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Short Communication

EVIDENCE FOR GP-ZONE FORMATION IN AN Al-3% Zn ALLOY

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The presence of small GP-zones in an Al-3 wt% Zn solid solution aged at temperatures below 80° is inferred from calorimetric reversion studies, although this composition lies outside the miscibility gap of the accepted phase diagram. The size of the zones is about 1 to 1.5 nm, as measured by high resolution electron microscopy.

A phase diagram study of the Al—Zn system has been published in 1983; figure 1 shows the solubility curves of the stable and metastable phases according to the extensive literature survey of Murray [1]. The α-solvus has only been determined above 2.2 at% Zn (110°). The coherent metastable miscibility gap in which Guinier–Preston zones (spherical, ellipsoidal GP-zones, α'_R-phase) appear has been plotted at the aluminium-rich side using data derived mainly from X-ray, electrical resistivity and thermoelectric power measurements.

No metastable phase should precipitate during room temperature (RT) aging of Al-alloys containing $\leq$3 wt% Zn. The present work reports experiments performed on an Al-3% Zn alloy which show, however, the existence of a small quantity of GP-zones. These have been detected by calorimetry and observed by high resolution electron microscopy.

Experimental

An Al-alloy of the following composition was kindly prepared and analysed by Cégédur–Péchiney: (3.0$\pm$0.1) wt% Zn or 1.26 at% Zn, 0.0026 wt% Fe, 0.0028% Si, 0.0037% Cu, <0.001% Mg, <0.002% Ti, <0.001% Cr, <0.0005% Mn. The 1 mm

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thick specimens were first homogenised at 400° for 6 h, then at 275° for 1 day before being air-cooled to RT. Most of the samples were rapidly introduced into a differential microcalorimeter of the Tian–Calvet type operating at 30°. Other air-cooled specimens were kept at RT for 4 weeks, or at 40, 60, 80 and 100° for 5 days,

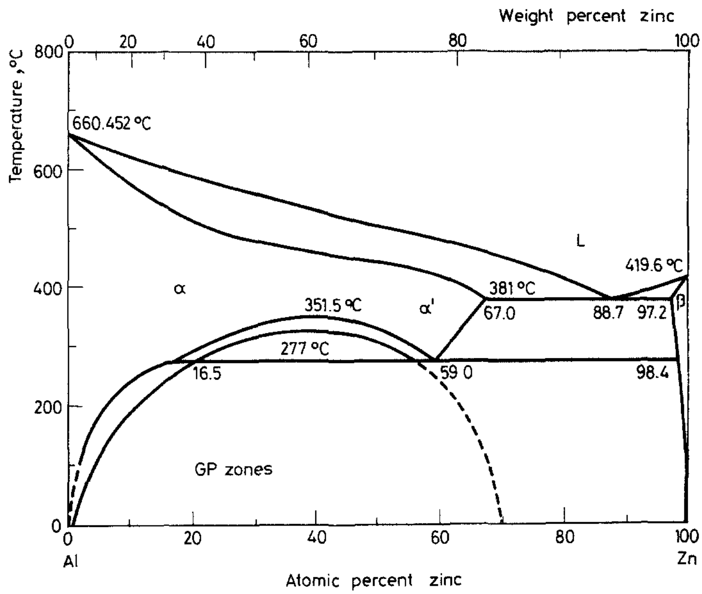

Fig. 1 Phase diagram of the Al—Zn system redrawn from [1]

before being analysed by differential scanning calorimetry (DuPont, model 990), at a heating rate of 20 K min^{-1}; the RT-aged samples were also studied by electron microscopy. For this purpose, they were thinned by electropolishing at −20° in a solution of 25% nitric acid and 75% methyl alcohol, using a Struers apparatus (model Tenupol). The foils were examined under an electron microscope Jeol 200 CX operating at 200 kV (spherical aberration coefficient: 1.05 mm).

Results

1. Calorimetric studies

By isothermal microcalorimetry, a heat release may be observed for up to 5 h when air-cooled solid solutions are examined at 30°. It follows that the Al-3% Zn alloy already lies slightly inside the coherent miscibility gap and exhibits formation of GP-zones, the only phase which appears on low temperature aging. As the heat release is strongest at the very beginning of aging, when no calorimetric measurements are possible, it is necessary to determine the total heat effect by DSC: samples aged at different temperatures were heated in the analyser to about 170°. Figure 2 represents the curves obtained on solid solutions kept for 5 d at RT (A), 40°

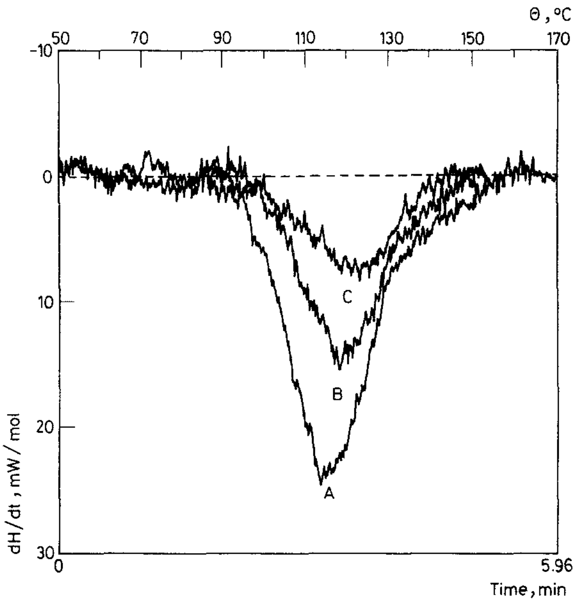

Fig. 2 Thermal effects accompanying the dissolution of GP-zones in an Al-3% Zn alloy aged for 5 d at RT (A), 40° (B) or 60° (C). DSC scans at 20 K min^{-1}

(B) or 60° (C); the heat effects dH/dt which accompany the reversion of GP-zones are plotted as function of time or temperature. Dissolution enthalpies of 1.9 (A), 1.0 (B) and 0.6 $J \cdot mol^{-1}$ (C) are obtained by integration. The noise of the apparatus becomes visible at the high magnification used, but the existence of a reversion process is beyond doubt. It no longer appears, if the alloy has been aged at 80 or 100°.

2. Electron microscopic observations

It is rather difficult to reveal the presence of GP-zones in this alloy, as their dimensions and volume densities are quite small. High magnification images obtained with a large objective aperture ($\sim 10^{-2}$ rad) allow observations of GP-zones by phase contrast, as previously reported [2]. In the present case, the best images have been achieved by high resolution electron microscopy with (111) planes near a diffraction position giving rise to the formation of lattice fringes in a symmetrical position. GP-zones have been detected in different regions of the sample. It can be seen from figure 3 that they do not exist to the right of the dislocation line shown on this micrograph; this may be related to a possible motion of the dislocation within the sample. Although the observed image has not yet been

Fig. 3 High resolution image showing the (111) plane lattice fringes (taken in symmetrical position). GP-zones are visible as dark spots of irregular shape extending over several lattice fringes. A dislocation is also present, to the right of which GP-zones are absent over some distance

compared with a computed image, it is likely that at small defocuses the reticular distance on the lattice image allows an estimation of the sizes of the GP-zones; they are about 1 to 1.5 nm in width.

Conclusions

The formation of GP-zones in aluminium alloys containing 15, 10 [3–5], 7 [6] and 6 [7] wt% of zinc has been previously examined by means of thermal measurements, diffraction contrast, phase contrast and high resolution electron microscopy. The present calorimetric studies indicate the existence of a very small amount of a coherent phase even in Al-3% Zn alloys aged below 80°. These GP-zones have not been detected by measurements of other physical properties but are confirmed by electron microscopic observations. High resolution electron microscopy shows that their sizes are about 1 to 1.5 nm.

It is evident from fig. 1 that the highest temperature of GP-zone formation in Al-3% Zn alloys (~80°) lies closer to the extrapolated α-solvus than to the proposed GP-zone solvus. The metastable phase boundary needs to be reinvestigated carefully.

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