Letters

Zone formation during room temperature ageing of Al–4% Cu–0.8% Si–0.8% Mg

In a recent publication [1] the variation of the hardness of a complex aluminium precipitative hardening alloy, of the L70 type and of composition Al–4% Cu–0.8% Si–0.8% Mg–0.7% Mn–0.5% Fe*, with ageing time at 130, 160 and 190° C was correlated with transmission electron microscope observations of precipitate morphology. It was established that the peak hardness after both 160 and 190° C ageing was associated with coherent θ' precipitate particles and the subsequent limited overageing at these temperatures was controlled by the slow growth of θ' particles. In contrast, ageing at 130° C gave a series of hardness time plateaus, which were ascribed to the sequential precipitation of GPI zones, θ'' and θ' precipitate. However, at all three ageing temperatures and particularly at 130° C, there was evidence during the inital stages of ageing for the formation of complex zones of the GPB type (Al–Cu–Si–Mg), as well as GPI zones. In this note, the precipitation hardening of Al L70 at room temperature is reported and correlated almost entirely with the formation of GPB type zones.

Specimens of Al L70 in sheet form (thickness = 1.25 mm) were solution treated at 500° C for 2 h and quenched into water at room temperature. At this temperature, the specimens age hardened, as shown in Fig. 1, with the hardness increasing from an as-quenched value of 87 VHN to a maximum value of 133 VHN after 48 h and then remaining constant for times up to 1000 h. For comparison, the previous results [1] on ageing at 130, 160 and 190° C are also plotted. It can be seen that initially the room temperature results closely parallel those measured after 130° C ageing. Thin foils were prepared from the quenched and room temperature aged specimens and examined in a JEOL–JEM 7 electron microscope. A micrograph typical of all the conditions examined, from ~ 1 to 1000 h, at room temperature, is shown in Fig. 2. It can be seen that:

(1) the dislocations were in the form of helices, with variable diameter (650 to 1800 Å) and pitch. Orientation measurements indicated that the helices were parallel to the projections of ⟨1 1 0⟩ on the foil surface;

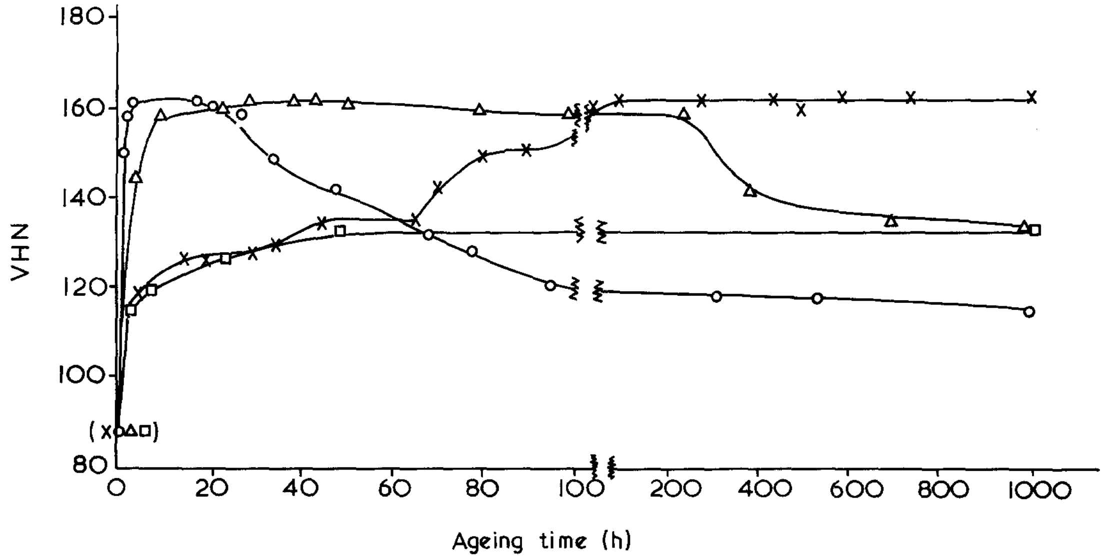

Figure 1 Hardness (VHN) versus ageing time at room temperature (□) compared with ageing at 130° C (+), 160° C (△) and 190° C (○). (Note change in scale at 100 h.)

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* wt %.

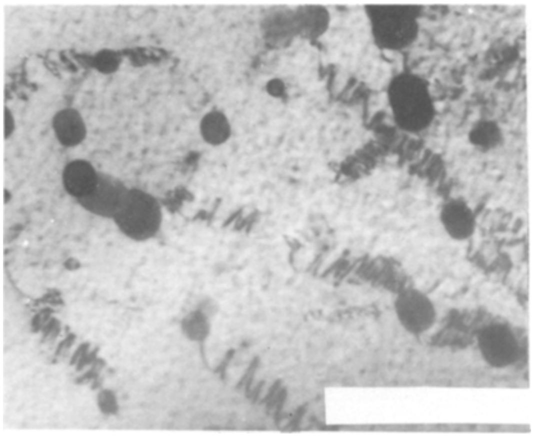

Figure 2 Helical dislocations, insoluble particles and mottled background in a room temperature aged specimen. (1 μm marker.)

(2) there was a complete absence of vacancy loops;

(3) numerous irregular particles remained after the solution treatment. These particles did not change in size during ageing;

(4) the background contained a fine mottled structure. However, the corresponding selected-area diffraction patterns did not reveal either the characteristic ⟨1 0 0⟩ streaking associated with GPI formation or any evidence for θ'', θ' or S′ precipitates. Hence, it appears that the hardening during room temperature ageing is associated with a complex zone of the GPB type which produces small lattice strains [3, 4].

We may assume that the helical dislocations were formed by the climb of screw dislocations with an associated total vacancy concentration (C_v) given by:

$$C_v = \pi r^2 N b \qquad (1)$$

where r is the helix radius, N is the number of turns per unit volume and $\boldsymbol{b}$ is the Burgers vector. Substituting values measured from Fig. 2 in Equation 1, gives the vacancy concentration required to produce the observed climb as between 1×10^{-4} and 8×10^{-4}. This value is less than the total solute atom concentration of Al L70. The subsequent stability of the helical dislocations during room temperature ageing (and under the electron beam), suggests that the vacancies producing climb were associated with solute atoms, which effectively pinned the dislocations prior and during zone formation. This effect would be in addition to the local pinning provided by the insoluble particules. It may also be concluded from the absence of vacancy loops during ageing, that the solute atom–vacancy interaction was sufficient to prevent vacancy clusters exceeding the critical number, suggested as ~ 10 vacancies for aluminium [5], required for collapse into a vacancy loop.

The solute atoms contributing to this process are likely to be Cu, Mg and/or Si, which are expected to remain largely in the quenched, supersaturated solid solution. (The solubility of Si in Al at 500° C is 0.8%, a level which is not affected by the presence of Cu and only slightly reduced by Mg, and the solubility of Mg in Al at 500° C is $\gg$ 0.8%, while Si does not precipitate at $< 190°$ C [6] or Mg_2 Si at $< 300°$ C [7, 8].) In contrast Fe and Mn are likely constituents of the particles which are insoluble at the solution treatment temperature.

The partition of vacancies between the Cu, Si and Mg solute atoms depends on the atomic concentration of the elements (C_{Cu}, C_{Si}, C_{Mg}), the solute atom–vacancy binding energies (E_{bCu}, E_{bSi}, E_{bMg}) and absolute temperature (T). Following [4] we assume that:

(1) all the Cu, Si and Mg atoms are in solid solution, with $C_{Cu+Mg} = 2.7$ at.% and $C_{Si} = 0.9$ at.%;

(2) the solute atom–vacancy binding energy is greater for Si than for Mg and Cu, with values of 3.2×10^{-20}, 1.6×10^{-20} and 1.6×10^{-20} J for E_{bSi}, E_{bCu} and E_{bMg}.

Then the partition of vacancies between (Cu + Mg) atoms ($C_{V(Cu+Mg)}$) and Si atoms (C_{vSi}) is given by [9]:

$$\frac{C_{v(Cu+Mg)}}{C_{vSi}} = \frac{C_{(Cu+Mg)}}{C_{Si}} \cdot \exp\frac{(E_{b(Cu+Mg)} - E_{bSi})}{kT}. \qquad (2)$$

Substitution in Equation 2 shows that at room temperature 6% of the vacancies are associated with (Cu + Mg) atoms and 94% with Si atoms.

Hence it is concluded the favourable partition of vacancies to silicon atoms in Al L70 at room temperature markedly alters the defect structure from that of the binary Al–Cu alloys and prevents formation of vacancy loops. It would also follow that the silicon atom vacancy association contributes to the zone formation during ageing, with a resultant GPB type zone of Al–Si–(Cu–Mg), rather than of a GPI (Al–Cu) zone.

GPB zones have also been noted [4] in the room temperature ageing of Al–2.5% Cu–1.2% Mg–0.24% Si, but in association with GPI zones. This result is consistent with the present findings as the partition of vacancies to silicon atoms was somewhat less favourable (~ 80%, cf.94%). The comparison may be further examined by utilizing the temperature dependence of the partition of vacancies given by Equation 2, as an increase in the ageing temperature of Al L70 to 130° C would reduce the partition of vacancies to silicon to 83%. Hence it is significant that GPI zones were tentatively identified during 130° C ageing of Al L70 and definitely established during higher temperature ageing (160 and 190° C).

These results suggest that the transformation from GPB zones to S′ precipitate, which has not been hitherto observed in Al L70, may be favoured at ageing temperatures between room temperature and 130° C, with the consequent possibility of novel properties for this commercially significant alloy.

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The topotactic decomposition of calcite group carbonates

The structural transformation which occurs in the decomposition of calcite group carbonates was reported [1] to exhibit conservation of the hexagonal layers, but elsewhere, [2], it was shown that the $(1 0 \bar{1} 4)_c$ cleavage faces become the $(1 1 0)_o$ plane family of the oxide. (c = carbonate, o = oxide). These two results are contradictory. In a study of the two-fold transformation of calcite crystals into oxide and then into hydroxide one of us [3] also found preferential orientations which cannot be explained by [1] and so a new study was appropriate.

The texture of the "pseudomorphs" which result from the decomposition of cadmium carbonate crystals has been completely investigated. The results of this investigation and their interpretation will be summarized here and these interpretations, supported by correlations between the two structures, will be published in more detail later [4].

The X-ray diffraction patterns of the decomposed crystals were obtained with the $[0 0 1]_c$ axis of the habit oriented along the rotation axis of a cylindrical camera, and with no crystal oscillation occurring during the exposures. The layer-lines of the patterns (Fig. 1) reveal a fibre texture in which the fibre axis shows a "pseudo-triad symmetry".