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Pre-precipitation of Al–Zn alloys in the range 30 to 40 wt % Zn

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Isothermal pre-precipitation in Al–Zn alloys, for the range between 30 and 40 wt % Zn at room temperature, has been investigated by means of small angle X-ray scattering (SAXS) experiments. Being consistent with previous results it is shown that the kinetics of decomposition strongly depend on Zn concentration. A sharp decrease of the decomposition rate is observed for values of between 32 and 34 wt % Zn. For concentrations of 38 and 40 wt % Zn no quenched vacancies effects are observed and SAXS spectra are very much broader than in dilute alloys. The correlation with the kinetics of precipitation of high temperature transition phases is pointed out.

1. Introduction

Pre-precipitation in binary solid solutions is a well known reaction occurring when the system is rapidly quenched from the high temperature homogeneous state. In particular the kinetics of decomposition of Al–Zn alloys has been extensively investigated during the last decades and the main information has been obtained by small angle X-ray scattering (SAXS) experiments [1]. Several structure models have been proposed to explain the ring shape of SAXS patterns [2–5]. At present it is generally accepted that, during early stages of pre-precipitation, Guinier-Preston (GP) zones are formed by spinodal decomposition [6, 7], according to the theories of Cahn [8] and Cook [9]. On the other hand, later stages have been explained in terms of a metastable miscibility gap and the existence of certain degree of ordering occurring between the zones, according to a model confirmed by Bonfiglioli and Guinier [5].

Most of the studies on the kinetics of decomposition were carried out on dilute Al–Zn alloys (up to 30 wt % Zn). It was found that the evolution of quenched samples during isothermal ageing is extremely fast [5]. For instance, the associated coefficient of atomic interdiffusion for Al–Zn30 (Al–30 wt % Zn) is about nine orders of magnitude larger than the corresponding equilibrium value, according to the results reported by this author [7]. This behaviour is currently explained in terms of the high atomic mobility due to the over saturation of vacancies retained by the fast quench.

More concentrated alloys have been studied less thoroughly. We know, however, that they show important differences in the kinetics of decomposition. For instance, Graf and Genty [10] reported that the size of the SAXS ring in Al–Zn40 is very much larger than the observed in Al–Zn10. Furthermore, Rundman in his thesis work [11] found no evolution of quenched Al–Zn40 alloys at room temperature. This is sharply different behaviour compared with that observed for concentrations up to 30 wt % Zn. Up to now a satisfactory explanation for this behaviour has not been attempted.

The purpose of the present paper is to provide further SAXS experimental information about the kinetics of pre-precipitation in Al–Zn alloys, in the range 30–40 wt % Zn. The emphasis will be made on the differences observed between dilute and concentrated alloys.

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2. Experimental procedure

Two sets of small angle X-ray scattering results are reported in this paper. One concerns the as-quenched state and the subsequent isothermal decomposition at room temperature of 30 and 40 wt% Zn alloys. In this case SAXS experiments were carried out with a device already described [12, 7], by using a low temperature camera (−150° C) to avoid any evolution of the samples during the measurements.

The second experiments refer to the final pre-precipitation state for intermediate compositions between 30 and 40 wt% Zn, aged completely at room temperature. These measurements were performed in a commercial Rigaku SAXS goniometer equipped with a graphite monochromator. CuKα radiation was used in both sets of experiments.

Samples of nominal composition 30, 32, 34, 36, 38 and 40 wt% Zn were prepared starting from pure materials, Al 99.999% and Zn 99.9999%, following the procedure already described [7]. The samples were homogenized at 400° C for one hour and then quenched in a cold bath, as is indicated for each experiment.

3. Results

SAXS curves for the Al–Zn30 alloy aged at room temperature (20° C) are shown in Fig. 1. The samples were quenched into a saturated sodium chloride solution at −5° C. The intensities $j_n(2\theta)$ (infinite height collimation conditions) are expressed in absolute units (a.u.) of scattering power per electron.

TABLE I Isothermal decomposition at room temperature of the Al–30 wt% Zn alloy (Fig. 1).

t (sec)	$j_n(2\theta)_{max}$ (a.u.)	$2\theta_{max}$ (degrees)
0	10.8	2.10
30	20.0	1.45
60	24.4	1.20
∞	56.2	0.75

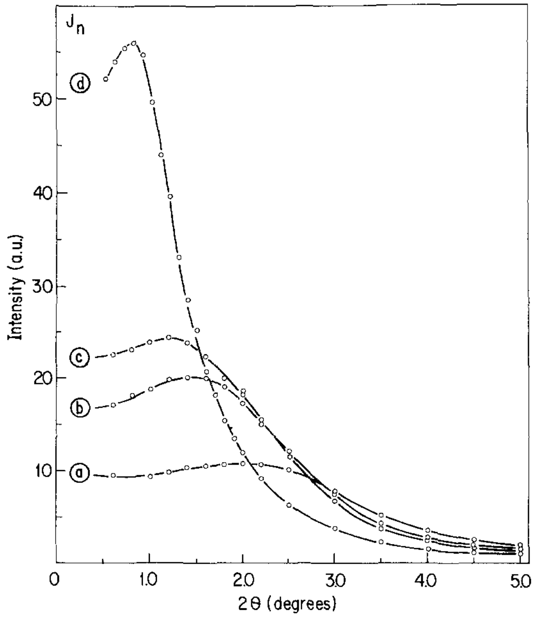

Figure 1 SAXS curves for the Al–30 wt% Zn alloy. Isothermal decomposition at 20° C: (a) as quenched; (b) 30 sec; (c) 60 sec; (d) completely aged.

As it can be seen, the evolution of this alloy is extremely fast. The total increase factor of the intensity maximum is 5.2, Table I. A continuous shift of the SAXS spectra towards smaller angles is observed, leading to the intersection of the scattering curves (cross-over point) just after 60 sec.

Fig. 2 shows the results for the Al–Zn40 alloy. In this case the sample was quenched into an eutectic Cl_2Ca solution at −55° C. This procedure was preferred in order to get a faster quench. Curve (a) corresponds to the as-quenched state and curve (b) to the final state of pre-precipitation. In agreement with previous results [11] the rate of evolution of this alloy at room temperature is almost negligible. The total increase of the intensity maximum just amounts to 10%, and no shift of the spectrum is observed. The intensity for the final state is clearly smaller than that observed in the Al–Zn30 alloy and the maximum is located at a larger angle (see Table II).

Final state of pre-precipitation was also analysed for intermediate compositions: 30, 32, 34, 36, 38 and 40 wt% Zn. The scattering curves are shown in Fig. 3. The samples were quenched into a water bath at 0° C and the measurements were performed

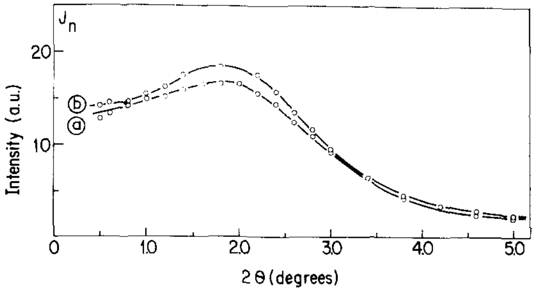

Figure 2 SAXS curves for the Al–40 wt% Zn alloy. Isothermal decomposition at 20° C: (a) as quenched; (b) completely aged.

TABLE II Isothermal decomposition at room temperature of the Al–40 wt % Zn alloy (Fig. 2).

t (sec)	$j_n(2\theta)_{\max}$ (a.u.)	$2\theta_{\max}$ (degrees)
0	16.8	1.9
∞	18.8	1.8

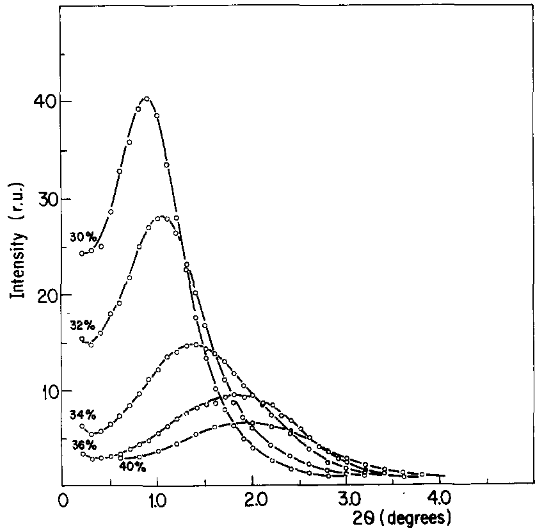

Figure 3 Final state of decomposition at room temperature of Al–Zn alloys in the range between 30 and 40 wt % Zn. The intensities are expressed in relative units. The curve for 38 wt % Zn has been omitted in order to avoid confusion in the drawing.

at room temperature. The slit system was aligned to give a primary beam with a Gaussian intensity distribution along its height. SAXS intensities expressed in relative units (r.u.) were normalized to primary beam intensity, thickness and composition of the samples. Fig. 3 show the progressive modification of the scattering curves as the Zn content increases from 30 to 40 wt % Zn.

4. Discussion

In a previous work [7] it was found that the decomposition of the Al–Zn30 alloy at −45° C could be satisfactorily explained in terms of the spinodal mechanism [8], if random fluctuation effects [9] are taken into account. Although this alloy should also be inside the spinodal at room temperature [6], the purpose of the present experiments was not to carry out a quantitative test of Cahn's theory. The evolution of this alloy at room temperature is excessively fast and, as we see in Fig. 1, we should limit our analysis just to the first 30 sec or less, in order to consider only the early stages of decomposition.

However, a qualitative analysis of the results will still allow the understanding of some important features of the pre-precipitation kinetics. The existence of an intensity maximum in the as-quenched state means that some degree of decomposition has occurred during the quench. This is a complex process occurring at varying temperatures during the continuous cooling. A detailed analysis of this process has been recently carried out for the quasi-binary system B_2O_3–PbO–Al_2O_3 glass [19]. After 30 sec of decomposition, Fig. 1, SAXS intensity grows for all the range of scattering angles studied. The first two curves do not show any intersection or a cross-over point. This behaviour could be consistent with the spinodal mechanism if random compositional fluctuations are present. When fluctuation effects are negligible, intersection of the scattering curves must occur at a critical wave number $k_c = k_m\sqrt{2}$, k_m being the wave number of the spectrum component with maximum growth rate [8]. The magnitude of k is related to the scattering angle 2θ by the relation $k = 4\pi(\sin\theta)/\lambda$, λ being the wave length of the radiation employed. On the other hand we know that the fluctuation term has the effect of shifting the cross-over point towards larger k values. In fact such behaviour was observed for the decomposition of this alloy at −45° C [7]. At this temperature the cross-over point was observed in the 6 to 7° 2θ angular range.

As the ageing proceeds we observe after 60 sec the intersection of curves (b) and (c) (Fig. 1) and a shift of the maximum intensity towards smaller angles. Now, this behaviour is no longer expected when the linear theory is satisfied. It is rather associated with the beginning of a coarsening process occurring during later stages of pre-precipitation [13]. The same behaviour has been observed at −45° C but in this case coarsening starts after between 90 and 120 sec.

According to the results previously obtained by Bonfiglioli and Guinier the behaviour of the Al–Zn30 and more dilute alloys is similar, showing a slow and progressive change of the kinetics and structural properties as the Zn content increases. The evolution at constant temperature inside the spinodal during first stages of decomposition follows linear Cahn's theory, corrected by the fluctuation term. For these alloys, up to 30 wt % Zn, the kinetics of decomposition is extremely fast (Fig. 1), showing an interdiffusion coefficient which is very much larger than the corresponding equilibrium value at the ageing temperature. We must recall however that this behaviour is currently observed in several systems during pre-precipitation [1]. It is usually explained in terms of the over saturation of vacancies retained during the quench. For Al–Zn30 the interdiffusion coefficient during decomposition at −45° C is nine orders of magnitude larger than the calculated equilibrium value [7].

Now, in comparing the kinetics of pre-precipitation of dilute Al–Zn alloys, up to 30 wt % Zn, with the Al–Zn40 and more concentrated alloys we found important differences. It can be seen in Fig. 2 that the evolution at room temperature of the Al–Zn40 is extremely slow with the total increase of the maximum intensity being just about 10%. These results are summarized in Table II. Here, no effects of over saturation of vacancies seem to be present. SAXS spectrum is much broader than the 30 wt % Zn alloy and the position of the maximum is located at a larger angle for the final state.

Equivalent results were published before by Graf and Genty [10], who reported a larger radius of the SAXS ring for Al–Zn40 in comparison to that observed in Al–Zn10. It is apparent that these authors were comparing final states of pre-precipitation for both alloys. Rundman [11] also found no evolution at room temperature for the concentrated alloy. The isothermal decomposition of this alloy at 65° C was in agreement with the linear spinodal theory [11, 14], but in this case another difference with dilute alloys was observed: no evidence of random fluctuation effects was detected.

Now we will analyse the final pre-precipitation state for compositions between 30 and 40 wt % Zn (Fig. 3). According to the early model for GP zones in Al–Zn alloys [2, 4], later confirmed by Bonfiglioli and Guinier [5]. The final state of pre-precipitation can be explained in terms of a two density model: small coherent regions enriched in solute atoms (GP zones) are isotropically distributed within the depleted matrix. This distribution, however, is not at random. On the contrary there is some degree of short range order "between" the zones leading to a quasi modulated structure, which accounts for the ring shape of SAXS patterns.

We can calculate the average size of GP zones using Guinier's law [15] to approximate the curves of Fig. 3. Furthermore we know that the angular position $2\theta_m$ is related to some average interparticle distance $\Lambda_m = 1/s_m$, being $s_m = 2(\sin\theta_m)/\lambda$. On the other hand, in terms of a modulated structure model Λ_m is a good approximation of the wave length of the principal spectrum component. In Table III are listed the values of maximum intensity, angular position $2\theta_m$ and radius of giration R_G of the zones, calculated from Fig. 3.

TABLE III. Final state of pre-precipitation at room temperature.

Wt % Zn	Maximum intensity	$2\theta_{max}$ (degrees)	R_G (Å)
30	40.4	0.90	21.6
32	28.1	1.05	18.4
34	14.8	1.40	14.1
36	9.60	1.80	13.6
38	7.50	2.10	12.4
40	6.60	1.95	11.6

It can be seen that for compositions larger than 30 wt % there is a sudden change of the scattering patterns: the final intensity maximum starts to decrease while it shifts towards larger angles. The size of the zones becomes progressively smaller leading to a continuous broadening of SAXS spectra. Increasing effects of an anomalous decay of vacancies during the quench are observed. Alloys with 34, 36 and 38 wt % Zn rapidly approach the behaviour of the Al–Zn40. On the other hand Al–Zn30 behaves as a dilute Al–Zn alloy. The change of the kinetics of decomposition must occur between 32 and 34 wt % Zn, since for this range the major change of maximum intensity is observed.

The reason why concentrated alloys do not show over-saturation of vacancies after the quench nor random fluctuation effects during the first stages of pre-precipitation is not well understood. However, from the present and previous results it is apparent that the different behaviours of concentrated alloys have to be investigated in relation to the process of decomposition occurring at high temperatures, during the continuous cooling. The decomposition during the quench in Al–Zn alloys could be correlated with the kinetics of precipitation of transition phases observed at temperatures between 150 and 225° C. We know that spherical GP zones are followed by the rombohedral semicoherent R phase, incoherent α' cubic phase and zinc β [16, 17], during the isothermal ageing at high temperature.

According to recent results, at present under elaboration [18], the rate of precipitation of transition phases at 200° C rapidly increases with

Zn content in the range of concentrations between 30 and 34 wt %. Furthermore, there is convincing evidence that these phases are very transient in concentrated alloys and this is consistent with the smaller sizes of GP zones observed during pre-precipitation (Table III). Further investigation on the kinetics of transition phases and its correlation with the pre-precipitation process would be worthwhile.

5. Conclusion

The rate of isothermal evolution of Al–Zn alloys during pre-precipitation strongly decreases for Zn concentrations greater than 30 wt %. SAXS spectra, for the final state, show a decreasing maximum intensity and progressive broadening with Zn concentration. For dilute alloys (up to 30 wt %), the oversaturation of vacancies after the quench allows for the large interdiffusion coefficient. Alloys with 36, 38 and 40 wt % Zn show an anomalous decay of vacancies during the quench and a smaller size of GP zones in the final state. The change of kinetics occurs mainly in the range between 32 and 34 wt % Zn. A correlated behaviour, to be reported in a later paper, has been observed for the kinetics of precipitation of high temperature transition phases.

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