Small-Angle Neutron Scattering of Single Crystals of Aged Aluminium–13 at. % Magnesium Alloy

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Abstract
X-ray, neutron and electron diffraction experiments have revealed the existence of internally ordered Guinier–Preston zones in Al–(8 to 15 at. %)Mg alloys; diffuse satellites oriented along <100> directions are observed near Bragg peaks and give rise to modulated contrasts by TEM. A small-angle neutron scattering experiment has been carried out on single crystals and a model is proposed for the interpretation of the observed pattern. The existence of concentration modulations is related to alignments of spherical GP zones along <100> directions.

Introduction
The formation of Guinier–Preston zones characterizes the early stages of phase separation in supersaturated solid solutions (Dauger, Guillot & Caisso, 1971; Bernole & Graf, 1972) resulting from the quenching of Al–Mg alloys (8 to 15 at. %). GP zones are approximately spherical as observed by transmission electron microscopy (Bernole, Graf & Guyot, 1973; Dauger, Denanot & Caisso, 1973) and X-ray scattering (Dauger, Guillot & Caisso, 1974). Their ordered internal structure has been determined by neutron diffraction (Dauger, Boudili & Roth, 1976) and has been confirmed by TEM (Boudili, Denanot & Dauger, 1977). However, this model does not explain the observations (X-ray and electron diffraction patterns) of satellites oriented along <100> near fundamental reflections. In addition, these satellites give rise to a modulated contrast by TEM; bright-field electron micrographs show one direction of modulation for \( g = (h00) \) and two directions for \( g = (hk0) \), which means that this microstructure appears through a strain contrast mechanism (parameter modulation). Again, this is the situation for high-angle X-ray scattering and therefore, except for their internal order and their shape (dark field electron microscopy), most of the information related to GP zones has been derived on the basis of lattice distortions.

In order to detect the so-called anisotropy in fluctuations of magnesium concentration, we have carried out small-angle neutron scattering experiments on single-crystal specimens. This study is restricted to the interpretation of the SANS pattern. A quantitative study of its dependence upon alloying and thermal history will appear in a subsequent paper.

Experimental conditions and results
A slice parallel to (110) was machined from an Al–13at. % Mg single-crystal obtained by the strain-anneal method; the slice was quenched and aged during several months at room temperature. The experiments were performed at the Laue–Langevin Institute High Flux Reactor on the D17 diffractometer, with a wavelength of about 11 Å.

The resulting pattern shows a continuous ring of scattered intensity with large reinforcements of the maxima along <100> directions. Intensity maps have been drawn (Fig. 1) under two orientations of the crystal with respect to the beam direction [<(100) and (110)] in order to illustrate this particular pattern.

Profiles of SANS intensity were obtained along all the <100> and <110> directions consistent with the previous specimen orientations, they are given in Fig. 2 (arbitrary units). Whatever the orientation, the intensity remains the same along analogous directions.

It is worth mentioning that:
(i) whatever the direction, the intensity has a maximum which is located at approximately the same position,

![Fig. 1. Small-angle neutron scattering: intensity maps in (100) and (110) planes.](image-url)
(ii) the maximum along \( \langle 100 \rangle \) is about twice that along \( \langle 110 \rangle \),
(iii) despite the fact that the particles are already large at this stage of aging (100 Å in diameter), no diffuse streak at larger angles is observed in any direction.

These features suggest that the anisotropy in the scattering pattern is mainly due to the distribution of the particles and that it is independent of their shape.

**Interpretation**

It is not possible to interpret such a pattern with the classical method, in which it is assumed that the particles are distributed at random, this method being appropriate to measurements carried out on polycrystals (Raynal, Roth, Bernole, Guyot & Graf, 1973; Raynal & Roth, 1975). An alternative model has therefore to be built in which the spatial distribution of the particles can be adjusted to provide a satisfactory simulated intensity along each direction of observation. We postulate that the statistical distribution of the projections of the distances between first neighbours in the direction of observation is a function, \( h(x) \), which fulfils the following conditions (model of a deformed one-dimensional atomic lattice; Guinier, 1956):

\[ h(x) \, dx \] is the probability for the distance between two first neighbours to be between \( x \) and \( x + dx \).

\( h(x) \) is normalized; \( \int_{0}^{\infty} h(x) \, dx = 1 \).

(c) The distance between neighbours \( n \) and \( n + 1 \) does not depend upon that between \( n + 1 \) and \( n + 2 \) neighbours.

(d) The mean value of \( x \) is given by

\[ a = \int_{0}^{\infty} x h(x) \, dx \]

and \( \Delta \) is the root mean square.

\[ \Delta^2 = \int_{0}^{\infty} h(x) (x - a)^2 \, dx \]

The scattering intensity can be expressed as

\[ I(s) = A a F^2(s) Z(s) \]

where \( F(s) \) is the scattering amplitude from a single particle with radius \( R \),

\[ F(s) = \frac{3 \sin(2\pi s R) - (2\pi s R) \cos(2\pi s R)}{(2\pi s R)^3} \]

\[ Z(s) = \frac{1 - \exp(-4\pi^2 s^2 \Delta^2)}{1 + \exp(-4\pi^2 s^2 \Delta^2) - 2\exp(-2\pi^2 s^2 \Delta^2) \cos(2\pi sa)} \]

\( A \) is a constant and \( s \) is the modulus of the scattering vector in the direction concerned.

\( I(s) \) depends on three parameters, \( R \), \( a \) and \( \Delta \), which are determined by fitting the calculated intensity to the experimental observations. Obviously, the same values of \( R \) and \( \Delta \) must be taken in the simulation along any direction of observation.

A good agreement between the simulated and the experimental curves (Fig. 3) is shown; the difference observed at very small angles (curve b) is related to experimental errors in this angular range and to the

Fig. 2. SANS intensity profiles in different directions.

Fig. 3. Comparison between calculated intensity and experimental points, \( R = 47 \, \text{Å}, a_{100} = 110 \, \text{Å}, a_{110} = 82 \, \text{Å}, \Delta = a/3 \).

Fig. 4. Linear pair correlation function \( P(x) \) obtained with the fitted parameters and a normalized Gaussian distribution function.
simplicity of the model. Each experimental point corresponds to the average of three measurements carried out in different equivalent directions: \(\langle 001 \rangle\) and \(\langle 010 \rangle\) in the \(\langle 100 \rangle\) plane and \(\langle 001 \rangle\) in the \(\langle 110 \rangle\) plane for curve 2(a); \(\langle 011 \rangle\) and \(\langle 011 \rangle\) in the \(\langle 100 \rangle\) plane and \(\langle -110 \rangle\) in the \(\langle 100 \rangle\) plane for curve 2(b).

The fitted mean radius of zones (47 Å) is fully consistent with the corresponding data derived from TEM observations (Dauger, Boudili & Roth, 1976).

The mean distance \(a\) is 1.34 times larger along \(\langle 100 \rangle\) (\(a_{\langle 100 \rangle} = 110\) Å) than along \(\langle 110 \rangle\) (\(a_{\langle 110 \rangle} = 82\) Å).

It is not possible to derive a straightforward interpretation of the obtained value of \(\Delta = a/3\). However, this parameter is related to the width of the statistic \(h(x)\), and it can be connected with the degree of order of the one-dimensional lattice. We can illustrate for example this linear distribution by postulating a Gaussian variation of \(h(x)\):

\[
h(x) = \frac{1}{\Delta \sqrt{2\pi}} \exp \left[ -\frac{(x - a)^2}{2\Delta^2} \right].
\]

Then, the fitted values of \(a\) and \(\Delta\) lead to the following quite reasonable pair of correlation functions (Fig. 4) written in the form:

\[
P(x) = \sum_{n=1}^{\infty} \frac{1}{\Delta(2\pi n)^{1/2}} \left\{ \exp \left[ -\frac{(x-na)^2}{2n\Delta^2} \right] + \exp \left[ -\frac{(x+na)^2}{2n\Delta^2} \right] \right\}.
\]

Discussion

Our conclusion is that, for the nearest neighbours, the GP zones are in a more or less ordered arrangement on a simple cubic lattice whose axes are the same as those of the parent matrix. This fact does not imply the existence of a 'paracrystal' but demonstrates the existence of concentration modulations and of alignments along \(\langle 100 \rangle\) directions.

We have tried to observe this structure by TEM but, in this Al–13% Mg alloy aged at room temperature, the evidence is shown only by satellites and modulated contrasts on bright-field micrographs. Nevertheless, in Al–16at.% Mg aged at 333 K, such zone alignments are visible (Gault, 1978) on dark-field micrographs (Fig. 5), because in this case there are less particles but they are larger.

In addition, we can evaluate in this model the mean volume fraction \(\beta\) of GP zones: \(\beta \approx \frac{4\pi}{3} \left( \frac{R}{a_{\langle 100 \rangle}} \right)^3\) and we obtain \(\beta = 32.6\%\), a large value which is consistent with that derived in the same alloy (\(m = 13\%)\) from the proposed concentrations inside \((m_z = 25\%)\) and outside the particles \((m_M = 7.5\%)\).

Finally, all salient features of X-ray, neutron or electron scattering patterns and of TEM observations are explained by this model of internal \(L_{12}\) ordered spherical GP zones aligned with a more or less diffuse periodicity along the three \(\langle 100 \rangle\) directions. The Al–Mg system is a new example in which phase separation and ordering occur simultaneously, with a modulated structure, and it is valuable to compare it with systems such as Cu–Ti (Laughlin & Cahn, 1975; Datta & Sofia, 1976) or Ni–Ti (Laughlin, 1976; Tsujimoto, Hashimoto & Saito, 1977).

Further discussion has then to be devoted to the early mechanism of this transformation; homogeneous nucleation and growth process or, more likely, initial spinodal decomposition.

References


