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On the Reversion of G P Zones in Al-10% Zn and Al-10% Zn-0.1% Mg Alloys

Most of the previous studies on spherical GP zones, which characterise the pre-precipitation process in the Al–Zn alloys, were related to their formation and growth [1-5]. However, very few of them have been concerned with reversion, i.e. dissolution of the GP zones that results when the solid solution containing them is heated above a given temperature. This temperature is determined, for a given composition of the alloy considered, by the metastable miscibility gap which seems to control the formation of such zones [3, 5].

The aim of this note is to present some results of small angle X-ray scattering during reversion of GP zones in Al–10% Zn and Al–10% Zn–0.1% Mg (wt %) alloys. The latter system has become interesting through the study of the atomic diffusion mechanisms by which the zones are formed [6-8]. Structural analogies and differences between those two alloys were recently pointed out; particularly it has been shown that segregation in the ternary alloy may be assumed to be also controlled by a metastable miscibility gap [9]. No data are available, however, on the reversion of this alloy.

The measurements were carried out with a device already described elsewhere [9-11] under such conditions that the "infinite beam" approximation was justified. The scattered intensity is expressed on an absolute scale in terms of the function $j_n(s)$ [5], where $s = 2 \sin\theta/\lambda$, 2θ being the scattering angle and $\lambda = 1.54$ Å the X-ray wavelength (Cu $K\alpha_1$). The exact compositions and characteristics of the alloys were given in a previous work [9]. After a solution-treatment at 300° C the specimens were quenched in water at 0° C and aged for several days at room temperature. The scattering curves were then measured for both alloys (time $t = 0$ of the reversion treatment). Subsequently, the samples were given successive reversion treatments in a glycerine bath at 110 ± 2° C. After each treatment the scattering curve was measured at room temperature. Although there is no appreciable change in the alloys during holding at room temperature, nevertheless the specimens were stored in liquid nitrogen between the measurements. Ten scattering curves were obtained for each alloy. Some of the curves are shown in fig. 1a and b. Other curves have been

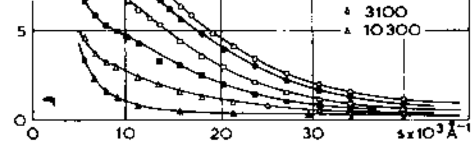

Figure 1 Scattering curves observed during reversion at 110° C. In order to avoid confusion, not all the measured curves are shown. For the same reason the figure is limited to scattering angles equivalent to $s = 45 \times 10^{-3}$ Å^{-1}, though measurements were made up to $s = 60 \times 10^{-3}$ Å^{-1} ($s = 2\sin\theta/\lambda$).

omitted in order to avoid confusion in the drawing. The scattered intensities are greater for the ternary alloy, in agreement with previous results [9]. A general decrease of the intensity can be observed even for times as short as 20 sec. For increasing reversion times this decrease becomes more pronounced. Simultaneously, the inflection point of these curves becomes less marked and shifts towards smaller values of s, and eventually disappears.

The average GP zone radii R have been calculated from the experimental curves by the classical method due to Guinier [12]. The integrated intensity

$$2\pi \int_0^\infty s\, j_n(s)\, \mathrm{d}s\,,$$

which is proportional to $(x_1 - \bar{x})\,(\bar{x} - x_2)$, has also been calculated. In this last expression x_1 and x_2 are the atomic concentrations of Zn in the zones and the matrix, respectively, and $\bar{x}$ is the mean atomic composition of the alloy. The corresponding values are plotted as a function of time in fig. 2a and b. It can be seen that up to about 200 sec of reversion the zone radius remains constant within the error of the measurements, but the integrated intensity shows a marked decrease. For times longer than 200 sec the decrease of both parameters is clear.

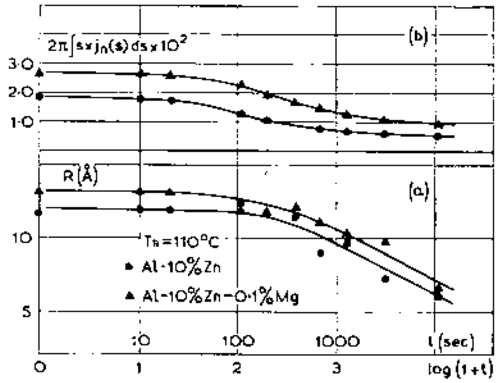

Figure 2 Variation of the GP zone radius and the integrated intensity during reversion at 110° C.

It is interesting to observe that for both alloys considered, the variation of the experimental curves during the reversion process is similar, and the parameters obtained from these curves behave in the same way.

The analysis of the scattering curves for high s values gives an idea of the uniformity in composition of the GP zones and the matrix [5, 12]. For the case of spherical homogeneous GP zones separated by a sharp interface from the matrix, itself considered of uniform composition, the scattered intensity decreases according to the s^{-3} law (Porod's law) [5, 12]. In our experiments this law is well satisfied for the curves corresponding to times shorter than 200 sec, but is no longer obeyed at greater times. The results for times longer than 200 sec are, however, uncertain, due to the poorer accuracy in the measurement of weak scattered intensities, which are of the same order of magnitude as the air-scattering. In any case, the fact that the law ceases to be obeyed for ageing times equivalent to those at which a clear decrease of the zone radii and the integrated intensity are observed, is doubtless meaningful. Taking into account all these observations, an attempt can be made here to give a description of the reversion process.

During the initial stages ($t < 200$ sec) the smaller GP zones begin to dissolve. This lessens the concentration difference between the remaining zones and the matrix, the result being an observable decrease of the integrated intensity. Nevertheless, the dissolution of the smaller zones does not result in a perceptible change of the radius as determined by Guinier's law, since this method gives an average radius which is primarily determined by the size of the larger zones [12]. In these early stages, the fact that Porod's law applies shows that zones and matrix maintain a uniform concentration and are separated by sharp interfaces. The sudden decrease of the zone radius which follows after 200 sec shows that even the larger zones have started to dissolve; at the same time the composition difference between zones and matrix decreases appreciably, which explains the remarkable decrease of the integrated intensity.

Although in these later stages the non-fulfilment of Porod's law may have an ambiguous interpretation owing to the aforementioned reasons, it is perfectly understandable that at this stage of evolution, the conditions for this law to apply are not fulfilled (uniform composition of GP zones and matrix, sharp interfaces separating them). When some zones start to dissolve, the mean distance between the remaining ones increases, so that they tend to form a system of "infinitely" distant particles. The displacement of the inflection points towards smaller values of

s and its eventual disappearance can thus be explained. It is interesting to compare this behaviour with that observed during the formation and growth of the GP zones. In this formation process the scattering curves show an inflection point immediately the intensity becomes observable. This means that the GP zones have an ordered distribution with an average distance between neighbouring zones from the earliest stages of their formation that can be detected by X-rays [5, 9, 13]. This distance increases with the ageing time, the experimentally determined zone radius increasing at the same time. This means that some zones grow at the expense of others which are being dissolved. During reversion, however, the atoms which come out of the dissolved zones do not migrate to other zones, but increase the mean solute concentration of the matrix. (Actually the solute atoms are not distributed entirely at random in the matrix but tend to form small clusters of two or three atoms [13]). With the rapid decrease in the number and average size of the zones, the system tends towards the isolated particles model.

The observed evolution, similar in both alloys, leads to the conclusion that reversion occurs in the same way in both cases. Particularly, in fig. 2 it can be seen that the zone radii and the integrated intensity vary in the same way in both alloys. It can then be inferred that the presence of Mg atoms does not appreciably alter either the structure or the rate of diffusion of the Zn atoms in the ternary alloy. This latter fact agrees with the interpretation given by Gould and Gerold [7], and Perry [8]. These authors suggest that the Mg atoms have a passive role, trapping vacancies when GP zones begin to form and releasing them afterwards, the overall result being only a lengthening in the time of growth. In the reversion process examined by us, however, the Mg atoms would have no effect.

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