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A Resistometric Study of Excess Vacancies in Al—Cu—Mg Alloys

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SUMMARY

Zone formation in Al - 3 wt.% Cu - 1 wt.% Mg alloys has been studied by resistivity technique, with a view to investigating the nature of excess vacancies in these alloys. Excess vacancies in these alloys are very strongly bound. The zones forming in these alloys are likely to be rich in vacancy concentration. When quenching of a solution treated alloy is interrupted for a minute above zone solvus temperature, the mode of vacancy annealing during interruption above 380°C is probably different from that below 300°C. In certain cases of interruption of the quench a diffusional barrier to zone formation has been observed and a mechanism for this has been proposed.

1. INTRODUCTION

Large supersaturation of vacancies and solutes can be obtained by quenching an age-hardenable aluminum alloy from the single phase to the two phase region of the phase diagram. Annealing out of these excess vacancies continues during quenching and aging, and the movement of the quenched-in vacancies accelerates the rate of zone formation. The mechanism of diffusing out of these excess vacancies may be modified by the solute vacancy interactions prevailing in the alloy system.

In Al - Cu - Mg alloys dislocation loops and helical dislocations are known to form by vacancy condensation [1,2], their size and number depending on composition, quenching rate and aging temperature. Although Sen and West [3] have reported an increase in quenched-in vacancy concentration in these alloys with increasing quenching rate, detailed investigation by electron microscopy [1] shows that the effect of quenching rate on clustered vacancy concentration is usually small.

Excess vacancies may modify the mechanical properties of aluminum alloys by altering the zone formation and precipitation characteristics. But, for Al - Cu - Mg alloys aged at room temperature, the tensile properties remain insensitive to the quenching rate [1]. However, Silcock [4] and Rajan [5] have observed an increase in peak hardness at 130 - 200°C with decreasing quenching rate, although a reverse trend has been noted by Sen and West [6].

A detailed study of the behaviour of excess vacancies by using resistivity techniques in complex systems like Al - Cu - Mg is not generally favoured because the resultant data are too complicated owing to superimposing effects of (a) solute depletion, (b) scattering by zones and (c) complexities of interactions of solutes and vacancies. The zones cause a resistance increase which masks the increase caused by quenched-in excess vacancies themselves. It has been proposed by Entwistle and Perry [7] that if the vacancy aided zone growth model is accepted, the rate of zone formation itself is a measure of the vacancy concentration. Thus, in the present investigation, zone formation in Al - Cu - Mg alloys has been measured by using a resistivity technique, to study the nature of excess vacancies in these alloys. In particular, the mechanism of vacancy annealing

TABLE 1

Composition of the alloys (wt.%)

Alloy	Cu	Mg	Si	Fe	Ag	Al
A	2.95	1.08	0.13	0.08	0.23	Bal.
B	3.07	1.05	<0.01	<0.01	—	Bal.

that occurs during isochronal interruption of quenching has been investigated.

2. EXPERIMENTAL

The chemical composition of the alloys is listed in Table 1. The alloys were chill-cast, homogenised for 24 hours at 450°C, hot forged to 15 mm square rods and later to 5 mm thick slabs.

Wires of 0.6 mm diameter were used for resisitivity measurements. The specimens were solution treated in air for 24 hours at 500°C ±5 degC. Quenching was performed by simply dropping the specimen into water at 30°C, unless otherwise stated. The specimen was transferred to an ice bath within 3 seconds of quenching. The quenching could be interrupted by dropping the specimen from 500°C into a salt bath for a minute and then rapidly transferring the specimen into water at 30°C; the time taken during this transfer was about one second. The temperature of quench-interruption (T_i) was always above the zone solvus temperature ($T_{G.P.}$) of these alloys [8]. In certain cases the salt bath temperature was the same as the solution treatment temperature. The aging was carried out in an oil bath and the aging temperature (T_A) was controlled to ±0.1 degC.

The resistances were measured with a Kelvin double-bridge and all measurements were made at 0°C using an ice bath. With this set-up ($\Delta\rho/\rho$) minimum up to 10^{-5} could be measured and the data have good reproducibility.

3. RESULTS

The alloys are aged isothermally and variations of the resistivity of alloy A at 70°C and 150°C and of alloy B at 150°C against time are plotted in Figs. 1 - 3. The effects of prior quenching in water or acetone or interrupting the quench at different T_i on the resistivity of the alloys have been demonstrated here. The

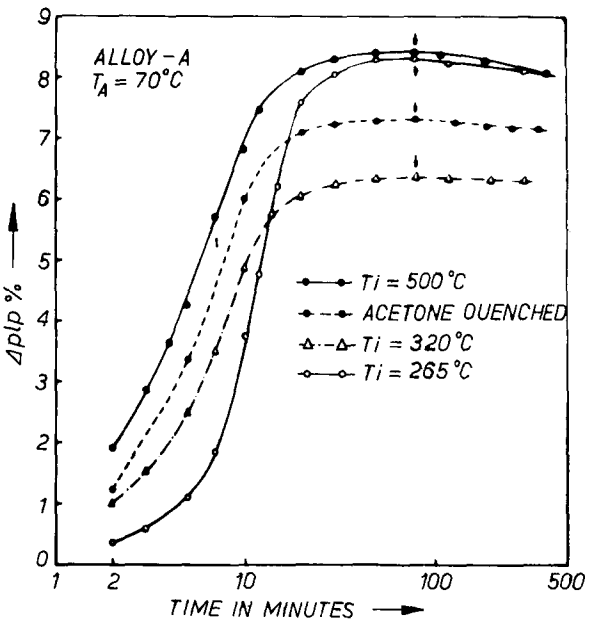

Fig. 1. Variation of resistivity of alloy A with time at 70°C, following pretreatments as indicated; the arrows indicate the resistivity-peak positions.

plots show the typical increase in resistivity which is indicative of zone formation. Zone formation may occur during quenching and aging. However, when the alloys are quenched

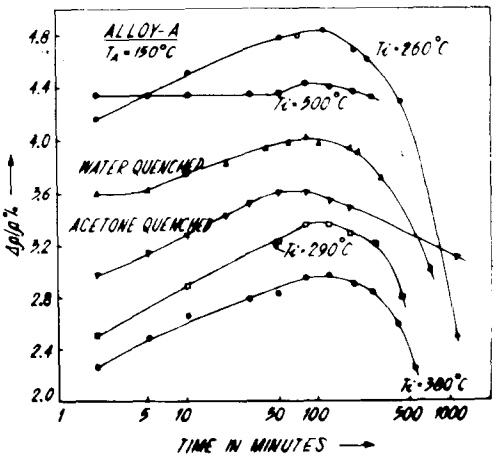

Fig. 2. Variation of resistivity of alloy A with time at 150°C, following pretreatments as indicated.

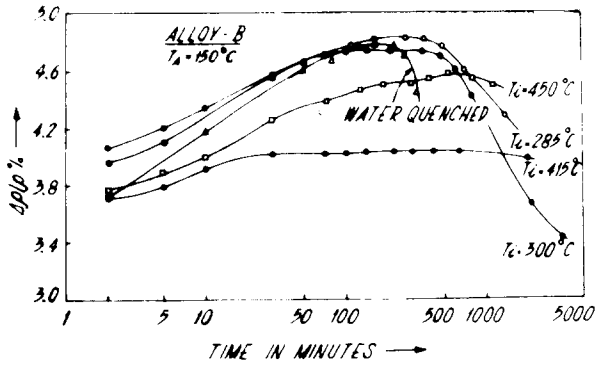

Fig. 3. Variation of resistivity of alloy B with time at 150°C, following pretreatments as indicated.

into acetone, the as-quenched resitivity decreases by less than 0.05% (not shown in figures) and a decrement of the peak resistivity as compared with the water quenched specimen results (*cf.* Figs. 1 and 2). With slower quenching rates, the concentration of quenched-in vacancies usually decreases and more time is available for zone formation during quenching. The results of acetone quench, therefore, indicate that zone formation in these alloys during quenching is negligible.

Zone formation during aging is likely to be modified by a change in vacancy configuration by quench-interruption. However, from the resistivity plots (*cf.* Figs. 1 - 3) it may be clearly seen that the resistivity peak changes considerably owing to the prior quench interruption, although the time to reach the peak remains virtually unaffected. For any particular aging temperature the variation of the resistivity maxima, $(\Delta\rho/\rho)_{max}$, with quench interruption temperature is plotted in Fig. 4. It is found that the peak resisitivity first decreases with decreases of T_i up to 300°C. However, when T_i is less than 300°C, an increase in zone density is observed.

For aging of alloy A at 70°C, the rate of increase in resistivity ($d\rho/dt$) is calculated numerically from the measured values and plotted against the time of aging in Fig. 5. The following points may be noted from this plot:

(i) When the alloy is quenched from the salt bath kept at solution treatment temperature, *i.e.* for T_i = 500°C, the aging rate continually decreases and the maximum aging rate is higher than that following the quench-interruption at $T_i < 500$°C.

(ii) For T_i = 265°C, the zone formation rate is small to begin with, increases to a maximum and then decreases continually.

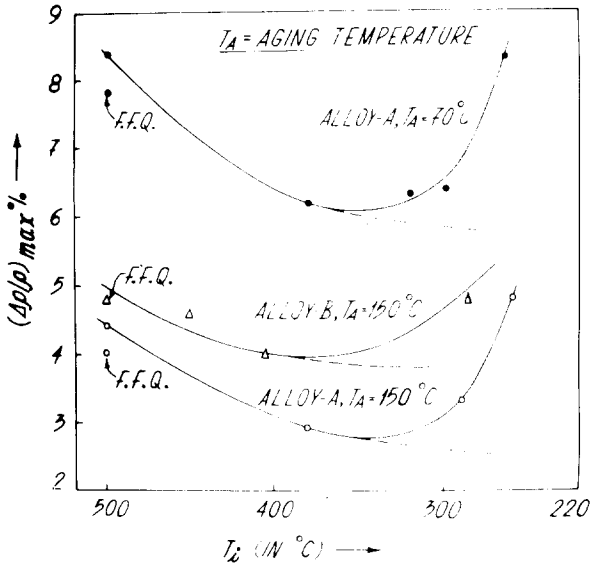

Fig. 4. Variation of resistivity maxima of isothermal aging with the temperature of quench interruption; F. F. Q. corresponds to aging following a free-fall-quench into water from 500°C.

(iii) The maximum rate aging, $(d\rho/dt)_{max}$, is greater when T_i is 265°C than when T_i is 320°C.

In fact, the aging rate is lowest for T_i = 300°C and an approximate calculation shows this reaction rate to be about twenty times faster than the rate in the presence of equilibrium

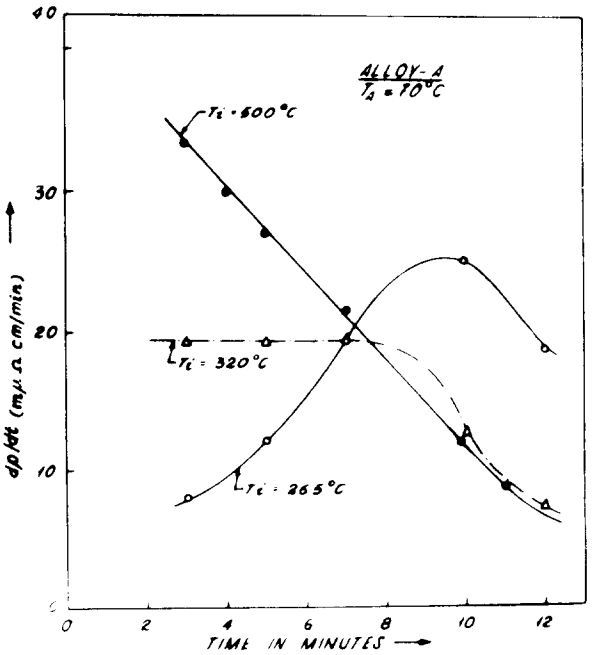

Fig. 5. Rate of increase in resistivity during zone formation as a function of time.

concentration of vacancies at 300°C. Thus, the quenched-in vacancy decay time in these alloys is very large. The vacancies in these alloys are very strongly bound by solute atoms or zones.

The ascending part of the resistivity curves of alloy A aging at 70°C is fitted to an equation

$$X = 1 - \exp\left(-\frac{t}{t_{max}}\right)^m \quad (1)$$

where $X = \Delta\rho/\Delta\rho_{max}$.

t_{max} = time required to reach resistivity peak, and this yields a value of $m = 0.95$ for specimens quenched from 500°C. With a decrease of T_i, m continually increases; when T_i is 320°C, m has a value equal to 1.2; for T_i = 265°C, $m = 1.2$ up to about 7 minutes of aging, after which m increases to 2. Hence, the aging reaction following quench interruption at different temperatures is not isokinetic.

4. DISCUSSION

The exact relationship between the zone size and the resistivity is not known. In the present study it is assumed that during the early stage of aging, the resistivity change is predominantly controlled by the rate of zone formation. Moreover, the resistivity peak is believed to occur at a critical zone size [9,10]. Hence, the time to attain resisitivity peak is related to a given degree of aging, provided that the zone size distribution does not change. Thus, the height of the resistivity peak may be taken as a measure of the zone density.

The zone density of the alloys currently investigated changes considerably with T_i (*cf.* Fig. 4). The effect may be attributed to (i) diffusing out of excess vacancies and (ii) solute depletion due to precipitation that occurs during holding at the quench-interruption temperature. However, it may be noted that at 70°C the zone density in alloy A is the same as that of an uninterrupted quench (*i.e.* T_i = 500°C). Therefore, the overall solute supersaturation is not affected by the quench-interruption at 265°C. Also, the change in the shape of the reaction rate curves (*cf.* Fig. 5) and the value of 'm' in eqn. (1) that occur owing to the quench interruption cannot be explained by solute depletion during holding at T_i. Hence, at any particular aging temperature, the zone density is predominantly controlled by the vacancy annealing mechanism that is operative during the prior quenching operation.

The dependence of zone density on vacancy configuration suggests possibly that vacancies are present as a chemical constituent of the zones forming in these alloys. The hardness data of Sen and West [6] support such a hypothesis. Moreover, stress induced rearrangement of clusters of solute atoms has also been observed in Al - Cu - Mg - Si alloy and the greatly accelerated rate of ordering has been attributed by Berry [11] to the presence of excess vacancies at the zones.

For any particular aging temperature the plot of zone density against T_i yields a U-shaped curve (*cf.* Fig. 4). As T_i decreases, more and more excess vacancies are annihilated and therefore the zone solvus line would shift downwards [12,13] as schematically shown in Fig. 6. The effective solute supersaturation will decrease with a decrease of T_i and the zone density during subsequent aging lowered. However, if the same mode of vacancy-precipitation is operative at all T_i, the curves in Fig. 4 would have been monotonic as shown by the dashed line in the diagram. Deviation from the monotonic trend probably indicates that the mode of vacancy-precipitation at $T_i < 300$°C is different from that at $T_i > 380$°C. The mechanism of vacancy-annealing at $T_i < 300$°C may be similar to that proposed by Turnbull [14] and Kimura [15]; the vacancies may be trapped at small vacancy clusters or dislocation loops during interruption of the quench at a temperature where zones are not forming. These loops can act as sources of vacancies at the aging temperature by shrinking. That the vacancy sinks operative at $T_i < 300$°C are aiding zone

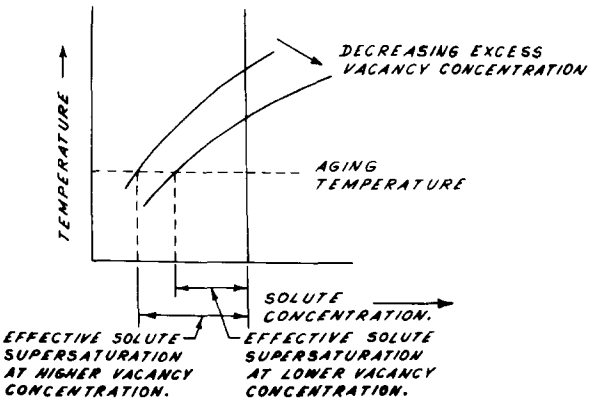

Fig. 6. Schematic illustration of the change in solute supersaturation with excess-vacancy concentration.

formation after an initial transition period, is supported by the present data. The $(d\rho/dt)_{max}$ is higher for T_i = 265°C than that for T_i = 320°C (*cf.* Fig 5) which implies that more vacancies are retained at the former T_i. But the initial sluggish rate of zone formation at T_i = 265°C may be attributed to some diffusional barrier to zone formation which may result from the temporary 'locking' of excess vacancies at the sinks operating at $T_i < 300$°C.

5. CONCLUSIONS

In Al - Cu - Mg alloys quenched-in excess vacancies are very strongly bound. In these alloys zone density is sensitive to the vacancy configuration. The zones forming in these alloys are likely to contain excess vacancies in themselves. For aging at any particular temperature, variation of zone density with temperature of isochronal quench-interruption is not monotonic. When quenching is interrupted for a minute at temperatures above $T_{G.P.}$, the mode of vacancy-precipitation at $T_i < 300$°C is different from that at $T_i > 380$°C. The vacancy sinks operative at $T_i < 300$°C are probably aiding zone formation after an initial transition period and a mechanism of action of these sinks has been proposed.

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REFERENCES

1 D.L. Robinson and M.S. Hunter, Met. Trans., 3 (1972) 1147.
2 R.N. Wilson, J. Inst. Metals, 97 (1969) 80.
3 N. Sen and D.R.F. West, J. Mater. Sci., 3 (1968) 266.
4 J.M. Silcock, J. Inst. Metals, 89 (1960 - 61) 203.
5 T.V. Rajan and M.N. Saxena, Indian J. Technol., 7 (1969) 348.
6 N. Sen and D.R.F. West, in The Mechanism of Phase Transformation in Crystalline Solids, Inst. Metals Monograph No. 33, Inst. Metals, London, 1969.
7 K.M. Entwistle and A.J. Perry, J. Inst. Metals, 94 (1966) 24.
8 S.K. Pabi and A.K. Mallik, to be published.
9 N.F. Mott, J. Inst. Metals, 60 (1937) 267.
10 H. Herman, J.B. Cohen and M.E. Fine, Acta Met., 11 (1963) 43.
11 B.S. Berry, Acta Met., 7 (1959) 741.
12 D.W. Pashley, M.H. Jacobs and J.T. Veitz, Phil. Mag., 16 (1967) 51.
13 M.S. Jacobs and D.W. Pashley, The Mechanism of Phase Transformation in Crystalline Solids, Inst. Metals Monograph No. 33, Inst. Metals, London, 1969.
14 D. Turnbull and R.L. Cormia, Acta Met., 8 (1960) 747.
15 K. Kimura and J. Okamoto, Mater. Sci. Eng., 4 (1969) 39.