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Pre-precipitation in Al/Zn and Al/Zn/Mg Alloys Studied by Small-Angle X-ray Scattering

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Results of small-angle scattering of X-rays for Al/10% Zn and Al/10% Zn/0.1% Mg (wt %) alloys during ageing at 20° C are presented. According to these results, the form and the structure of Guinier-Preston zones in both alloys are the same. Nevertheless, the values of the radius and the zinc concentration reached by the zones are higher in the ternary alloy than in the binary one. On the basis of a recently proposed model for pre-precipitation in Al/Zn alloys, it is possible to give a convenient quantitative description of the alloys studied hereby. Structural models advanced by other authors on the basis of resistometric studies are discussed in the light of the present results.

1. Introduction

This paper is concerned with an application of the scattering of monochromatic X-rays at small angles. This technique, apart from its biological applications, has found particular use in the study of the early stages of phase transformation in alloys, because it is particularly sensitive to the presence of randomly dispersed, small regions of enhanced scattering power. In the early stages of ageing of supersaturated alloys, one frequently obtains "Guinier-Preston (G P) zones" [5]. These are merely regions of matrix lattice (sometimes lath-shaped, sometimes spherical, according to the alloy system under investigation) which are enriched in solute. The form of the small-angle scattering plots, and especially the position of any scattering maxima, permits the estimation of the average diameter or thickness, which may be less than 10 Å, and the number of these zones per unit volume of alloy. The considerable experimental complexities of this technique, and the necessary corrections, are detailed in a classic book by Guinier and Fournet [13].

In recent years, several studies have been made of the variation of electrical resistivity in Al/Zn alloys during precipitation processes [1-4]. As is well established, these processes are characterised from the structural point of view by the formation of G P zones [5].

As a result of these experiments using electrical resistivity, it has been possible to obtain important information concerning the influence of crystal defects (especially vacancies) on the kinetics of pre-precipitation, and the activation energies which appear to govern the process have been calculated [1-4]. These studies have been extended by the introduction of defects produced by plastic deformation [6] and neutron-irradiation [7] and also by adding small percentages of magnesium, which is thought to have a strong binding energy with vacancies [8-10]. The results of the experiments using resistivity are thus very complete.

At present, theories to account for the observed variations of electrical resistivity in terms of atomic phenomena (such as the formation of G P zones) are not well established. Interpreting the results of resistivity measurements at the atomic level is impeded by the almost total absence of structural information during the early stage of pre-precipitation, where resistivity changes most rapidly.

Very recently, a detailed quantitative study has been made of Al/Zn alloys at low temperature by small-angle scattering of X-rays [11].

Through these experiments, it has been possible to observe the early stages of pre-precipitation, and so suggest a model for the structure of G P zones and their formation. In the present work, we have used the same method to study alloys of Al/10% Zn and Al/10% Zn/0.1% Mg, for which detailed resistivity measurements are available, and we have been able to give a suitable quantitative description. We then analysed the structural models suggested by the resistivity measurements.

2. Experimental Methods

The alloys were prepared from metals of high purity (Al 99.999%, Zn 99.9999%, and Mg 99.9999%). Melting was carried out in an electrically heated, alumina crucible under an argon atmosphere. After a homogenisation anneal of 48 h at 500° C, the ingot was rolled to a convenient thickness. The compositions according to chemical analysis were Al/10.1% Zn, and Al/10.0% Zn/0.085% Mg (figures are for weight per cent unless otherwise indicated). The samples, in the form of sheets of about 0.1 mm thickness, were homogenised at 300° C and quenched into water at 0° C. They were then transferred and kept in liquid nitrogen.

To measure the small-angle scattering, we used a General Electric diffractometer, which was operated with a strictly monochromatic beam [12] under conditions such that the "infinite beam approximation" [13] was justified. The intensity of the scattered beam is expressed on an absolute scale by the function $j_n(s)$, which depends only on the nature of the sample [11, 14]. The parameter s has its usual significance: $s = 2 \sin \theta/\lambda$, where 2θ is the scattering angle and λ is the X-ray wavelength. The small-angle scattering results were determined immediately after quenching and after various ageing times at 20° C. The measurements were always made at $-150°$ C, at which temperature there is no appreciable ageing. To carry out these measurements, we used an apparatus which allowed the specimens to be placed in position without ever being heated above the indicated temperature [15]. The ageing anneals were carried out in a conventional themostat.

In order to calculate the compositions of the G P zones of the matrix by the method due to Gerold [16], we also studied the alloys of nominal compositions: Al/20% Zn; Al/20% Zn/0.1% Mg; Al/30% Zn; and Al/30% Zn/0.1% Mg. (The compositions as determined by chemical analyses were respectively: Al/19.7% Zn; Al/19.6% Zn/0.09% Mg; Al/29.3% Zn; and Al/29.7% Zn/0.088% Mg.) These were prepared and measured in the above way. The study was limited, however, to two results per alloy determined after several days ageing, and after a further five days.

3. Results

The scattering curves of Al/10% Zn and Al/10% Zn/0.1% Mg are given in figs. 1a and 1b. In both cases, they have a "ring" form, with a maximum which becomes more marked with increased ageing. The form of the curves at the smallest value of s is distorted by the geometrical consequences of a long beam; this distortion reduced the distinctiveness of the small-angle peak.

The values of the integral corresponding to alloys of 20 and 30% Zn are an average of two measurements made with a five-day interval.

A "Guinier plot" [13], constructed from experimental curves, in every case embodies a linear part sufficiently well defined to permit calculation of the radius of gyration of the G P zones. Assuming the zones are spherical and uniform in composition, the radius of gyration immediately gives the zone radius. Its variation as a function of ageing-time is given in fig. 2a. It can be seen that the values of the zone radius in the two alloys are similar until an ageing-period of approximately 30 min has elapsed. After this, the zones in the ternary alloy grow larger than those in the binary alloy.

With sufficiently high s values, Porod's theory [13], which predicts a reduction of the scattering intensity according to an s^{-3} law, is obeyed. Analysis of the tails of the curves, measured immediately after quenching, was not, however, conclusive owing to their feeble intensity. Where the composition of the zones and the matrix are known (see later in study), Porod's theory makes it possible also to calculate the radius of the G P zones, assuming they are spherical. The R' value found by this method is always smaller than that of the R value taken from the Guinier plot [13]. Comparison of R and R' gives an indication of the distribution of zone sizes.

From each experimental curve, we have calculated the integral

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

whose variation as a function of time is given in

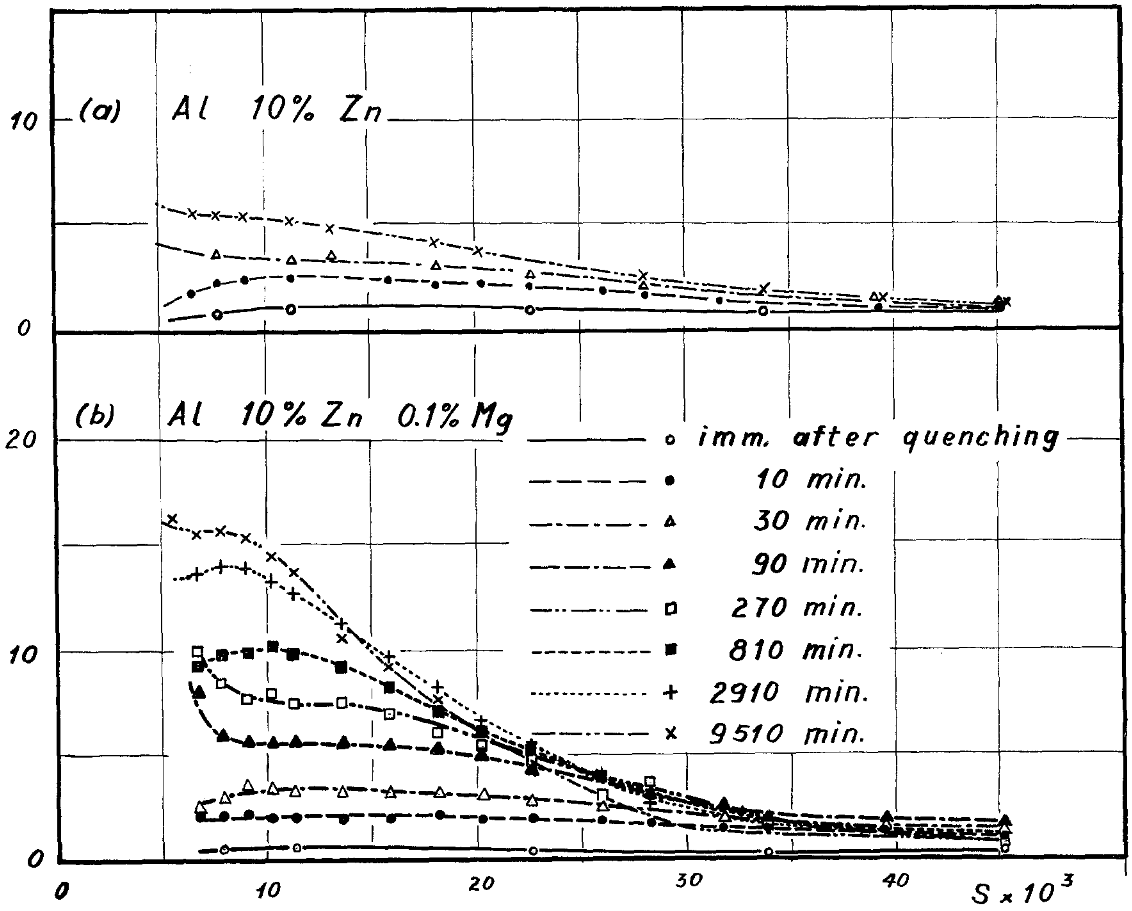

Figure 1 Scattering curves observed during the isothermal ageing at 20° C. To avoid confusion, not all the observed curves for the Al/10% Zn alloy are represented. For the same reason, the figure is limited to $s = 40 \times 10^{-3}$ Å^{-1} though measurements were made up to $s = 68 \times 10^{-3}$ Å^{-1}.

fig. 2b. In comparing the curves of fig. 1 with the plot of fig. 2b, it must be remembered that fig. 1 does not show the full range of s over which the measurements were made. The curves cross near $s = 30 \times 10^{-3}$, and thus the integrals for the various curves differ less than might appear from fig. 1. In the case of the binary alloy, the value of the integral is similar to the stationary value. This characterises what is known as the "limiting state" [11]. For the ternary alloy, on the other hand, the initial value of the integral is small, and the integral increases so that, at the limiting state, it has a value larger than that of the binary alloy. The integrals at the limiting state of the alloys Al/20% Zn, Al/20% Zn/0.1% Mg, Al/30% Zn, Al/30% Zn/0.1% Mg behave in the same way: for the same value of zinc, the integral of the ternary alloy is larger. Our results are given in tables I and II.

4. Structure of the Alloys Al/10% Zn and Al/10% Zn/0.1% Mg

Bonfiglioli and Guinier [11] proposed the following scheme for the G P zones and their development during isothermal ageing in Al/Zn alloys: the spherical G P zones are formed from a homogeneous solid solution which undergoes spinodal decomposition [17], which causes them to be remarkably regularly distributed in the matrix. These zones, which are initially small with composition close to the average composition of the alloy, and always coherent with the matrix, become enriched with zinc, and some grow at the expense of others. At the same time, the matrix is depleted of zinc. The zones and the

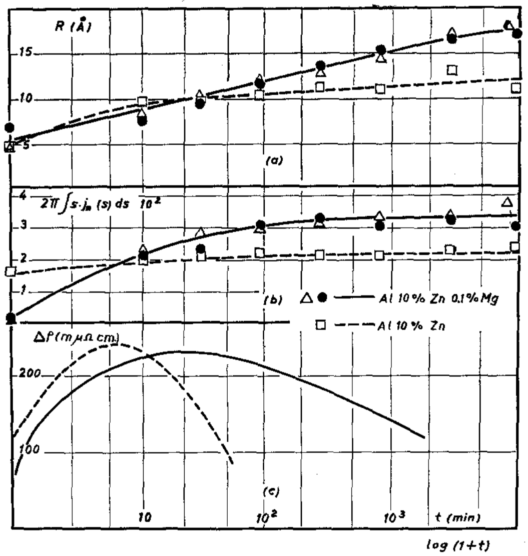

Figure 2 Curves (a) and (b) show the variation of the G P zone radius and the integrated intensity, respectively, with the isothermal ageing-time at 20° C. For the Al/10% Zn/0.1% Mg alloy, two measurements with two different samples (● and △) were made to check the reproducibility. However, in the text only the data corresponding to the first are reported. Curve (c) – resistivity versus ageing-time at 20° C, obtained from Panseri and Federighi [1, 8].

TABLE II

Alloy	$2\pi\int_0^\infty s j_n(s)\,ds \times 10^{-2}$
Al/20% Zn	5.91*
Al/20% Zn/0.1% Mg	6.98
Al/30% Zn	8.56
Al/30% Zn/0.1% Mg	10.65

*The values of the integral quoted for the alloys containing 20 and 30% Zn are the means of two measurements made at five-day intervals.

matrices finally attain compositions corresponding to the metastable miscibility gap at the ageing-temperature. In this condition, the intensity no longer varies with time: this is the limiting state. From these constant values of the integral, measured for three alloys with different zinc contents, it is possible to evaluate, using Gerold's method [16], the fractional concentrations of zinc in the zones (x_1) and in the matrix (x_2). Using this method, three pairs of values x_1 and x_2 are obtained, corresponding to the atomic concentration of zinc in the G P zones and in the matrix; they should coincide within experimental error. For the three alloys Al/10% Zn, Al/20% Zn, and Al/30% Zn, aged at 20° C, we found the following respective values: $x_1 = 0.73$, $x_2 = 0.020$; $x_1 = 0.75$, $x_2 = 0.020$; $x_1 = 0.77$, $x_2 = 0.024$. The average is $x_1 = 0.75$, $x_2 = 0.022$. These values are different from those given by Gerold [16]: $x_1 = 0.69$; $x_2 = 0.018$. The difference can be attributed to errors in the absolute measurements which are not the same in the two cases. In particular, Gerold's method of measuring the energy in the incident beam differs from ours [12, 16]. Once the composition of x_1 and x_2 are known, it is possible to calculate the radius of the R' zones by Porod's law, the number of zones per unit volume, and a radius r_0 which determines a spherical volume containing, on average, only one zone. This last calculation gives an idea of the distribution of zones in the matrix.

In the transitional state preceding the limiting state, it is possible to find the compositions of x_1 and x_2 only by using an additional hypothesis. Bonfiglioli and Guinier [11] assume that the

TABLE I

t (min)	Al/10% Zn			Al/10% Zn/0.1% Mg		
	$2\pi\int_0^\infty s j_n(s)\,ds$ $\times 10^{-2}$	R (Å)	R' (Å)	$2\pi\int_0^\infty s j_n(s)\,ds$ $\times 10^{-2}$	R (Å)	R' (Å)
0	1.60	4.5	—	0.17	4.5	—
10	1.96	9.2	5.6	2.07	7.3	7.2
30	2.06	9.8	5.9	2.28	9.4	7.3
90	2.14	10.1	6.0	3.00	11.6	6.6
270	2.08	11.0	6.0	3.21	13.4	6.3
810	2.06	10.7	5.2	2.97	15.1	9.4
2910	2.22	12.7	6.0	3.14	16.5	9.8
9510	2.31	10.8	5.8	2.95	17.0	9.8

total volume of the G P zones does not vary during *the course of* isothermal ageing. Thus, when x_1 and x_2 are known, it is possible to calculate the same parameter in the transitional as in the limiting state, and the results are given in table III. Using the G P zone radii taken from Guinier's model, and the radius r_0, we calculated the scattering curves by means of the Zernicke-Prins equation [13] assuming a distribution function of the $P(r)$ zones as follows:

$$P(r) = 0 \text{ where } r < r_0 \qquad (1)$$
$$P(r) = 1 \text{ where } r > r_0$$

These curves certainly have the "ring" form, but the maximum always occurs at s values greater than those given by the corresponding experimental curves. The effect of an "infinite beam" on a scattering curve at its maximum is to reduce that maximum in the direction of smaller s values [18]. The agreement between the experimental and calculated curves is therefore satisfactory.

We shall now consider whether it is possible to describe the structure of Al/Zn/0.1% Mg according to the system proposed for Al/Zn alloys.

There are obvious analogies between experimental results for Al/10% Zn and Al/10% Zn/0.1% Mg. The scattering curves always have a "ring" form in both alloys, and Guinier's and Porod's laws both hold. Moreover, the variation of the integral

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

as a function of time is very similar in both alloys: it grows from the initial value towards a steady state. Similarities in the variation of the zone radii are also found, although the increase of these radii is more pronounced in the ternary alloy.

These facts lead us to conclude that, in the Al/10% Zn/0.1% Mg alloy, there is a segregation of zinc atoms into zones with similar structure and form to those in Al/Zn alloys. We shall therefore attempt to describe them by the same structural model.

Gerold's method [16], when applied to the limiting state of the three alloys Al/10% Zn/0.1% Mg, Al/20% Zn/0.1% Mg, and Al/30% Zn/0.1% Mg, gives the following pairs of values for composition in the zones and in the matrices:

$$x_1 = 0.83 \qquad x_2 = 0.013$$
$$x_1 = 0.86 \qquad x_2 = 0.014$$
$$x_1 = 0.85 \qquad x_2 = 0.15$$

The three pairs of values coincide within the approximation of the calculation. The average is $x_1 = 0.83$, $x_2 = 0.014$.

It appears, then, that segregation in the Al/Zn/0.1% Mg alloys is governed by a metastable miscibility gap, as in the Al/Zn alloys. The limits of the gap are, however, different in the two cases: at the limiting state, the G P zones are richer in zinc in the ternary alloys, and the matrix is more depleted.

Having ascertained the compositions in the zones and in the matrix and assuming the same hypothesis as for the binary alloy (that the total volume of the zones is constant throughout isothermal ageing), we were able to calculate the same parameters as for the Al/10% Zn alloy. The results of these calculations are shown in table III. Using the values of R and r_0 and the function $P(r)$ given in (1), we calculated, by means of the Zernicke-Prins equation, a series of scattering curves which had, as previously, a "ring" form. However, the position of the maxima always occurs at larger values of s than in the corresponding experimental curves. The agreement is, therefore, satisfactory, taking into

TABLE III

t	Al/10% Zn				Al/10% Zn/0.1% Mg			
(min)	$N/V \times 10^{-18}$ (zones/cm^3)	r_0 (Å)	$x_1(t)$	$x_2(t)$	$N/V \times 10^{-18}$ (zones/cm^3)	r_0 (Å)	$x_1(t)$	$x_2(t)$
0	84	14	0.661	0.024	93	14	0.233	0.037
10	10	29	0.727	0.022	22	22	0.707	0.019
30	8.3	31	0.744	0.022	10	29	0.738	0.018
90	7.7	32	0.749	0.022	5.5	35	0.830	0.015
270	5.8	34	0.748	0.022	3.5	41	0.869	0.014
810	6.2	34	0.745	0.022	2.5	46	0.838	0.014
2910	3.8	40	0.771	0.021	1.9	50	0.860	0.014
9510	6.2	34	0.785	0.020	1.7	52	0.835	0.014

account the effect of the "infinite beam" approximation.

5. Discussion

The most immediate result of our experiments is to show that, in the ternary alloy Al/10% Zn/0.1% Mg, the form and structure of G P zones, and the form of their development are effectively the same as for the binary alloy Al/10% Zn. Gerold and Gould reached the same conclusion; although they assert that the intensity integral at a given ageing-temperature is independent of the magnesium content, and this does not agree with our findings. There are nonetheless notable differences between the two alloys: segregation is more severe in the ternary alloy. In its final stages, in fact, higher values are found for the radius and the zinc concentration in the G P zones than are found in the binary alloy. This probably arises because the process of short-range diffusion by which the zones develop is different in the two alloys [19]. However, we cannot give a valid explanation on the basis of our results.

The work of Panseri and Federighi [1, 8] with alloys of Al/10.2% Zn and Al/9.8% Zn/0.1% Mg seems to lend itself to analysis in the light of our results. Given the similarity of the composition of the alloys and the thermal treatment, it is possible to make quite a direct comparison.

Panseri and Federighi's conclusions concerning the structure of the alloys they studied may be summarised as follows.

(*a*) In precipitation in an Al/10% Zn alloy, all the G P zones, assuming they have a constant composition, reach the same size at the same time, at a given ageing-temperature. More particularly, they reach a critical size which gives rise to a characteristic maximum value for resistivity curves as a function of isothermal ageing-time. This has the result that the height is proportional to the number of zones per unit volume, which depends entirely on the ageing-temperature.

(*b*) Not taking kinetic modifications into account, pre-precipitation occurs in the Al/10% Zn/0.1% Mg much in the same way as in the binary alloy Al/10% Zn. The form and structure of the G P zones are the same in the two alloys; at a given ageing-temperature, the number of zones per unit volume is also the same.

Bartsch [9] refutes this last point. He suggests that, in the ternary alloy, there are "segregation complexes" which differ from G P zones. Our results do not confirm this theory. However, the similarity between the alloys of Al/10% Zn and Al/10% Zn/0.1% Mg, as supported by our experiments, appears more limited than Panseri and Federighi suggest. According to our results, only the form and structure of G P zones are the same in the two alloys.

In fig. 2c, we have plotted the resistivity curves as a function of ageing at 20° C, as taken from Panseri and Federighi's work with alloys quenched from 300° C. It can clearly be seen that, when maximum resistivity is reached, the intensity integral has still not acquired a stable value. This means that the composition of zones and the matrices changes, and the composition cannot be considered constant until the limiting stage is reached.

Table I shows that at any moment in development the radii of the zones measured by Guinier's and Porod's laws are different. This shows that there is always a widespread distribution of zone sizes. There is, therefore, no justification for the supposition that all G P zones reach the same size at the same time.

Although one can calculate, from fig. 2a, G P zone radii corresponding to the resisitivity maxima, there is no direct comparison with the radii given by Panseri and Federighi. In fact, these authors find, for the Al/10% Zn alloy, a critical radius 11Å, taken from a diagram (fig. 14, reference 1) which has the zone sizes found by Graf [20]. But these values are in turn determined by the angular position of the scattering ring. This gives a parameter which, although not precisely defined, is nearer to the diameter than to the radius of the G P zones [13].

Independently of this fact, fig. 2a shows that the values of the zone radii in the two alloys are similar until 30 min of ageing. Given that the structure of the G P zones is the same in both cases, the critical size, if it exists, must be the same; and the resistivity maximum should occur at a similar time in the two alloys. However, this maximum was observed after 5 min in the binary alloy and after 20 min in the ternary alloy. This does not seem to confirm that the maximum occurs when the G P zones reach a critical size, but this result is inconclusive. In fact, even if the radii of the calculated zones are similar in the two alloys, a different distribution of sizes occurs in the two cases. Moreover, experimental error at short ageing-times is considerable.

As for number of zones per unit volume, this diminishes in our model during isothermal ageing as $1/R^3$, and there is no direct relationship with ageing-temperature.

6. Conclusions

With small-angle X-ray scattering measurements alone, it is not possible to establish more conclusively the structure of alloys, without having recourse to more or less arbitrary hypotheses. Our study of Al/Zn and Al/Zn/0.1 % Mg alloys has, however, brought to light some analogies and differences not previously observed.

As for a quantitative description of the structure, this was based on the model of Bonfiglioli and Guinier [11] (with its limitations as already described by these authors). However, for the early stages of pre-precipitation which we have succeeded in measuring, with a refrigerated sample, there had previously been available only those models suggested by resistometric observations. The description given in this work is based upon X-ray scattering experiments, which are much more directly related to the structure than are the resistivity measurements.

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