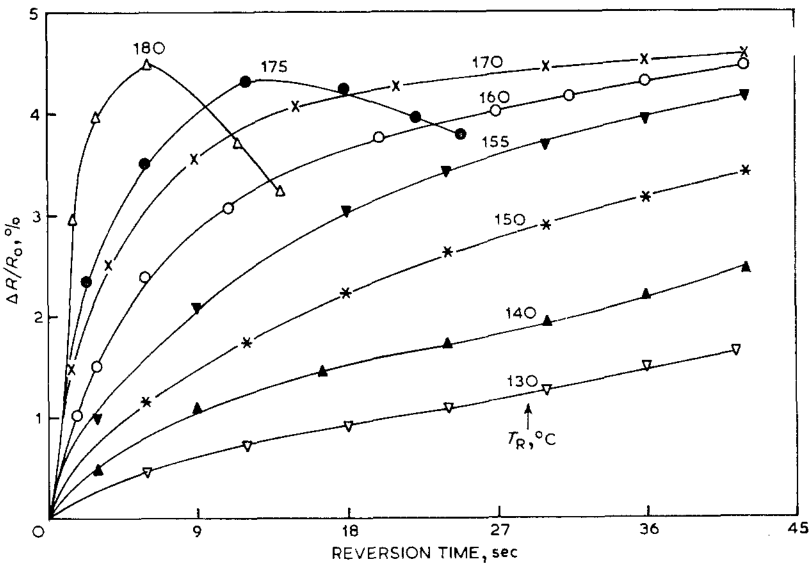

Figure 7 Percentage change in resistance as a function of reversion time at different temperatures. The specimen was quenched from 580° C and pre-aged for 250 min at 50° C.

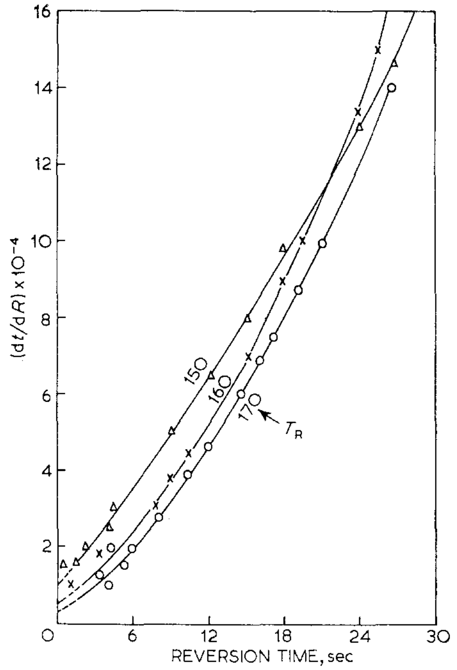

Figure 8 The variation of the reciprocal of resistance change with time for the reversion temperatures indicated.

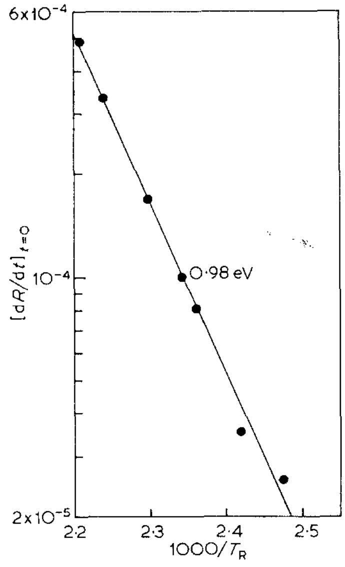

Figure 9 Estimation of the activation energy for reversion by the "initial rate" method, as indicated in the text.

in fig. 12. The peak height, which is normally supposed to represent the number of zones, is found to decrease with increasing pre-ageing time. The times for complete reversion and for the peak in resistivity are both longer, the longer the pre-ageing time. In fact, they increase linearly with the logarithm of the pre-ageing time (fig. 13) since the available vacancy concentration inside and outside the zones becomes negligible after prolonged ageing prior to reversion.

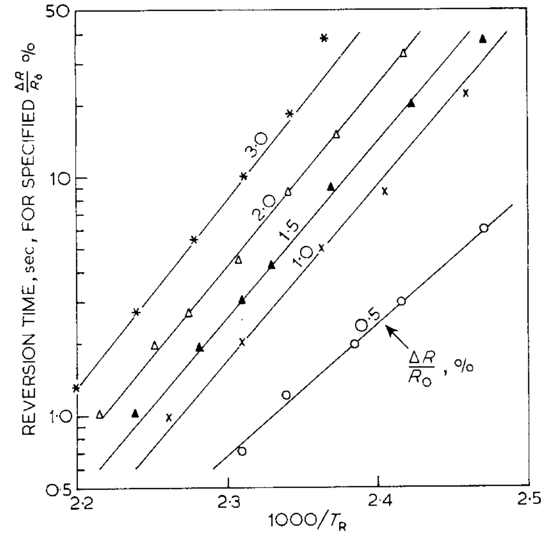

Figure 10 Estimation of the activation energy by the "cross-cut" method for different values of $\Delta R/R_0\%$, as indicated on the curves.

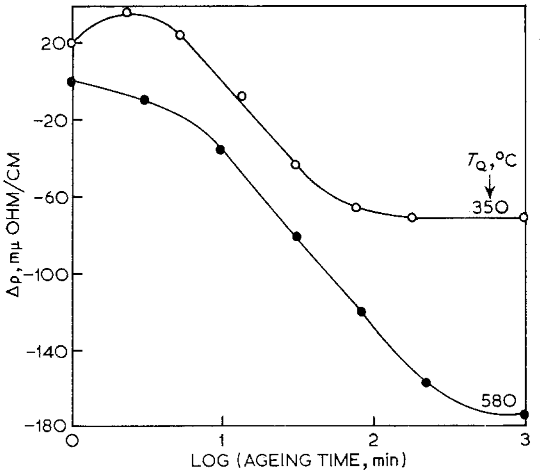

Figure 11 Effect of quenching temperature on the isothermal ageing at 25° C.

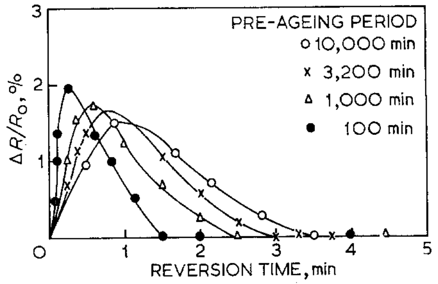

Figure 12 Resistance change during reversion for different pre-ageing periods indicated.

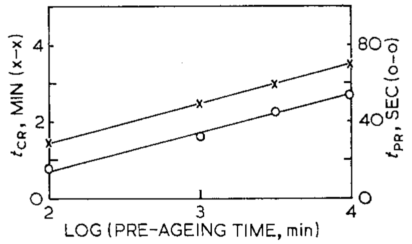

Figure 13 Variation of time for complete reversion (t_{CR}) and time-to-peak during reversion (t_{PR}) with the logarithm of pre-ageing time.

4. Discussion

4.1. Solute-Vacancy Interactions

Because of the interaction of the vacancies with the solute atoms in an alloy, it is generally known that the energy of formation of vacancies in alloys is smaller than in pure metals [15]. In Al–1.3 at.% Ag alloy, a value of 0.70 eV was obtained for the vacancy formation energy and 0.10 eV for the solute-vacancy binding energy (section 3.1). In a dilute alloy with 0.64 at.% Ag, we had earlier reported [7] a value of 0.61 eV for E_F' and 0.13 eV for E_B^{v-Ag}. The variations of E_F' and E_B^{v-Ag} are thus interdependent, and the nature of the solute, particularly its melting point with respect to the matrix, plays an important role in this connection. It has been shown [16] that where the melting point of the solute is higher than that of the matrix (as in the present case), the diffusion coefficient decreases with increasing solute concentration. Diffusion coefficient is given by the relation:

$$D = D_0 \exp\left[(E_F + E_M' - E_B^{v-Ag})/kT\right] \qquad (5)$$

where E_F is the vacancy formation energy in pure aluminium, E_M is the effective migration energy of a vacancy-silver atom pair and E_B^{v-Ag} is the vacancy-silver atom binding energy. Turnbull and Treaftis [17] have shown that the migration energy does not vary much with the solute concentration. A similar observation was also made in the present investigation: the migration energy for Al–1.3 at.% Ag alloy was 0.53 eV, which is not much different from that for Al–0.64 at.% Ag alloy [7]. In view of the constancy of E_M^{Ag} with concentration, any decrease in the diffusion coefficient, due to an increase in the concentration of silver, should result in an increase in the vacancy formation energy, in view of the higher melting point of silver compared with that of aluminium.

The migration energy of 0.53 eV is, in fact, the apparent migration energy of a silver atom, i.e. the effective migration energy of a vacancy-silver atom pair, E_M', minus the v–Ag binding energy, E_B^{v-Ag}. Hence the activation energy for silver diffusion in the Al–1.3 at. % Ag alloy would be $E_F + (E_M' - E_B^{v-Ag}) = 0.76 + 0.53 = 1.29$ eV. This is comparable with the activation energy for silver diffusion in Al–1.26 at. % Ag alloy, which has been determined by Beerwald as 1.5 eV [18].

In view of the negligible size difference between aluminium and silver atoms, it seems unlikely that an appreciable stress field would be generated by cluster formation in the alloy. This would entail a low value for v–Ag binding energy, resulting from the electronic interactions due to the valency difference between aluminium and silver atoms. As expected, the v–Ag binding energy in Al–1.3 at. % Ag is only 0.10 eV, while it was 0.13 eV in Al–0.64 at. % Ag alloy reported earlier [7]. These values are to be compared with those in the literature [19–26]: the values vary from 0.08 to 0.4 eV depending on (i) the experimental methods employed (ii) the silver concentration in the alloy (iii) the matrix and (iv) the temperature of measurement. Resistometric studies in this laboratory (8, 19, 20] on the influence of 0.01, 0.03, 0.08 and 0.10 at. % Ag additions on the clustering of Zn atoms in an Al–4.4 at. % Zn alloy, gave 0.23, 0.21, 0.20 and 0.18 eV respectively for the v–Ag binding energy, thus bringing out the effect of concentration on the binding energy.

4.2. Kinetics of Reversion

Resistance peaks were attained at a shorter time for higher reversion temperatures (fig. 7). The peaks could be due to the attainment of a critical size by the dissolving zones or due to the formation of intermediate or equilibrium phases [4]. However, the peak was reached at too short a time for the new phase to form (fig. 7). Hence, the resistance maximum is considered to correspond to a critical size of the dissolving G–P zones, implying thereby, that reversion is an inverse process of zone formation.

As discussed earlier (section 3.3) the activation energy for reversion varies with reversion time from an initial value of 0.98 eV to a value of 1.46 eV at later stages. Due to partial reversion at lower and medium temperatures, the zone diameter and density are likely to vary for a given change in resistance. A change in resistance equivalent to $\Delta R/R_0\% = 0.5$ (fig. 7) is so small that the zone diameter and density may be considered to be independent of the reversion temperature. For higher changes in resistance, where there can be a possible influence of zone diameter and density, the activation energy was in fact found to be independent of these. Hence, one can conclude that while the activation energy determined is almost independent of zone density and size distribution, it varies from 0.98 to 1.46 eV with the reversion time.

The resistivity, ρ, of the specimen is a function of the concentration, C_Z, of the zones, their size, r, and the number, N, so that:

$$\frac{d\rho}{dt} = \frac{\delta\rho}{\delta C_Z} \cdot \frac{dC_Z}{dt} + \frac{\delta\rho}{\delta r} \cdot \frac{dr}{dt} + \frac{\delta\rho}{\delta N} \cdot \frac{dN}{dt} \qquad (6)$$

In the initial rate method of activation energy calculations, we are interested in $(d\rho/dt)$ at $t = 0$. Corresponding to this situation, N is a constant and $(dN/dt) = 0$; and also $\delta\rho/\delta r = 0$ since just before the commencement of reversion, the zones have grown to such a size that their resistivity contribution is almost independent of their size. Hence at $t = 0$, we have:

$$\frac{d\rho}{dt} = \left(\frac{\delta\rho}{\delta C_Z} \cdot \frac{dC_Z}{dt}\right) \qquad (7)$$

For the resistivity changes observed during reversion, and the resistivity contribution of a silver atom, it can be shown that at least one silver atom should be emitted per second at a median reversion temperature such as 155° C. The silver atoms can be shown to migrate a distance of 0.5 Å in 1 sec at this temperature. Hence, for the dissolution of zones to keep going, the already emitted Ag atoms should diffuse away from their positions, giving room for fresh atoms. The reversion phenomenon is thus diffusion-controlled, and the activation energy for reversion can be identified as the activation energy for diffusion. In such a case, dC_Z/dt should be proportional to D_{Ag}, the diffusion coefficient, subject to the reasonable assumption that $\delta\rho/\delta C_Z$ is independent of the reversion temperature.

The diffusion coefficient is given by the expression [6]:

$$D_{Ag} = c_V[1.1 \exp(-E_M^{Ag}/kT)] \qquad (8)$$

where E_M^{Ag} is the apparent migration energy, which is a constant. The variation observed in the activation energy for reversion (section 3.3) reflects changes in the diffusivity with time and from equations 7 and 8 it follows that this would in turn be due to changes in the available vacancy concentration during the course of reversion.

4.3. Mechanism of Reversion

In arriving at the mechanism of reversion, one has to bear in mind the parallelism between the activation energies for reversion and for the fast and slow reactions in Al–Ag alloys: the activation energy for reversion from the fast reaction stage is 0.49 eV and the value for reversion from the slow reaction stage varies from an initial value of 0.98 eV to a final value of 1.46 eV (section 3.3), while the apparent activation (migration) energy increases from 0.53 eV corresponding to the fast reaction to 1.25 eV corresponding to the slow reaction [6]. This parallelism implies that both the processes might involve the same operating mechanism. The slow reaction has been explained either in terms of the vacancy-trapping effect of the zones or the vacancy-loop interactions. It is now necessary to examine which one would be operating in the reversion process.

The difference between the activation energies for the slow and fast reactions is (1.25 − 0.53) eV or 0.72 eV. If the slow reaction mechanism involves the vacancy-trapping effect of the zones, this value should represent the vacancy-zone binding energy and the vacancy concentration in equilibrium with the zones should be proportional to $\exp(-0.72/kT)$. This concentration should remain constant with time until complete dissolution which, in turn, means that the activation energy should remain constant during the entire period of reversion. But the present results contradict this prediction, since the activation energy for reversion was found to vary with time.

According to the mechanism based on the vacancy-loop interaction, the slow reaction is prompted by the vacancy concentration in equilibrium with the dislocation loops [3, 6]. For ageing conditions similar to the present investigation, the dislocation loops have been shown to have a radius of 20 Å and a density of 3×10^{12} cm^{-3} [6]. The concentration of vacancies in equilibrium with the dislocation loops just at the end of ageing at T_A (which would be the same as at the beginning of reversion) is given by

$$c_V \simeq \exp\left[-\left(E_F' - \Delta E\right)kT_A\right] \tag{9}$$

Here, E_F' is the vacancy formation energy and ΔE is the increase in the energy of the dislocation loop on absorbing a vacancy. The value of ΔE would be the difference between the activation energy for silver diffusion as determined by tracer techniques (which is 1.5 eV for Al–1.3 at.% Ag alloy [18]) and the activation energy for the slow reaction (which is 1.25 eV as determined by resistivity measurements [6]); thus a reasonable value for ΔE is 0.25 eV.

When the specimen attains the reversion temperature, T_R, the vacancy concentration changes to $\exp[-(E_F' - \Delta E)/kT_R]$; this is in excess of the thermal equilibrium vacancy concentration characteristic of T_R by a factor of $\exp[\Delta E/kT_R]$. The specimen would, in course of time, lose this excess vacancy concentration in an attempt to attain the thermal equilibrium value, $\exp[(-E_F'/kT_R)]$. Mathematically this implies that the value of ΔE should change from its original value of 0.25 eV to almost zero, which is possible only if we assume the competitive growth of loops. The loops grow in their size according to the relation [3]

$$\Delta E = \frac{5.2}{r_l} \tag{10}$$

where r_l is the radius of the loop and when loops grow sufficiently large ($\simeq$ 100 Å in radius) ΔE is negligibly small.

The time required for the emission of a vacancy from a loop is approximately given by [5]:

$$t = 10^{-14} \exp[(E_F' + E_M^{Ag} - \Delta E)/kT] \tag{11}$$

where E_F' and E_M^{Ag} are the vacancy formation and migration energies respectively. With the present values of $(E_F' + E_M^{Ag}) = (0.70 + 0.53) = 1.23$ eV and $\Delta E = 0.25$ eV, t is found to be about 4.8×10^{-3} sec at 150° C and much shorter at higher temperatures. The vacancy jump frequency is high enough to permit the jumping of vacancies from one loop to another, thus facilitating the growth of some loops at the expense of others; this process is easier because of the high density of dislocations. On the other hand, there is not much scope for the permanent sinks like grain boundaries and straight dislocations to absorb the excess vacancies because of the possibly large distances between them. Thus, the competitive growth of the dislocation loops appears to be mainly responsible for the decay of the excess vacancies during reversion. Dislocation loops larger than 100 Å in diameter have actually been observed by Cohen *et al* [27] in reverted Al–Zn and Au–Ni alloys and by Thomas [28] in aged Al–Ag alloys.

The commencement of reversion would correspond to a vacancy concentration of $\exp[-(E_F' - \Delta E)/kT_A]$. The loop radius is almost constant at this stage and the activation energy for silver diffusion would be given by $(E_F' - \Delta E + E_M' - E_B^{v-Ag})$ which in the present case works out to be 1.04 eV. The activation energy for reversion obtained by the initial rate method is 0.98 eV. As reversion proceeds, the loops become sufficiently large by a process of competitive growth as mentioned earlier, and ΔE becomes negligibly small, so that the activation energy for silver diffusion would now be given by $(E_F' + E_M' - E_B^{v-Ag}) = 1.29$ eV. The time to bring about $\Delta R/R_0\% = 1.0$ to 3.0 (fig. 7) is sufficient enough to permit competitive growth of the loops. During this stage, the diffusion of silver is aided by the vacancies in equilibrium with the large dislocation loops. The value of activation energy for the later stages of reversion, obtained by the cross-cut method ($\simeq$ 1.4 eV), would correspond to this stage, and the dependency of the activation energy for reversion on the reversion time is a direct consequence of the variation of the vacancy concentration during reversion.

5. Conclusions

(i) In Al–1.3 at.% Ag alloy, the vacancy formation and migration energies were found to be 0.70 and 0.53 eV respectively. The vacancy-silver binding energy was evaluated as 0.10 eV.

(ii) During reversion at 175° C, the time to reach the peak and the time for complete reversion were both found to vary linearly with the logarithm of the pre-ageing time.

(iii) The activation energy for reversion is found to vary from 0.98 to 1.46 eV with reversion time. This is identified as the activation energy for silver diffusion. Based on the vacancy cluster mechanism, the variation in activation energy with reversion time is attributed to changes in the vacancy concentration in equilibrium with small dislocation loops.

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References

1. D. Turnbull, H. S. Rosenbaum, and H. N. Treaftis, *Acta Metallurgica* **8** (1960) 277.
2. D. Turnbull and R. L. Cormia, *ibid* **8** (1960) 747.
3. J. Okamoto and H. Kimura, *Mater. Sci. Eng.* **4** (1969) 39.
4. K. Asano and K. Hirano, Fall Meeting of the Institute of Metals, Japan (1968) [as mentioned in Ref 5 below].
5. H. Shimizu and H. Kimura, *Mater. Sci. Eng.* **5** (1969/70) 127.
6. K. N. Murty and K. I. Vasu, communicated to *Mater. Sci. Eng.*
7. *Idem, Mater. Sci. Eng.* **5** (1969/70) 251.
8. K. S. Raman, E. S. D. Das, and K. I. Vasu, *J. Mater. Sci.* **5** (1970) 105.
9. M. Kiritani, *J. Phys. Soc. Japan* **20** (1965) 1834.
10. H. Kimura, A. Kimura, and R. R. Hasiguti, *Acta Metallurgica* **10** (1962) 607.
11. W. DeSorbo, H. N. Treaftis, and D. Turnbull, *ibid* **6** (1958) 401.
12. A. J. Perry, *ibid* **14** (1966) 1143.
13. F. C. Duckworth and J. Burke, *Phil. Mag.* **14** (1966) 473.
14. M. Murakami, O. Kawano, and Y. Murakami, *Acta Metallurgica* **17** (1969) 29.
15. W. M. Lomer, *Monogr. Ser. Inst. Metals* **23** (1957) 79.
16. R. F. Mehl, F. N. R. Hines, and K. A. von den Steinen, *Metals and Alloys* **13** (1941) 41.
17. D. Turnbull and H. N. Treaftis, *Bull. Amer. Phys. Soc.* **1** (1956) 334.
18. A. Beerwald, *Z. Elektrochem.* **45** (1949) 789.
19. K. S. Raman, E. S. D. Das, and K. I. Vasu, *Current Sci.* **38** (1969) 130.
20. E. S. D. Das, K. S. Raman, and K. I. Vasu, Paper presented at the Conference on "Materials Science and Research India", Bangalore (1970).
21. M. Ohta and F. Hashimoto, *J. Phys. Soc. Japan* **19** (1964) 1987.
22. F. Hashimoto, *ibid* **20** (1965) 336.
23. M. Ohta, F. Hashimoto, and T. Tanimoto, *Memoirs of the School of Engg. Okayama Univ.* **3** (1968) 39.
24. M. Ohta and F. Hashimoto, *J. Phys. Soc. Japan* **19** (1964) 133.
25. *Idem, Trans. Japan Inst. Met.* **6** (1965) 9.
26. D. R. Beaman, R. W. Balluffi, and R. O. Simmons, *Phys. Rev.* **134** (1964) A532.
27. J. B. Cohen, O. F. Kimball, M. Meshii, and K. Rundman, *Acta Metallurgica* **14** (1966) 545.
28. G. Thomas, *Phil. Mag.* **4** (1959) 1213.

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