Small-Angle X-ray Scattering Map of an Al–4 wt % Cu Alloy after Spinodal Decomposition

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A single-crystal of Al–4 wt % Cu having small GP zones was rotated in the plane normal to a quasi-point-collimated X-ray beam. Measurements of the scattered intensities in the plane of rotation of the sample allowed the construction on a map of the scattering in the reciprocal plane. This map is more complicated than the 'scattering cross' expected from thin platelets parallel to the three sets of \{100\} planes.

Introduction

The presence of anisotropic spinodal decomposition in Al–4 wt % Cu has been shown by small-angle X-ray scattering (Naudon, Delafond, Junqua & Mimault, 1976). The first observation, of a scattering ring from a polycrystalline sample, was in fact made possible by the association of several experimental conditions: (i) the use of Cu Kα radiation, which broadens out the scattering pattern to twice the width of that with Mo Kα radiation, which is usually used in the study of this alloy. (ii) Our small-angle X-ray camera was working with linear collimation and a bent-crystal monochromator, which, as a result of the precise convergence of the X-ray beam, reduces the uncertainty in the central angular region of the pattern, even when the power is quite large. (iii) The use of a sealed xenon–methane linear position-sensitive detector, which registers the scattering pattern by accumulation and allows measurement of the very weak scattered intensities given by the Al–Cu alloys in the early stages of spinodal decomposition.

Spinodal decomposition in Al–4 wt % Cu alloy was recently confirmed by electron-microscopic investigation (Rioja & Laughlin, 1977). They observed diffuse satellites to all fundamental reflections after 5 hours of aging at room temperature.

The X-ray scattering ring or the satellites in the electron diffraction pattern imply the existence of real-space modulations, as was first pointed out for the Al–Zn system by Bonfiglioli & Guinier (1966) when considering Cahn's (1961) theory of spinodal decomposition.

It is now well established that modern spinodal-decomposition theories predict a peak in the small-angle X-ray scattering intensity distribution (for example, Langer, 1973). Here we want to stress the fact that, when we speak of an X-ray peak (or ring in isotropic systems) relevant to the spinodal mechanism, this peak appears at the very beginning of the decomposition process and always shifts toward the primary beam. It is at the same time associated with the observation of a maximum in electrical-resistance measurements and a characteristic behaviour of the static magnetic susceptibility. Furthermore, the two mechanisms of GP zone formation, nucleation–growth and spinodal decomposition, have been distinguished in the Al–Cu system, as in Al–Zn alloys, and will be reported elsewhere.

Anisotropy of the spinodal decomposition in the Al–Cu system has been observed in the study of a single crystal, in which the [001] axis was parallel to the incident X-ray beam and normal to the long dimension of the position-sensitive detector. When the sample was rotated about this axis, a maximum was found on each of the four branches of the scattering cross. This means that the platelets are regularly spaced along the direction normal to their planes. By choosing a \langle 100 \rangle-direction streak (A) and a \langle 110 \rangle-direction streak (B), we observed differences in the first accumulations following the quench, i.e. at the beginning of the spinodal-decomposition process.

In order to get a more accurate small-angle pattern we have carried out this same study on the spinodal-decomposition anisotropy in Al–Cu alloys under other experimental conditions. However, before describing this new experiment it is necessary to make a critical analysis of the previous one.

Fig. 1. Single-crystal Al–4 wt % Cu quenched from 540°C into air at 20°C. 4 min accumulation after aging for 75 min along (A) and 80 min along (B). A square represents $2.83 \times 10^{-2}$ Å$^{-1}$ for s and 32 counts for the scattered intensity.
Comments on the former experiment

In order to restrict the measured scattered intensities to the beginning of the aging, just after the quench, the accumulation times were limited to four minutes. Two curves of the former experiment, corresponding to a quench into air, which greatly reduces the decomposition rate compared with a water quench, are shown in Fig. 1. The accumulation along orientation (A) corresponds to an aging time of 75 min and the other (B) corresponds to 80 min. The accuracy on the intensity scale is not very good since a square represents only 32 counts. Nevertheless, the experiment could be performed with a direct-beam cross section in the plane of the sample of 0.5 x 3 mm and with horizontal-slit aperture before the linear detector of 5 mm.

It can be seen in the central region of Fig. 1 that there is a rather important deformation of the small-angle pattern in the (001) reciprocal plane of the Al-4% wt Cu single crystal. Consequently, cross sections (A) and (B) of the scattered intensities near the central beam were altered by adjustment of the geometrical conditions, so as enhance the measurements of the small differences a little farther from the centre, between weak intensities along the (A) and (B) directions, which are needed to point out the anisotropy of the spinodal decomposition.

Description of the new experiment

By reducing in height the convergent monochromatic beam a quasi-point collimation is obtained. We chose a beam cross section of 0.5 x 1 mm for the sample and an aperture of 1 mm for the linear slit just before the detector. The distance between the sample and the detector is 130 mm and gives a slight vertical divergence. With these conditions the rotation of the sample about an axis parallel to the beam is equivalent to the rotation of the linear detector in the plane normal to the X-ray beam. In this case however, the intensity is much lower than in the previous experiment and it is not

![Graphical representation of the experiment results](image-url)
possible for the sake of accuracy to have only four minutes' accumulation. In addition, measurements for several different sample rotations must correspond to the same metallurgical state of the sample, that is to say no evolution must occur during the time necessary to carry out a set of measurements.

The Al-4 wt% Cu single crystal was quenched from 540°C into water and aged for 14 h at 60°C. Such an aging temperature is located in the spinodal region of the thermodynamic diagram, as we know from magnetic susceptibility measurements and in situ small-angle scattering which allowed us to locate the spinodal temperature at 140°C for this Al-4 wt% Cu alloy (Mimault, 1977). Finally, 5000 s was chosen for the accumulation times in order to get an accurate enough intensity scale; this time gives 256 counts for a square on the visualization screen.

Results

The different cross sections of the scattering along the (A) and (B) directions are indicated on the two schemes of Fig. 2, where the beam stop is represented by a vertical segment. Some of the scattering patterns are also shown on Fig. 2. The one indicated (A)0 is centered on the X-ray axis and (A)2 corresponds to an accumulation made when the linear position detector and its horizontal slit were raised up 2 mm.

No evolution was detected at room temperature during the time required to obtain the 13 scattered-intensity recordings. That is not very surprising because the precipitation process in the Al-Cu system is always slow at room temperature (Guinier, 1952) and even more so after aging at 60°C.

We can see on the (B)0 recording, obtained with good collimation and with no artifact of the slit geometry included, that a scattering maximum is obtained along the [110] direction. This maximum is lower than the one along [100] and its angular position is also different. This important fact is shown at the bottom of Fig 2 through the superposition of (A)0 and (B)0. The ratio between these two peaks is approximately \( \frac{1}{2} \), the one along [110] being closer to the primary beam than the one along [100]. With only (A)0 and (B)0 recordings it would be possible to suppose that the periodicity of a set of GP zones in a [100] plane is not only along a (100) direction but also along all other directions in this plane, because the spinodal decomposition gave a regular arrangement of the zones in this plane. However, such a feature cannot be explained so easily because the small-angle X-ray scattering pattern is more complicated. The map of the iso-intensity points has been reconstituted with different cross sections along (A) and (B) directions. The result is shown in Fig. 3, which for evident symmetry reasons is schematized for the whole pattern. The values 3, 2.5, 2, 1.5, 1 and 0.5 on the curves indicate the height in squares of the scattering on the cross sections shown on Fig. 2.

This map of the scattering in reciprocal space indeed looks like a cross, but in the central region it has the form of two pairs of butterfly wings. Let us note that in reciprocal space the streaks are in a plane tangent to the Ewald sphere. Consequently, part of the scattering density along the streaks is not effective in producing these patterns, although in the central region the result is good.

Discussion

The shape for the scattered intensity distribution, like butterfly wings, shown in Fig. 3 has previously been observed (Guillot, 1973; Guillot, Dauger & Caisso, 1973) from an identical single crystal of Al-4 wt% Cu alloy. That experiment was carried out on a Manenc system giving the scattering in the vicinity of a 200 reflexion and the result was obtained on a film. The crystal was quenched from 540°C and aged two months at 20°C.

It is advisable to say that much care must be taken when a scattering-pattern shape like butterfly wings around the 200 Bragg reflexion is compared with similar observations in the vicinity of the central peak. In reality, lattice distortions play an important part in the scattering pattern for the higher angles when coherent GP zones are present in a crystal, especially for Al-Cu alloys (Guinier, 1952), but the influence of the crystallographic distortions or displacement disorder is negligible in the central area of the reciprocal space relative to that of the substitutional disorder (Guinier, 1959). Nevertheless, the small-angle scattering pattern does not have the expected form of the well-known cross given by platelets parallel to the {100} planes of the crystal.

Now one can say that the butterfly-wings-like scattering around the 200 reflexion has an origin analogous to that giving a similar pattern near the origin of reciprocal space, except that around 200 the wings are not symmetric because of the distortions created by GP zones. Computer simulations were made by Guillot to explain this particular form of the scattering near the 200 reflexion and a promising approach to agreement with experiment was made when the influence of the surrounding GP zones was taken into account, that is to say when the correlations between a scattering GP zone and the others in its vicinity were allowed for. Such calculations must be carried out to explain the small-angle scattering pattern. We now have one less unknown parameter, the distance between the flat scattering centers in the perpendicular direction, but other parameters are still unknown.

As an example we can perform the following calculation for this single crystal of Al-4 wt% Cu alloy aged 14 h at 60°C in the spinodal region. It is assumed that GP zones are formed and the concentrations in this two-phase system are defined by the boundaries of a metastable miscibility gap.

![Fig. 3. Single-crystal Al-4 wt% Cu alloy quenched from 540°C and aged 14 h at 60°C. Equi-intensity contour map of the scattered intensities in the plane of the linear position detector normal to the [001] X-ray axis.](image-url)
In that case and according to Guillot, the copper concentration values are near 30 at.% for the GP zones and near 1% for the impoverished matrix solid solution. The volume fraction of the particles is then \( \beta = 0.025 \). The mean volume occupied by each zone (radius \( R \) and thickness \( h \)) is \( v = A^3 \) with \( A \sim 45 \AA \), given by the position of the scattering peak [cross section \( (A) \) in Fig. 2], and we have

\[
\beta = \frac{3\pi R^2 h}{v} = \frac{3\pi R^2 h}{A^3}.
\]

The factor 3 results from the existence of three sets of \{100\} planes.

When supposing a monolayer GP zone, we found that the diameter of the disc was 23 \AA, which result is consistent with the periodicity \( A = 45 \AA \) along a direction parallel to \langle 100\rangle.

It is concluded that this map with the particular form of butterfly wings should be explained in terms of not only the periodicities of the platelets normal to \langle 100\rangle directions, but also the correlations both between these platelets and those in their habit planes and, probably, between platelets in the three sets of \{100\} planes.

References


**Neutron Small-Angle Scattering Study of Phase Decomposition in Au–Pt**

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Isothermal decomposition of a Au–60 at.% Pt alloy, quenched from the solid as well as the liquid state, has been studied with the D11 neutron small-angle scattering spectrometer at ILL, Grenoble. An incident neutron wavelength of 6.7 \AA was used and measurements were carried out in the range of scattering vector \[ \beta = 4\pi \sin \theta / \lambda \] from \( 2.8 \times 10^{-2} \) to \( 21 \times 10^{-2} \) \AA\(^{-1}\). The preliminary results indicate that decomposition of this alloy at 550\(^\circ\)C takes place by a spinodal mode, although deviations were observed from linear spinodal theory, even at very early times. Slower aging kinetics were observed in liquid-quenched alloy as compared with solid-quenched. Liquid quenching is more efficient in suppressing quench clustering than is solid quenching. However, liquid quenching yields an extremely fine-grained material, which thereby enhances discontinuous precipitation at grain boundaries, competing with decomposition in the bulk. A Rundman–Hilliard analysis was used for the early stages of the spinodal reaction to obtain an interdiffusion coefficient of the order of \( 10^{-16} \) cm\(^2\) s\(^{-1}\) at 550\(^\circ\)C for the solid-quenched alloy.

I. Introduction

Spinodal decomposition has been described by several mathematical theories (Cahn, 1961, 1968; Langer, 1973). More recently attempts have been made (Marro, Bortz, Kalos & Lebowitz, 1975) to characterize such a decomposition process by means of computer simulation using Monte-Carlo techniques. In spite of these theoretical and computer simulation approaches to the understanding of this process, there is still inadequate correspondence to most of the reported experimental results.

From the experimental standpoint, the main requirements to obtain unambiguous information on the nature of the spinodal mechanism are the following: (i) The composition of the alloy to be studied should be at the center of a binary miscibility gap. (ii) Such an alloy should be quenched to high supersaturations so that limited quench clustering should have taken place.* The early stages of the temporal evolution of such a supersaturated solid solution can be most usefully followed by means of small-angle scattering (SAS) methods, since the SAS intensity is directly related to the Fourier transform of the composition fluctuations.

Rundman & Hilliard (1967), using Cahn's linear spinodal theory, have shown that the time-dependent intensity spectra, \( I(\beta, t) \), have a form

\[
I(\beta, t) = I(\beta, 0) \exp \left[ 2R(\beta t) \right].
\]

In this equation, \( \beta \) is determined from experimental diffraction data: \( \beta = (4\pi \sin \theta) / \lambda \), where \( 2\theta \) is the full scattering angle.

* Attempts to minimize quench clustering have been made by quenching from the melt (Agarwal & Herman, 1973), where cooling rates at least an order of magnitude higher than in conventional solid-quenching can be obtained.