Effect of matrix precipitation on cellular growth kinetics in an Al-28 at. % Zn alloy

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The reported existence of two metastable miscibility gaps in the aluminium-zinc (Al-Zn) system is confirmed by an electron microscopic study of precipitate reversion in an Al-28 at. % Zn alloy. The metastable Guinier-Preston (G.P.) zones are replaced above ~125°C within minutes by a metastable rhombohedrally distorted fcc phase (R-phase). Consequently, the recently published calculations for the growth rate of the cellular reaction in the 100 to 250°C temperature range are revised in accordance with the nature of the continuous precipitate ahead of the advancing cell boundary. The observed growth rates are now shown to agree most satisfactorily with current theories of cellular decomposition as controlled by cell boundary diffusion and influenced by continuous precipitation in the matrix.

1. Introduction

The extensive solid solution of zinc in aluminium has been subjected in recent times to several detailed investigations, mainly from the point of view of precipitate reversion [1-15] and lately also with reference to cellular (discontinuous) precipitation [16-18]. The solid solution extends to about 66 at. % Zn and occurs in three different fcc modifications, designated α, α' and α'' in the Al-Zn diagram (Fig. 1) and is involved in two monotectoid reactions, the first ($\alpha'' \rightleftharpoons \alpha + \alpha'$) concerned with the three isostructural phases and the second ($\alpha' \rightleftharpoons \alpha + \beta$) leading eventually to a mixture of essentially fcc Al and hexagonal close-packed (hcp) Zn at room temperature. With sufficient care it is possible to limit precipitation, both during the quench and at room temperature, in alloys containing up to about 35 at. % Zn, and then to follow the decomposition of the alloy through a succession of metastable equilibria to the two equilibrium terminal solid solutions at temperatures up to the lower monotectoid horizontal (275°C). Low angle X-ray scattering, electron microscopy, hardness and electrical resistivity measurements have been widely used by previous workers in their attempts to clarify the precipitation
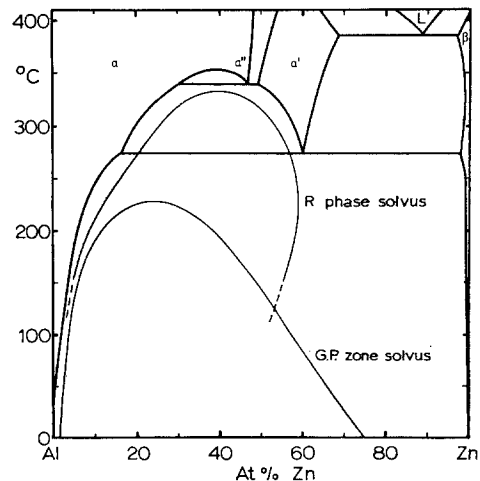

Figure 1 The aluminium-zinc phase diagram with proposed metastable miscibility gaps for the G.P. zones and the R-phase (from [15]).

sequences in this alloy. The complexity of the reversion process has recently been highlighted [15] and seems to have a direct bearing on the interpretation of the phenomenon of cellular precipitation in Al-Zn alloys, which has been recently observed *in situ* in a high-voltage

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electron microscope in the temperature range of 100 to 250°C [17, 18].

On quenching aluminium-rich Al-Zn alloys from single-phase regions to room or sub-zero temperatures, fully coherent G.P. zones are known to form rapidly. The zones are spherical to start with, but undergo a rhombohedral distortion on reaching a critical diameter which is about 60 Å at room temperature [1]. The Zn content of the zones can be estimated from values of integrated intensities of low-angle X-ray scattering and has been found to be around 70 at.% at room temperature. The latter value is dependent on the temperature of study and decreases with increasing temperature. R-phase is formed at higher temperatures either on direct quenching or by zone reversion. The kinetics of its formation are appreciably faster on reversion than on quenching and this partly coherent metastable precipitate has a rhombo-hedral structure derived by a simple compression in a direction perpendicular to the matrix {1 1 1} planes. The possible existence of two different reversion temperatures for the G.P. zones and the R-phase respectively has been conceded by several investigators [8-11] but only recently on the basis of experimental data from a large number of investigators, have two diff-erent metastable miscibility gaps (Fig. 1) been established [15]. The present study was under-taken to obtain direct electron microscopic evidence for the transition from G.P. zones to R-phase as postulated by the two proposed miscibility curves and, if necessary in the light of this evidence, to re-interpret the data on cellular growth kinetics recently reported for an Al-28 at.% Zn alloy [18].

2. Experimental procedure

The Al-Zn alloy was prepared from high-purity metals and contained 28.4 at.% Zn according to chemical analysis. It was cold-rolled to 125 μm thickness after homogenization at 400°C. Prior to ageing, all specimens were subjected to a uniform solution treatment at 400°C for 1 h followed by quenching in iced brine and then stored in liquid nitrogen to prevent further decomposition.

Since the proposed metastable miscibility curves (Fig. 1) suggest a possible change in the matrix structure around 120 to 130°C when the partially coherent R-phase replaces the fully coherent G.P. zones, a series of temperatures was chosen for ageing studies at five degree intervals in the range 80 to 150°C. The solution treated specimens were aged for 15 min and then quenched in iced brine. Thin foils were im-mediately prepared by electropolishing the specimens in a 20% solution of perchloric acid in ethanol at about −25°C. The foils were exam-ined expeditiously, generally within 20 min of the final quenching, in a Siemens Elmiskop 100 kV microscope. Zinc precipitation on the foil surface, which could be easily identified by dark-field microscopy, was nominal in all specimens at the commencement of electron microscopic observation, but increased very rapidly within minutes inside the microscope. Selected area electron diffraction was used to identify the different phases.

3. Experimental results

A typical microstructure obtained in our Al-Zn alloy at temperatures up to 120°C is shown in Fig. 2a. The microstructure consists of a high volume fraction of G.P. zones in the form of distorted spheres whose average size at 80°C was measured as around 60 Å in diameter. Fig. 2b shows an enlargement of the (2 2 0) reflection from a selected area diffraction pattern obtained from Fig. 2a. Apart from the high angle $(1 0 \bar{1} 3)$ zinc reflection due to the small amount of surface zinc, sidebands are clearly visible flanking the matrix reflection.

Unlike other alloy systems where sidebands have been observed from plate-like precipitates [19, 20], the sidebands in Fig. 2b are not strongly crystallographic in their direction and this is consistent with the spherical zone morphology of Fig. 2a. The advantages of using sideband spacings to accurately measure very small precipitate sizes have been reported [20] and on this basis the calculation for Fig. 2b gave a value of 54 Å for the average zone size. Sidebands were also found when the alloy was aged for 1 h at room temperature after solution treatment and the average zone size was calculated as 38 Å in this case from the sideband spacings.

At and above about 125°C the matrix changes its appearance dramatically displaying a fine "tweed-like" precipitate (Fig. 3a) as in the early stages of spinodal decomposition in alloys of the Cu-Ni-Fe system [19]. This "tweed-like" pre-cipitate coarsens with increasing temperature reaching a few hundred Ångströms in size around 200°C. That this precipitate is R-phase was confirmed by a careful examination of the (2 2 0) matrix reflection (Fig. 3b). The presence
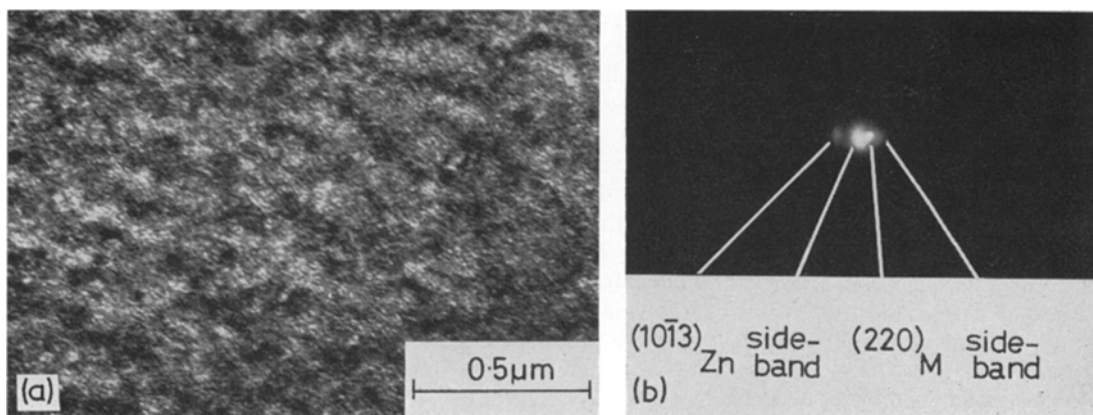
Figure 2 (a) G.P. zones in Al-28 at. % Zn alloy after ageing at 80°C for 15 min (b) The (220) reflection from (a) showing sidebands around the matrix reflection and the ($10\bar{1}3$) zinc reflection.
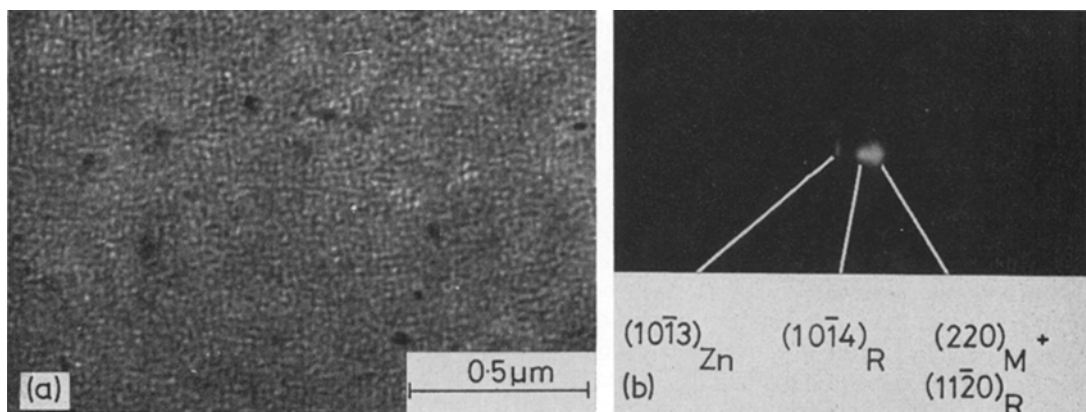

Figure 3 (a) R-phase in Al-28 at. % Zn alloy after ageing at 130°C for 15 min. (b) The (220) reflection from an area with the "tweed-like" precipitate showing matrix, R-phase and zinc reflections.

of R-phase causes a split around (220) with the ($10\bar{1}4$) R-phase reflection separated from matrix and ($10\bar{1}3$) zinc reflections. The lattice parameters of the R-phase calculated from the diffraction pattern of which Fig. 3b is an enlargement and from a number of other patterns were in satisfactory agreement with those reported earlier [10].

The temperature of 125°C is quite critical for the changeover in the matrix structure and seems to coincide almost exactly with the temperature obtained by the downward extrapolation of the suggested R-phase solvus on to the G.P. zone solvus (Fig. 1). As the R-phase and G.P. zones have the same Zn content at this temperature, it is likely that the former nucleates easily and pro-

fusely from the latter and grows rapidly replacing the zones within minutes. The kinetics of R-phase formation may well be somewhat different in more dilute alloys or single crystals, especially when the specimens are directly quenched to around this critical temperature from the single-phase region [12]. It is interesting to note, however, that the lowest temperature so far reported for isothermal formation of the R-phase on the basis of X-ray diffraction evidence has been 130°C for an Al-8.7 at. % Zn alloy single crystal [1].

4. Re-interpretation of cellular growth data

The cellular precipitation occurring in an

Al-28 at. % Zn alloy in the temperature range of 100 to 250°C has recently been shown [17, 18] to nucleate at the grain boundaries and to proceed at a linear growth rate, with the cell interface advancing steadily into the matrix containing the metastable precipitates. The authors of this investigation analysed the variation in the interlamellar spacings and growth rates for the cellular product as a function of temperature in terms of Turnbull's theory [21] of cellular growth, modified to include the retarding effect of continuous precipitation in the matrix [22, 23]. The experimental findings were reasonably consistent with a growth mechanism controlled by cell boundary diffusion and did not fit in with any model based on volume diffusion ahead of the cellular interface. The observed growth rates were found, however, to fall abruptly and well below the calculated values around 130°C and to continue to display a deviation from theory, albeit decreasing with increase in temperature, up to about 200°C. The present results indicate that the discrepancy in the growth rate is due to the sudden change in the nature of the metastable precipitate in the matrix above 125°C.

According to the modified Turnbull theory of cellular growth controlled by cell boundary diffusion, the growth rate G_B is given by

$$G_B = K.D_B\lambda/S^2$$

where K equals $(Co-Ce)/Co$, Co and Ce being metastable and equilibrium solute contents respectively of the matrix, D_B is the solute diffusivity along the cell boundary, λ is the thickness of the cell boundary (generally assumed to be 5 Å) and S is the interlamellar spacing. In the above expression, K and hence G_B, will be influenced by the composition of the metastable matrix as obtained from the relevant miscibility gap, i.e. as affected by the co-existing metastable precipitate, namely R-phase or G.P. zones. In the earlier calculations [18] only the metastable miscibility gap for the R-phase, based on very little experimental data [12] was available and was extrapolated to lower temperatures.

The variation of K with temperature is given in Fig. 4, as determined from the two metastable miscibility gaps already referred to and shown in Fig. 1. There is a possible overlap between the two metastable miscibility curves in the temperature range of 125 to 225°C, but our ageing experiments have clearly shown that the R-phase solvus should replace the G.P. zones solvus
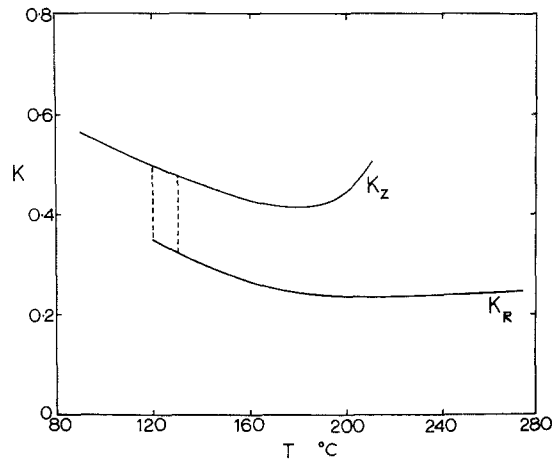

Figure 4 Variation of the concentration factor (K) with temperature for the Al-28 at. % Zn alloy. K has been calculated using the position of the metastable solvus for G.P. zones (K_Z) or the R-phase (K_R).

above 125°C for computing K in our calculations. It has to be stressed here, however, that the kinetics of R-phase formation is sensitive to specimen composition, size, shape and thermal history [10, 15] and the critical temperature of 125°C recorded by us may not be universally valid for all investigations on Al-Zn alloys. The actual temperature for the transition from G.P. zones to the R-phase on ageing is best determined under experimental conditions pertaining to each study.

The recalculated growth rates (G_B) are shown in Fig. 5 and display the same main characteristics as the observed growth rates, namely a
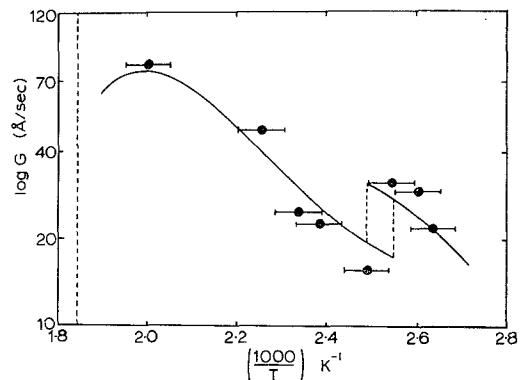

Figure 5 Comparison of experimental and calculated growth rates (G_B) with temperature for cellular precipitation in an Al-28 at. % Zn alloy.

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sudden drop around 125°C and a maximum around 225°C. The agreement between theory and experiment is now as good as can be expected in such studies with inevitable limitations such as uncertainty in the measurement of the actual temperature of the specimen while being observed in the electron microscope.

5. Conclusions

1. The existence of separate metastable miscibility gaps for the G.P. zones and the R-phase in the Al-Zn system has been confirmed by electron microscopy and diffraction.

2. The observed growth rates for the cellular precipitation in the Al-28 at. % Zn alloy recently reported [18] have been re-interpreted by using the G.P. zone solvus below 125°C and the R-phase solvus above. This leads to a significantly better agreement with the theoretically predicted growth rates based on a modified Turnbull theory of cellular decomposition.

Acknowledgements

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