Clustering Phenomena in Al-4.4 at. % Zn Alloy with 0.03 and 0.08 at. % Ag Additions

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The influence of 0.03 and 0.08 at. % Ag additions on the clustering of Zn atoms in an Al-4.4 at. % Zn alloy has been studied by resistometry. The effect of quenching and ageing temperatures shows that the ageing-ratio method of calculating the vacancy-solute atom binding energy is not applicable to these alloys. Zone-formation in Al-Zn is unaffected by Ag additions, but the zone-reversion process seems to be influenced. Apparent vacancy-formation energies in the binary and ternary alloys have been used to evaluate the v-Ag atom binding energy as 0.21 eV. It is proposed that, Ag and Zn being similar in size, the relative vacancy binding results from valency effects, and that in Al-Zn-Ag alloys clusters of Zn and Ag may form simultaneously, unaffected by the presence of each other.

1. Introduction

It has been recognised that the interaction between the quenched-in vacancies and solute atoms is of importance in understanding the nature and speed of the initial decomposition and the vacancy-aided clustering of solute atoms in quenched, age-hardenable alloys. It is now established that such a clustering process always precedes the true precipitation in age-hardening systems and is termed "pre-precipitation".

The pre-precipitation process has been extensively studied in Al-rich solid solutions with Zn, Ag, Cu and Mg. Comparison of the vacancy-annealing characteristics of these alloys with pure aluminium has given rise to the concept of a "binding energy", which is of the order of 0.1 to 0.3 eV for most solutes in the Al matrix. Consequently many methods of evaluating the vacancy-solute atom binding energies have been suggested [1], and quantitative estimates of binding energy made for a number of elements [2-16]. It is pointed out that this interaction is the one that causes either a retardation or acceleration of the pre-precipitation, when a small quantity of a ternary solute is added to an age-hardenable binary alloy. This, therefore, affords a simple method of comparing the rates of clustering in a binary alloy with and without

the third solute, from which the binding energy can be evaluated. This method has been employed extensively by Hashimoto and co-workers [2-11], Perry [13, 14] and Perry and Entwistle [12]. The method is based on the solid solution model of Lomer [17]; the vacancy concentration (atom fraction) in any alloy is given [14] by:

$$C_v{}^* = A[1 - ZC_1 + ZC_1 \exp(E_B{}'/kT_H)$$
$$- ZC_2 + ZC_2 \exp(E_B{}''/kT_H) - ZC_3$$
$$+ \ldots \ldots] \exp(-E_F/kT_H)$$
$$\approx A^* \exp(-E_F{}^*/kT_H) \qquad (1)$$

Here $C_1, C_2 \ldots$ are the atom fraction of the solutes of type 1, type 2, $\ldots$ and $E_B{}', E_B{}''$, $\ldots$ are the binding energies of the respective solutes to vacancy, Z is the co-ordination number of the matrix metal and E_F is the vacancy formation energy in the pure metal while $E_F{}^*$ gives the apparent vacancy-formation energy in the alloy, and A and A^* are constants. This equation obviously requires that (i) vacancies are singly distributed, (ii) there does not exist any appreciable interaction between the two solute species, (iii) vacancies are bound to only one type of solute at a time, and (iv) vacancy-solute pairs do not contain more than one solute atom.

If one can determine the vacancy concentration in the binary (C_v') and ternary (C_v'') alloys

and if E_B' or E_B'' is known, the other can be evaluated by applying equation 1 modified to the respective case. The method of Hashimoto and co-workers [2-11], Perry [13, 14] and Perry and Entwistle [12] is to obtain the ratio C_V'/C_V'' as equal to (i) the ratio of the initial rate of ageing in the binary to that in the ternary alloy, or (ii) the ratio of the time taken to reach the peak in resistivity during isothermal ageing of the ternary to that taken in the binary alloy under identical conditions.

On the basis of this:

$$\frac{C_V'}{C_V''} = \frac{(\text{Initial rate of ageing})_{\text{binary}}}{(\text{Initial rate of ageing})_{\text{ternary}}}$$

$$= \frac{(\text{Time-to-peak})_{\text{ternary}}}{(\text{Time-to-peak})_{\text{binary}}},$$

$$= \frac{[1 - ZC_1 + ZC_1 \exp(E_B'/kT_H)]}{[1 + ZC_1\exp(E_B'/kT_H) - ZC_1 - ZC_2 + ZC_2] \exp(E_B''/kT_H)]} . \quad (2)$$

The use of this equation requires that (i) the pre-exponential terms are similar in value, and (ii) the distribution of free and bound vacancies in the alloys at the homogenisation temperature and at the ageing temperature immediately at the point of quench is not much different. These requirements have been discussed by Ohta and Hashimoto [6] and Perry [14] in detail.

The systems Al-Zn and Al-Ag show a pronounced tendency to cluster. Because of the negligible misfit, the zones formed are spherical in both systems. It was, therefore thought that Ag additions to Al-Zn or Zn additions to Al-Ag provide an interesting alloy for study. Hashimoto et al [7, 8] have earlier reported some results on the effect of Ag addition to Al-4.4% Zn alloy. Shee et al [18] studied the effect of Ag on the ageing characteristics of an Al-6.8% Zn alloy. We earlier reported [19] the evaluation of v-Ag binding energy by the method discussed above. In the present paper we give results of resistivity increment on quenching, isochronal annealing and isothermal ageing of Al-4.4% Zn alloy with 0.03 and 0.08% Ag (all compositions are in at. %). Ag was selected for two reasons: (i) it has an atomic diameter close to that of Al and Zn, and it is not expected to interfere much with the formation of spherical zones in the alloy; and (ii) there is considerable interest in small Ag additions to commercial Al-based alloys to bring about uniform precipitation and enhanced resistance to stress-corrosion [20].

2. Experimental

The alloys were all prepared from super purity Al, high purity Zn and pure Ag. Cylindrical ingots 15 mm diameter and 200 mm long were obtained by melting and casting under purified argon. The homogenised rods were cold-rolled, in several stages, with intermediate annealing at 400° C, down to wires, 3 mm diameter, which were cold-drawn in diamond dies to 0.7 mm diameter. The analysis of the pure metals and the alloys are given in table I. Preparation of the specimens and the treatments given are discussed in detail elsewhere [19]. The specimen was made from a 2 m length of the wire, 50 cm on either end of which were rolled flat and split in two to serve as current and potential leads. The central 1 m length, wound into a helical coil 1 cm diameter and 3 cm long served as the specimen. Electrical resistivity measurements were made by the standard 4-probe potentiometric technique.

For isochronal annealing, stirred liquid baths maintained at 20° C intervals in the range — 20 to + 200° C, were used. These were controlled to within $\pm$ 0.1° C. For measuring resistivity increment on quenching, specimens were quenched into stirred ice/water mixture at 0° C and immediately transferred to liquid air, with an intermediate dip in alcohol or acetone at 0° C. For isothermal ageing, specimens were quenched to 0° C, and then immediately transferred to the ageing bath.

The resistivity values are reported in $m\mu\Omega$ cm ($= 10^{-9}\Omega$ cm) units. $\triangle\rho$ is calculated using the relation:

$$\triangle\rho = \frac{\rho_0(R - R_0)}{R_0},$$

where R and R_0 are the resistivity and resistance of the sample at the reference temperature (liquid air temperature for quenched-in resistivity measurements, ageing temperature for isothermal work and — 20° C for isochronal annealing), immediately after a quench from 200° C (lowest solutionising temperature used in this work), but with no ageing. The accuracy of measurement was 1 in 10^6 for resistance measurements. Reproducibility was better than $\pm$ 0.01%.

The quenching rates were recorded using a Tektronix-551 oscilloscope. It was in the range 2 to $5 \times 10^{4°}$ C sec^{-1} for the experimental conditions described above, and was considered to be high enough to trap vacancies efficiently.

TABLE I Compositions of pure metals and alloys made for the investigation

| Pure metal | Impurity content in ppm maximum | | | | | Alloy composition, at. % | | |
	Cu	Fe	Si	Pb	As	binary	ternary-1	ternary-2
Aluminium (99.997+)	5	5	20	—	—			
Zinc (99.995+)	—	20	—	20	0.1	4.38	4.39	4.40
Silver (99.99+)	—	—	—	—	—	0.00	0.03	0.08

3. Results

3.1. Isochronal Annealing

The process of decomposition of a quenched alloy can be qualitatively studied by an isochronal annealing procedure. In order to find out if Ag atoms exerted any influence on the decomposition of Al-4.4% Zn alloy, isochronal annealing experiments, at temperature intervals of 20° C and an annealing period of 2 min at each temperature, were carried out from − 20 to + 200° C with Al-4.4% Zn, Al-4.4% Zn-0.03% Ag and Al-4.4% Zn-0.08% Ag alloys quenched into stirred ice/water mixture from different temperatures in the range 200 to 500° C. Fig. 1 shows the percentage change in resistivity as a function of annealing temperature.

The data in fig. 1 show that there are three broad regions of change: (i) an initial increase at low temperatures, that reaches a maximum; (ii) a continuous decrease, after the maximum, to a plateau; and (iii) a second decrease in the temperature region of 120 to 140° C, which does not seem to depend on the quenching temperature. Similar observations have also been made by Panseri and Federighi [21] in an Al-4.4% Zn alloy.

The temperature at which the initial increase, observed at low temperatures, reaches a maximum and the magnitude of this increase at the maximum point are both dependent on the quenching temperature; increasing quenching temperature brings down the temperature at which the maximum in resistivity is observed. Region (i) is due to the formation of GP zones reaching a critical size. Further growth of these zones beyond the critical size results in the
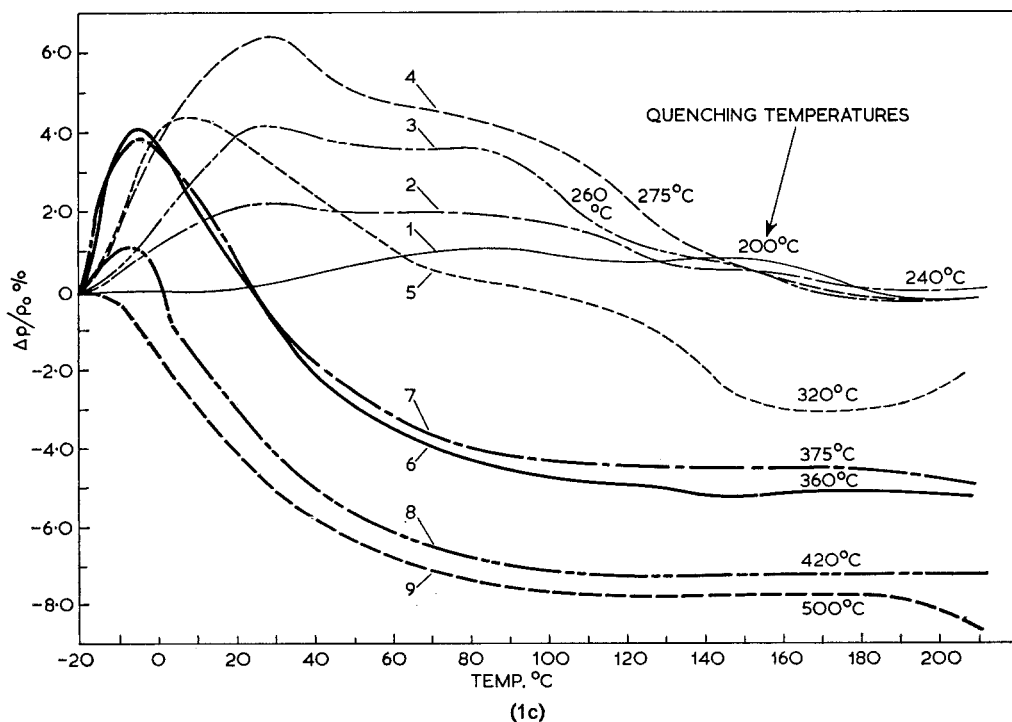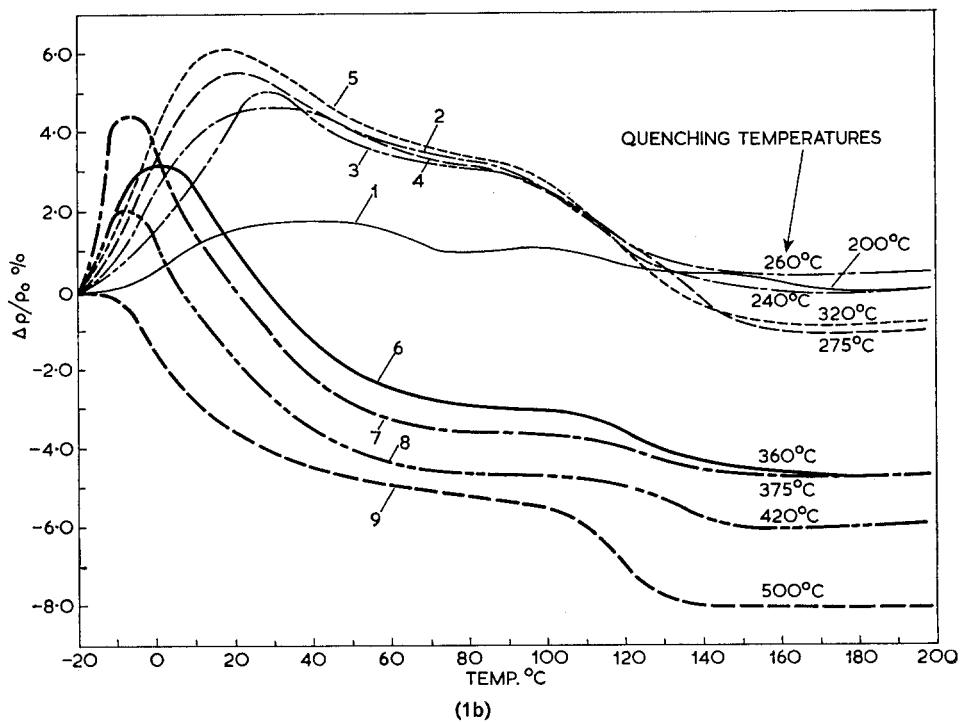

(1a)

(1b)

(1c)
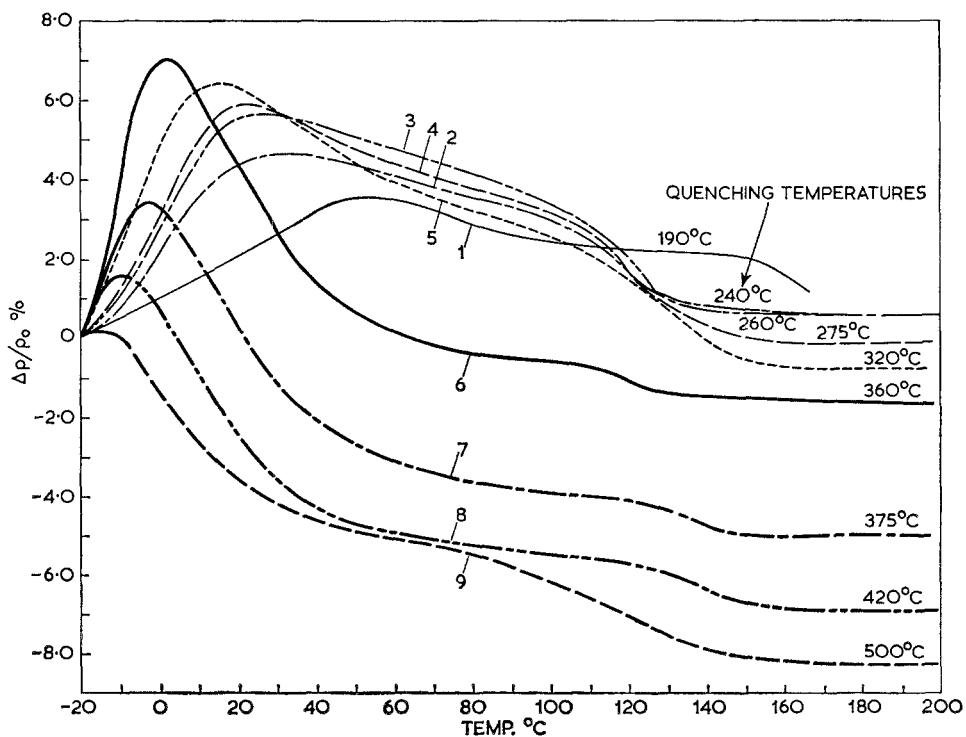
Figure 1 (a) Isochronal annealing characteristics in quenched Al-4.4% Zn alloy. 20° C steps; 2 min anneal at each temperature. (b) Isochronal annealing characteristics in quenched Al-4.4% Zn-0.03% Ag alloy. (c) Isochronal annealing characteristics in quenched Al-4.4% Zn-0.08% Ag alloy.

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decrease as in region (ii). Region (iii) is associated with a probable zone-reversion process, as was postulated by Panseri and Federighi [21]. This assumption is fairly well founded because the solvus temperature for GP zones in this alloy is 120° C [22]. Also, Krishnarao et al [23] working on an Al-4.4% Zn alloy, observed only the first two regions and not the third in the temperature range of − 80 to + 200° C, probably because in this alloy the GP zones are stable up to the monotectoid temperature (∼260° C). The general features of the isochronal curves have been discussed in detail by Federighi [24], for pure metals, and dilute and concentrated Al-based alloys.

We now make a comparison of the annealing characteristics of the binary alloy with those of the ternary alloys. It can be noticed that (i) in the ternary alloys the maximum increase in resistivity takes place after quench from a lower temperature; e.g. 360° C in the Al-Zn alloy, 320° C for Al-Zn-0.03% Ag alloy and 275° C for Al-Zn-0.08% Ag alloy. This seems to indicate that the presence of Ag atoms influences the zone-forming process in the Al-Zn alloy. Clustering is faster in ternary alloys and the maximum is reached for a low-temperature quench; this is further strengthened by isothermal annealing results (vide infra), and also with the observation that in Al-Ag alloys the clustering rate is very high [4]. (ii) The second decrease in the temperature range 120 to 140° C is observed for the binary alloy and for the Al-Zn-0.03% Ag alloy; for the Al-Zn-0.08% Ag alloy, it is observed only for low temperature quenches. When the quenching temperature is greater than 360° C, this second decrease is totally absent.

It is possible that in the Al-Zn-0.08% Ag alloy, quenched from high temperatures, the zones formed are different in nature from those in the other two alloys, and they may be more stable so that re-dissolution does not take place below 200° C.

The results from isochronal annealing experiments, being highly qualitative in nature, will be interpreted with the help of isothermal ageing results.

3.2. Quenched-in Resistivity

The increment in electrical resistivity produced upon quenching is a measure of the concentration of vacancies trapped-in, and the dependency of this on quenching temperature (fig. 2) can therefore be used to estimate the vacancy-

formation energy in metals and alloys. The shape of this plot has been discussed by Panseri and Federighi [21] and also by us [25]. The values of apparent vacancy-formation energy computed from the linear portion of the plot are 0.59, 0.53 and 0.52 eV respectively for the binary, Al-Zn-0.03% Ag and Al-Zn-0.08% Ag alloys. Although the difference in these values seems to be quite small it can be seen that the formation energy is reduced by the presence of Ag atoms. The low values of vacancy-formation energies can be easily explained to be due to clustering taking place during quenching. We are of the opinion that the extent of quench-clustering is even greater in the alloys containing Ag than in the binary alloy, and this varies with the quenching temperature. It is known that Ag-rich spherical zones are formed at considerably rapid rates in Al-Ag alloys [4]. This enhanced quench-clustering can be easily seen by comparing the resistivity increments produced after a quench from, say 400° C; the values in $m\mu\Omega cm$ are: 150 for the binary alloy; 190 for Al-Zn-0.03% Ag alloy and 330 for the Al-Zn-0.08% Ag alloy, all under identical conditions of quenching. The values of formation energy obtained by this method, therefore, cannot be used to evaluate the binding energy.

The above results however help to conclude that the presence of Ag atoms does influence the
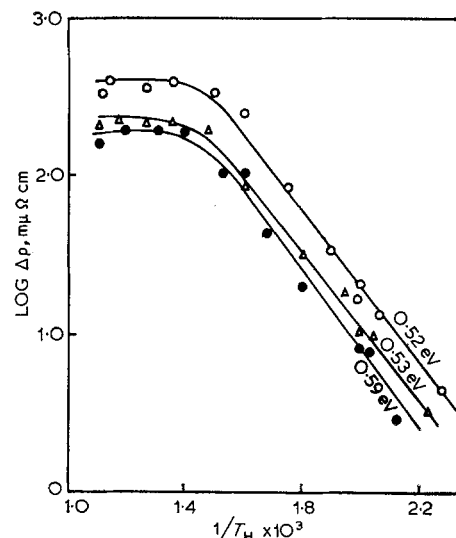

Figure 2 Plot of logarithm of quenched-in resistivity increment against reciprocal of quenching temperature. ●—● Al-4.4% Zn; △—△ Al-4.4% Zn-0.03% Ag; ○—○ Al-4.4% Zn-0.08% Ag.
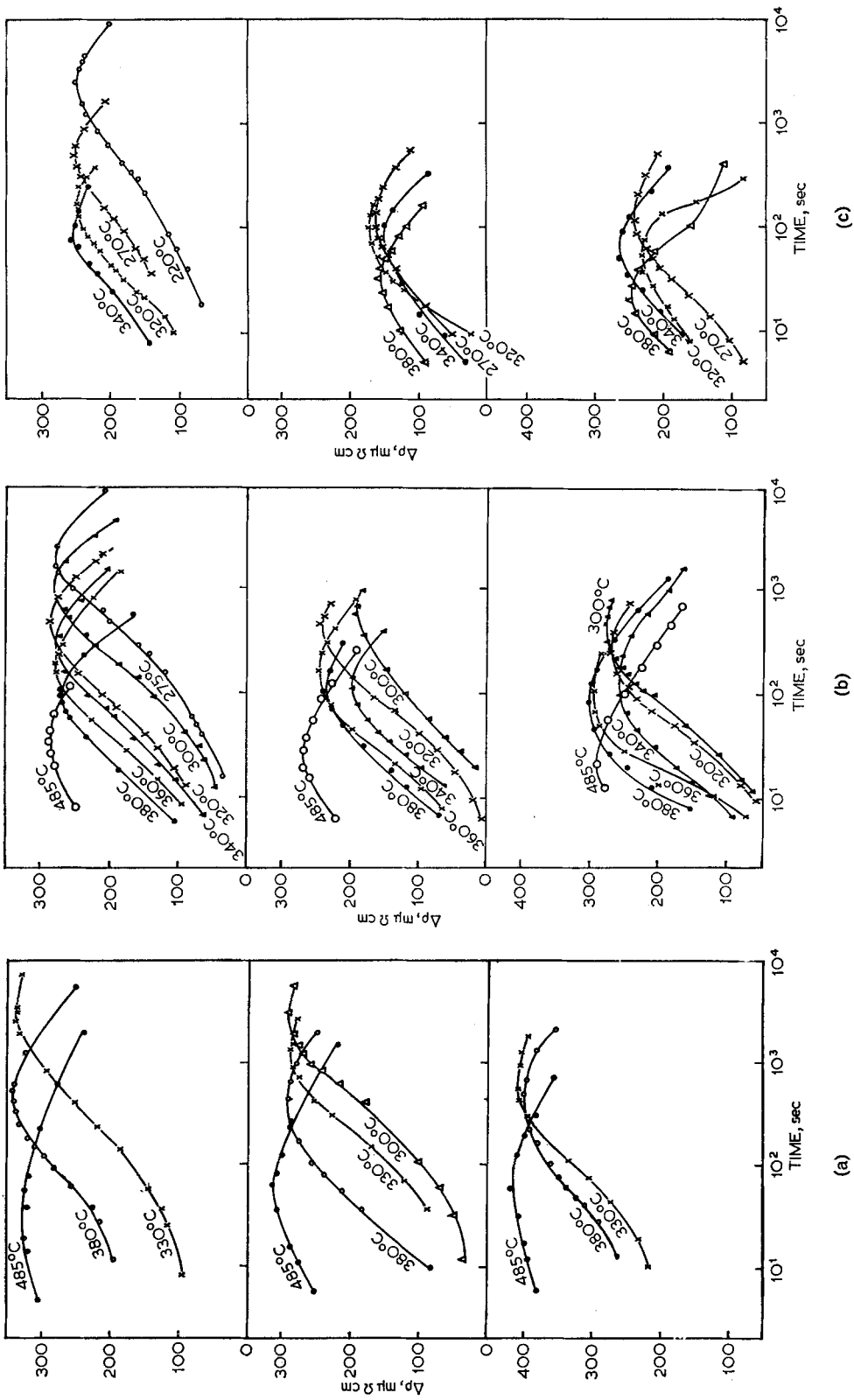
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Figure 3 Resistivity changes during isothermal ageing at different temperatures, after quench from a series of quenching temperatures in the three alloys. (a) Ageing at $T_A = -20°C$. (b) Ageing at $T_A = 0°C$. (c) Ageing at $T_A = 25°C$. Throughout: top, Al-4.4% Zn; middle, Al-4.4% Zn-0.03% Ag; bottom, Al-4.4% Zn-0.08% Ag.

kinetics of zone-formation in Al-Zn alloy. The nature of this influence will be discussed towards the end.

3.3. Isothermal Ageing
3.3.1. Effect of Quenching Temperature
Specimens quenched from a series of homogenisation temperatures were aged at − 20, 0 and 25° C, and the results have been summarised in fig. 3, and are in keeping with earlier findings by other authors [2-16, 21].

The increment in resistivity at the peak is almost independent of quenching temperature, but decreases with increasing ageing temperature. This is true for both binary and ternary alloys. A similar trend was reported for a number of ternary alloys based on Al-Ag, Al-Cu and Al-Zn by Hashimoto and co-workers [2-11], and for

Al-Zn-Mg alloys by Perry [14, 16]. But we earlier reported that in an Al-Zn-0.3% Be alloy [25-27], the magnitude of the resistivity peak is dependent on the quenching temperature, and this was interpreted as due to an interaction between the two solute species. In the present work, therefore, the independence of peak height of quenching temperature suggests that there is no appreciable interaction between Zn and Ag atoms in the quenched ternary alloy. However some X-ray evidence is needed to confirm this.

The times-to-peak can be used as a parameter to evaluate the activation energy for formation and migration in these alloys. The approach to peak is dependent on the number of quenched-in vacancies which, in turn (equation 1), is dependent on the quenching temperature (fig. 4).

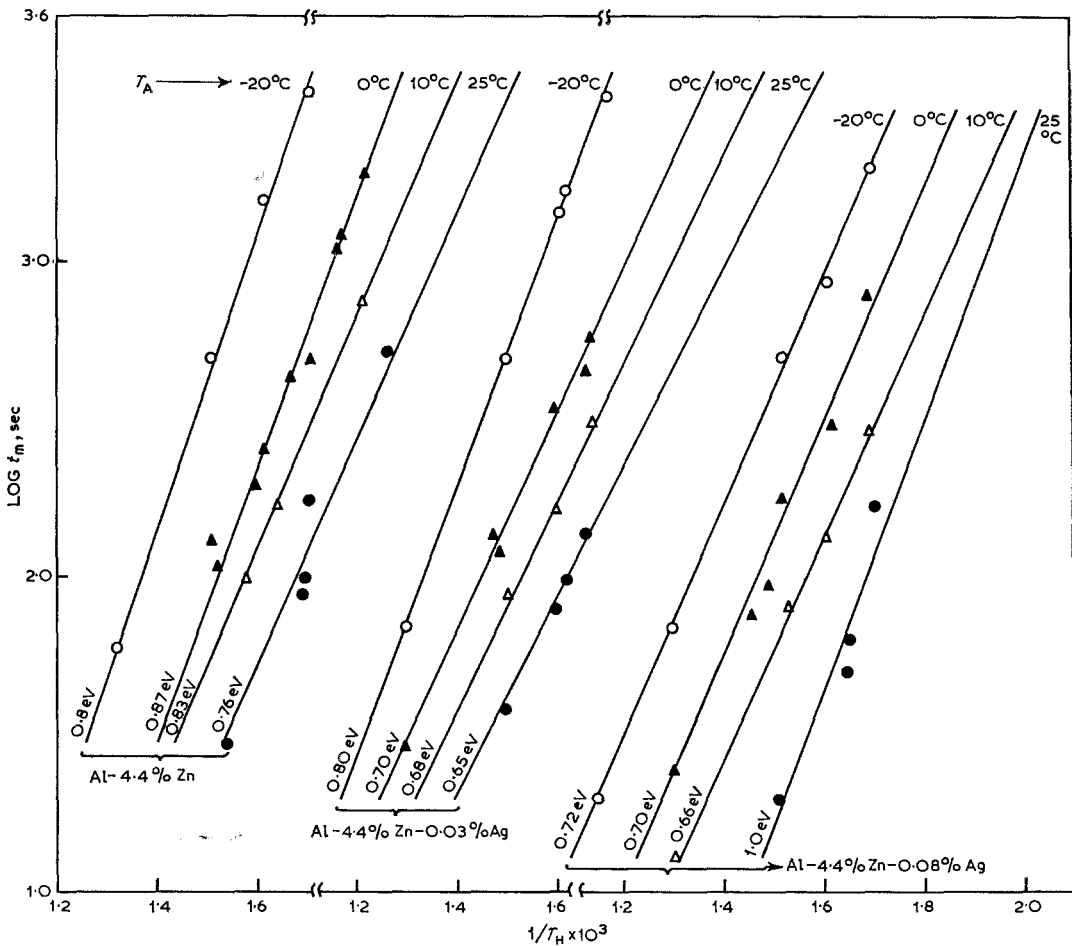We also evaluated the initial rate of ageing in

Figure 4 Activation plots of logarithm (times taken to reach the peak) against reciprocal quenching temperatures, for the three alloys.

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Figure 6 Plots of logarithm (times-to-peak) against reciprocal ageing temperature. ○—○ Al-4.4% Zn; △—△ Al-4.4% Zn-0.03% Ag; ●—● Al-4.4% Zn-0.08% Ag.

4. Discussion of Results

The isochronal and isothermal annealing data reported above clearly show that the presence of Ag atoms in the Al-Zn alloy does not appreciably alter the solute clustering process. However, the absence of a second resistivity decrease during the isochronal annealing of Al-Zn-0.08% Ag alloy, quenched from temperatures greater than 360° C (fig. 1), indicates that the nature of zones formed and their reversion on reheating depends on both the ternary solute concentration and the quenching temperature.

The dependence of resistivity-increment on quenching temperature as stated above cannot give an accurate estimate of the influence of Ag atoms on the kinetics of the clustering process, but the values of apparent activation energy evaluated from the Arrhenius-type plots (fig. 2) do indicate that there is a reduction in the value of the vacancy-formation energy; this means that Ag influences the kinetics to a certain extent. If we now compare the magnitude of the resistivity increments in the two ternary alloys, they are

higher than that in the binary alloy for all quenching temperatures. This can only indicate that the extent of clustering during the quench itself is even greater in the ternary alloy. At the point of quench, the resistivity is not only due to the arrested vacancies, but also due to the solute clusters formed, and any solute-vacancy pairs that may be formed. This is an indefinite factor, because the extent of quench-clustering depends on the quenching rate, which varies, even under identical conditions of quench, with quenching temperature and specimen size. It is however significant to note that the variation of $(\triangle \rho)$ quench with quenching temperature does follow an Arrhenius-type relationship.

The results obtained from isothermal ageing experiments will now be examined. The addition of a small amount of a ternary solute is assumed to trap the vacancies and thus cause a slowing down in the rate of clustering. For identical conditions of quenching and ageing therefore, the ternary alloy should age more slowly than the binary. From the ageing data given in fig. 3, it can be seen that there is a slowing down effect in the Al-Zn alloy by the addition of 0.03% and 0.08% Ag, but this occurs only above a certain quenching temperature (T_c), below which the ternary alloy ages faster than the binary alloy. The value of T_c depends on the concentration of the ternary solute as well as the ageing temperature. Thus, if we want to use the ratio of time-to-peak in ternary to that in the binary alloy to indicate the magnitude of the vacancy binding to Ag atoms as per equation 2, this ratio would vary with the temperature of quenching. The ageing ratio in this case continuously decreases with decreasing quenching temperature. Such a behaviour in the ternary alloy is quite normal as can be seen from the schematic diagram presented in fig. 7.

The formation energy in the ternary being smaller than that in the binary, the time-to-peak in the ternary alloy would be larger than in the binary for temperatures above T_c, but smaller than that in the binary alloy for temperatures below T_c. The temperature T_c at which the binary and ternary alloys age at equal rates (table II), varies with the ageing temperature as well as the ternary solute content.

As pointed out earlier, the dependence of the times to reach the peak in resistivity, or the initial rate of ageing on the quenching temperature [28] may be used to evaluate the activation energy for the formation of vacancies. The
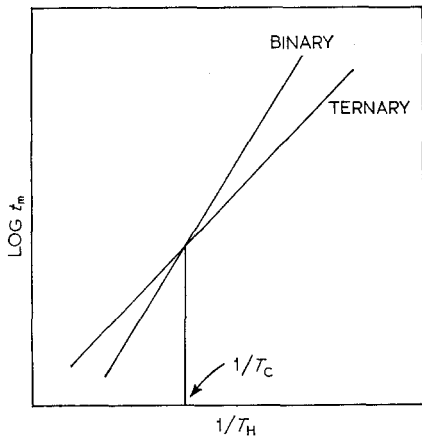
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Figure 7 Schematic diagram of log t_m vs. $1/T_H$ to show T_c.

evaluation of the activation energy by the times-to-peak method will however, be in error, as pointed out by Perry [14]. It is suggested that if, instead of considering the times-to-peak, the times taken to achieve given fractions of peak are used for the evaluation of vacancy-formation energy, then a plot of the formation energy values versus the respective fractions of peak extrapolated to zero ageing would give a corrected value. This has been done for the three alloys, to obtain the corrected values of formation energy. These values of formation energy were introduced in equation 1, with suitable modifications, to get the vacancy-solute atom binding energy. All the values are collected in table III.

The average value of v-Ag binding energy is evaluated as 0.21 ± 0.02 eV. This value is in good agreement with that obtained by Ohta and Hashimoto [4, 6, 7], who measured the effect of a third element of known binding energy on the ageing rate of Al-Ag alloy and back-calculated the binding energy of Ag using equation 1. In an earlier report [19], we had calculated the v-Ag binding energy to be 0.18 eV, by the ageing ratio method. The difference in the values reported then and the value calculated now is immediately apparent – that in Al-Zn-Ag ternary alloy, the ageing ratio is dependent on quenching temperature (fig. 7). This will lead to the inference that the vacancy distribution that takes place immediately at the point of quench is not independent of the relative vacancy distribution at the quenching temperature.

The fact that in certain ranges of quenching temperature, there occurs an acceleration in the ageing rate of a binary alloy by trace additions was indicated as an interesting case for study by Perry [14]. Murakami et al [29] observed an acceleration in the zone-forming process by ternary Zn and Mg additions in a Cu-2% Be alloy. However, there does not seem to be any particular significance that can be attached to the value of T_c evaluated above, although it may be pointed out that evaluation of T_c, which can be done for any set of alloys might help in obtaining solute-vacancy binding energy values that are unaffected by quenching and ageing temperatures.

The activation energy for migration of defects

TABLE II Maximum increase in resistivity ($\Delta\rho_m$) due to isothermal ageing, and values of quenching temperatures (T_c) at which the ternary alloys age at the same rate as the binary alloy at the indicated ageing temperatures

Ageing temperature, °C	Al-4.4% Zn $\Delta\rho_m$ m$\mu\Omega$ cm	Al-4.4% Zn-0.03% Ag $\Delta\rho_m$ m$\mu\Omega$ cm	T_c,°C	Al-4.4% Zn-0.08% Ag $\Delta\rho_m$ m$\mu\Omega$ cm	T_c,°C
−20	320	300	350	400	420
0	280	250	290	300	365
25	250	190	—	250	—
40	240	140	—	220	—

TABLE III Vacancy-formation energies and solute-vacancy binding energies

Alloy	from quenched-in resistivity	Vacancy-formation energy, eV from initial rate of ageing	from times-to-peak uncorrected	corrected	Solute-vacancy binding energy, eV
Al-4.4% Zn	0.59	0.58	0.81	0.70 ± 0.01	0.06 ± 0.02 (v-Zn)
Al-Zn-0.03% Ag	0.53	0.60	0.72	0.68 ± 0.01	0.21 ± 0.02 (v-Ag)
Al-Zn-0.08% Ag	0.52	0.60	0.70	0.64 ± 0.01	0.21 ± 0.02 (v-Ag)

in the three alloys works out to be 0.4 eV (fig. 6). This shows that the addition of Ag atoms does not influence the migration of Zn atoms in the alloy. The sum of the formation and the migration energies calculated above yields 1.0 to 1.1 eV for the activation energy E_D, for solute diffusion. This is in agreement with earlier reported values [30, 31]. The slightly smaller values obtained for the ternary alloys may indicate that the presence of Ag atoms may enhance the solute diffusion, thereby decreasing the value of E_D. The above results also suggest that the different types of vacancy-solute complexes formed in the ternary alloys are not very different from those formed in the binary, and that the solute diffusion during the initial stages of ageing in all these alloys is still largely controlled by the excess vacancies retained by the quench.

Ohta et al [7], from their studies on the effect of a third element on the initial ageing of Al-4.4% Zn alloys classified the elements into three groups as follows: (i) those that lower the ageing rate; (ii) those which do not affect the ageing rate; and (iii) those which influence the ageing rate besides interacting with Zn atoms, thus forming ternary zones.

Ag, Cu and Mn were in group (ii). It is possible that the quenching and ageing temperatures used by them (340 and 20° C respectively) for the Al-4.4% Zn-0.03% Ag alloy was near the respective T_c, so that the clustering rate was not influenced. In fact, in the present study, the Al-Zn-0.03% Ag alloy quenched from 300° C, (T_c for this alloy) and aged at 0° C, showed the same ageing rate as in the binary alloy (fig. 8). Similarly the Al-Zn-0.08% Ag and the Al-Zn alloy quenched from 370° C ($T_c = 365$° C for this alloy) aged at equal rates.

In kinetic studies of the above type, it is therefore necessary to make detailed investigations regarding the effects of quenching and ageing temperatures, and also the effect of temperature on the relative distribution of solute atoms and vacancies. An understanding of the exact nature of the influence of temperature on the binding energy is essential to permit comment about the ageing behaviour of ternary alloys, after quench from different temperatures. The presently available theories cannot explain how the same element can cause both acceleration and slowing down of the clustering rate in the binary alloy.

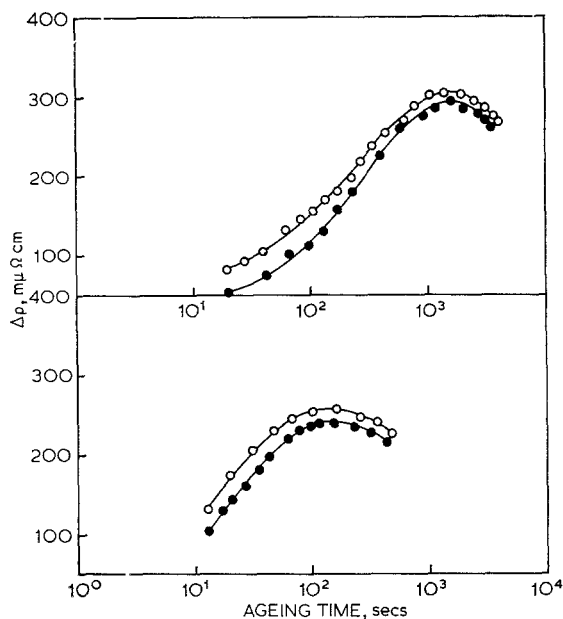In view of the fact that in the Al-Zn-Ag alloys,

Figure 8 Isothermal ageing curves for binary and ternary alloys, after quench from respective critical temperatures, showing that the two alloys age at equal rates. Top: ●—● Al-4.4% Zn; ○—○ Al-4.4% Zn-0.03% Ag; $T_H = 300$°C; $T_A = 0$°C. Bottom: ●—● Al-4.4% Zn; ○—○ Al-4.4% Zn-0.08% Ag; $T_H = 370$°C; $T_A = 0$°C.

both Ag and Zn have atom sizes very close to that of Al atoms, the chief contribution to the binding energy must be the electronic one. We have inferred above, from isothermal resistivity data, that there is no interaction between Zn and Ag atoms. The smallness of the effect of Ag on the ageing process in the Al-Zn alloy may lead one to think intuitively that both Zn and Ag form clusters separately, and simultaneously; particularly when the Ag concentration is appreciable. That this is so can only be confirmed from X-ray and electron-microscopy studies.

5. Conclusions

Al-Zn-Ag alloys provide an interesting case for studying the clustering process because both Al-Zn and Al-Ag systems exhibit similar ageing characteristics and both Zn and Ag atoms have atom diameters close to that of Al.

The presence of Ag atoms influences the kinetics of the ageing process in the Al-4.4% Zn alloy, but not the general ageing characteristics.

The zone-reversion process, indicated by the isochronal annealing experiments, seems to be influenced by both the quenching temperature and the Ag content in the ternary alloy.

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The influence of Ag on the clustering process is dependent on both the quenching and the ageing temperatures; above a certain quenching temperature T_c, there is a slowing-down effect, while below this temperature, there is an acceleration. The temperature at which there is no effect on the clustering rates is dependent on ageing temperature and Ag concentration.

Comparison of formation energies in the binary and ternary alloys yields 0.21 ± 0.02 eV as the average v-Ag binding energy. The activation energy for solute diffusion in the alloys is about 1.1 eV, indicating that diffusion in these alloys is also largely by a vacancy-aided mechanism. It is suggested that Zn and Ag form clusters independently.

Acknowledgement

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