Characterization of Two Different Types of Long-Period Ordered Alloys by High-Resolution Electron Microscopy

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Abstract

High-resolution electron microscopy can be used to differentiate between two structural models of long-period ordered alloys. These models differ in the nature of the disorder as seen in the stacking irregularities which can have planar boundaries as exemplified by Ag_3Mg or wavy boundaries as in AuCu II. In the composition range 22–27 at. % Mg, Ag_3Mg is built up with a regular arrangement of two kinds of structural layers, 1 or 2 $L1_2$ cells in thickness. Some stacking disorder exists, but this alloy can be locally described using a space-group notation and has the character of being an infinitely adaptative structure. High-resolution images have been used to show the perfect planarity of the boundaries in Ag_3Mg, thus demonstrating the way in which disorder is accommodated in this alloy.

1. Introduction

It is well known that a number of Al alloys (AuCu, $AuCu_3$, Cu_3Pd, Ag_3Mg, Au_3Zn, ...) order to exhibit periodic antiphase structures (PAP) over specific concentration ranges. The most striking feature of these PAP structures is that $\bar{M}$ (the mean antiphase half-long period) changes with concentration and takes on non-integer values as measured in units of **a**, the parameter of the disordered Bravais cell **a,b,c**.

Two theoretical models have been devised to explain these non-integer values together with the sharpness of the diffraction spots. In the first of these, Fujiwara (1957) has considered a more or less regular stacking along the antiphase direction **a** of antiphase domains of different lengths, which are always integers or half

integers* measured in units of **a**. The stacking is defined by a periodic step function of period $2\bar{M}$ which characterizes the antiphase sequence called 'regular arrangement with uniform mixing'. As a consequence, the domain boundaries are thin and planar over large areas. It is possible to introduce some disorder in the stacking, while keeping the same mean period, by considering a statistical distribution function of disturbance for the sequence: we then get an 'irregular arrangement with uniform mixing'. Such stacking disorder, sometimes known as that of 'the first kind' (see Guinier, 1964), does not change the geometry of the diffraction pattern or the sharpness of the spots, and affects only the intensities.

In the second model (Jehanno & Pério, 1964; Jehanno, 1965), non-integer values of $\bar{M}$ are accounted for by an order function of period $2\bar{M}$ which represents the probability of occupancy of one of the ordered sublattices by a given chemical species in the planes perpendicular to the antiphase direction. The disorder is then equally distributed in each boundary. As a result, the antiphase boundary spacing fluctuates around the $\bar{M}$ average value. The boundaries can no longer be planar and become sinuous with a uniform mean spacing. Hence, the structural difference between these two models lies in the manner in which the disorder arises. In Fujiwara's model, a perfect long-range correlation in the planes perpendicular to the antiphase direction reduces the disorder to a pure stacking disorder. In Jehanno & Pério's model, where a possible short-range correlation is introduced in the planes parallel to and near to the boundaries, they

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* For an antiphase vector of the first kind $(\mathbf{b} + \mathbf{c})/2$ (which is the case for all experimentally observed monodimensional antiphase alloys) half-integer values can be obtained only for $L1_0$ ordered, and not for $L1_2$.

fluctuate in spacing but have a uniform average separation (Fig. 1).

It appears that both the above classes of ordering behaviour exist, a fact which has already been pointed out (Guymont & Gratias, 1978, 1979). In this paper, we demonstrate, with the aid of high-resolution microscope images, that Ag_3Mg, in the concentration range 20–27 at. % Mg shows PAP ordering formulations (stable below about 653 K) which are best described by Fujiwara's model in contrast to AuCu II which orders in the manner described by Jehanno & Pério.

2. Structural model of ordered Ag_3Mg

Earlier X-ray powder and electron diffraction results (Schubert, Kiefer, Wilkens & Haufler, 1955; Fujiwara, Hirabayashi, Watanabe & Ogawa, 1958; Hähnis, Mäki & Paalassalo, 1971) led to the following conclusions on the structure of Ag_3Mg:

(1) From 20 to 22 at. % Mg, $\bar{M} = 2$; the structure is DO_{23}.

(2) $\bar{M}$ decreases from 2 to about 1·67 as the concentration of Mg is increased from 22 to 27 at. %.

(3) The structure may be analysed as a mixing of antiphase domains of lengths $M_1 = 1$ and $M_2 = 2$ in various proportions, but with some disorder along a to account for the apparently continuous variation of $\bar{M}$ with concentration.

A recent electron diffraction investigation (Guymont & Gratias, 1979) has suggested that $\bar{M}$ varies discontinuously with concentration, only taking on values which can be specified by well defined ratios. Fig. 2 shows the structure corresponding to composition 25 at. % Mg. This structure is conveniently denoted $2\bar{2}2\bar{1}$, using Fujiwara's notation (the numbers symbolize the lengths of the successive domains and the minus signs denote those domains which are in antiphase).

As the concentration of Mg is decreased the proportion of domains of length 2 increases with the long period until no domains of length 1 remain at about 22 at. % Mg. It is thus the proportion of domains of length 1 which is apparently correlated with composition (Fig. 3).
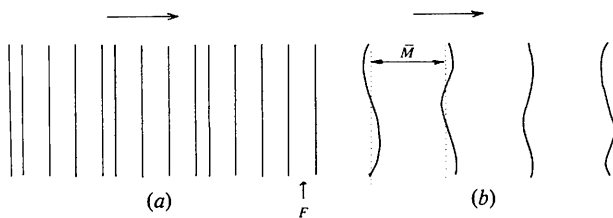
The following values of $\bar{M}$ have been identified for different alloy compositions: $\bar{M} = 10/6 = 1·667$ (26·5 at. % Mg); $\bar{M} = 7/4 = 1·75$ (25 at. % Mg); $\bar{M} = 18/10 = 1·8$ (24 at. % Mg); $\bar{M} = 26/14 = 1·86$ (23·5 at. % Mg); $\bar{M} = 2$ (22 at. % Mg).

All these results have been obtained disregarding any possible disorder of the first kind. The problem which thus arises is to determine how such disorder can be accommodated: either in the stacking sequence (stacking disorder) or in the boundaries themselves (as in Jehanno & Pério's model). It is not possible to distinguish between these two types of disturbance using diffraction data only because both models, provided that they correspond to the same statistical distribution function, give rise to the same diffraction intensities (homometric structures). The only way to settle the question then is to use high-resolution transmission electron microscope images.

3. High-resolution images of the ordering structures

The alloy preparation and subsequent foil-thinning techniques are described elsewhere (Guymont & Gratias, 1979). The observations were performed with a JEOL 120 CX provided with a top-entry goniometer
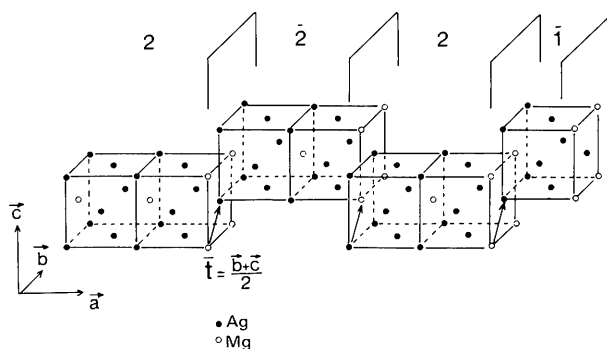

Fig. 2. $2\bar{2}2\bar{1}$ idealized structure of ordered Ag_3Mg ($b = c = 4$ Å; $a = 28$ Å).

Fig. 1. Schematic representation of the two types of disorder. (a) Fujiwara's model (F: stacking disorder). (b) Jehanno and Pério's model (fluctuating boundaries around an average spacing $\bar{M}$).
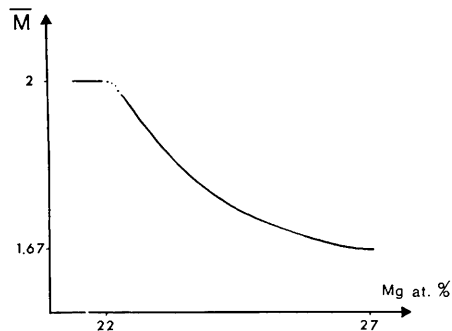

Fig. 3. Variation of the mean half period $\bar{M}$ versus the Mg concentration.

stage operated at 100 kV. (The spherical aberration coefficient C_s of the objective lens was $2 \cdot 5 \pm 0 \cdot 2$ mm.)

Image formation in the microscope, using selected diffracted beams, realizes a partial Fourier synthesis, but the transfer function of the microscope makes any simple correlations of image and structure rather difficult. Furthermore, the experimental conditions (e.g. foil thickness, defocus, exact local orientation of the sample, beam convergence and coherency) are generally not known with sufficient accuracy to trust the reliability of the calculated simulations without special care.

However, in the case investigated here, it is relatively simple to distinguish between the two types of disorder because of the perfect long-range order correlation in the planes perpendicular to the antiphase direction imposed by Fujiwara's model: the images taken in a plane containing the antiphase direction will be sensitive to fluctuations in the stacking sequence from a given superstructure row and give rise to rectilinear and parallel fringes, which are neither necessarily equispaced, nor of uniform intensity. On the other hand, boundaries in a material ordered as described by Jehanno & Pério's model will appear as sinuous, badly defined, blurred regions with a definite average spacing ($\bar{M}$). Fig. 4 shows a dark-field micrograph taken with a superstructure PAP row of $2\bar{2}\bar{2}\bar{2}1\bar{2}\bar{2}\bar{2}2\bar{1}$ ($\bar{M} = 18/10$) ordered Ag_3Mg. Typical interference fringes are observed: they are rectilinear, parallel and not equispaced. The defocus ($\varepsilon = -1000$ Å) has been chosen so that the stacking sequence can be clearly visualized. This general aspect is quite similar to images observed on Au_4Zn (Van Tendeloo & Amelinckx, 1977). The images of other Ag_3Mg structures for different compositions previously recognized by their diffraction patterns (Guymont & Gratias, 1979) are shown in Figs. 5 and 6. The proportion of domains of length 1 decreases with the Mg content. This type of ordering is already well known for mixed oxides where it is sometimes termed infinitely adaptive (see e.g. Anderson 1977). As a further illustration of this 'infinitely adaptive' behaviour, images of ordered arays of $(2\bar{2}\bar{2}1)$ and $(2\bar{2}\bar{2}\bar{2}1)_2$ sequences have been observed for intermediate compositions (Fig. 7). Here, $\bar{M} = 32/18$; there-
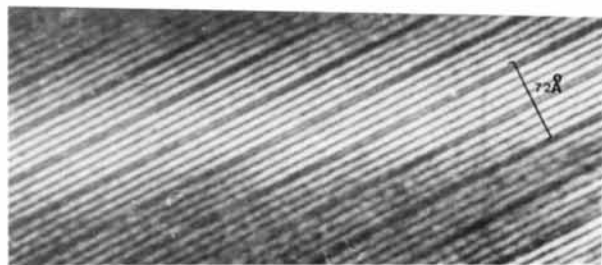
fore the long-period parameter $\mathbf{A}$ is 32 $\mathbf{a}$ ($a = 4$ Å). Other similar types of arrays that might result from other intermediate concentrations can be readily imagined. In spite of the high value (astonishing for a metallic alloy) of $\mathbf{A}$, this latter quantity will clearly always be expressible as $\mathbf{A} = (2n_2 + n_1)\mathbf{a}$ and consequently
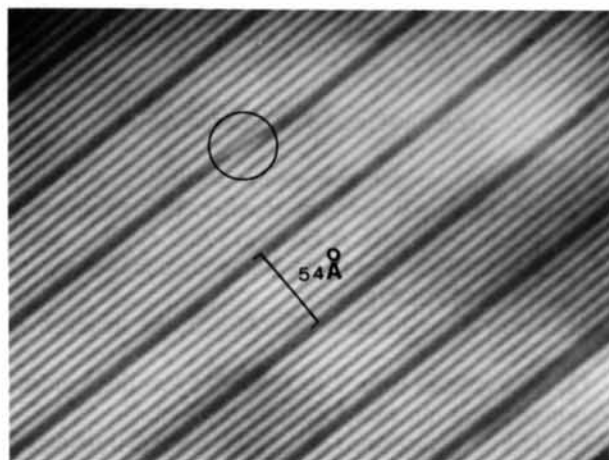
$$\bar{M} = (2n_2 + n_1)/(n_2 + n_1),$$

Fig. 5. Lattice image of an irregular arrangement with uniform mixing obtained after magnesium loss. (The diffraction pattern corresponds to the average structure: $2\bar{2}\bar{2}2\bar{2}\bar{2}2\bar{1}$, $\bar{M} = 15/8$.) Note the existence of disorder at the level of a boundary (encircled).
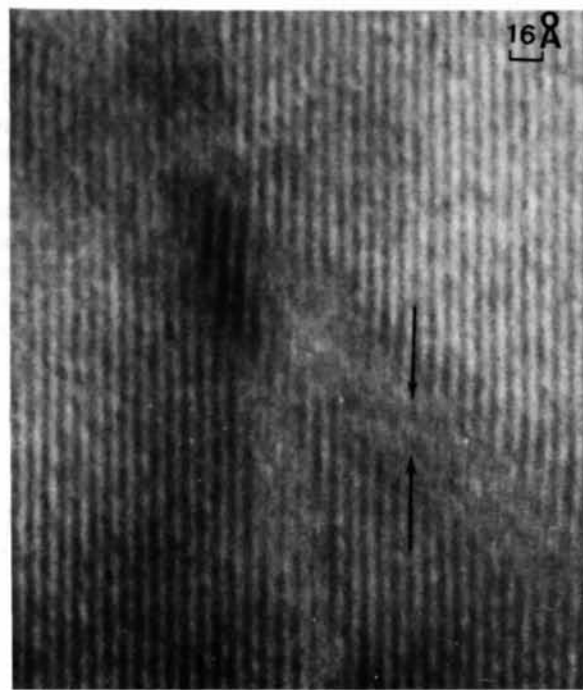

Fig. 6. DO_{23} structure $(2\bar{2})$ for 22 Mg at. % alloy. Note the presence of inclined antiphase boundaries.

Fig. 4. Lattice image of the $(2\bar{2}\bar{2}\bar{2}1)_2$ structure ($b = c = 4$ Å; $a = 72$ Å).

where n_1 and n_2 denote the number of domains of lengths 1 and 2 respectively.

All these structures are well described by the 'uniform mixing' model of Fujiwara and many arrays show no stacking disorder over a large distance in the **a** direction. The arrays are thus well described by the 'regular arrangement' terminology: the structure can then be locally described by a space group.

The images formed using a large objective aperture (diameter 0.45 Å^{-1}) with the sample in the Laue symmetric orientation and the undeviated beam on the optical axis exhibit the projected symmetry of the crystal (*via* its potential). For instance, the antiphase shift between adjacent layers is clearly visible in Fig. 8, in agreement with the proposed structure $2\bar{2}2\bar{2}1\bar{2}\bar{2}2\bar{2}\bar{1}$: the planar symmetry of the image is *cmm*, which is the projected group of the space group *Immm* of the structure.

In particular, the boundaries remain well defined planes with no disorder even on the scale of the unit cell. Further details of the contrast phenomena will be presented elsewhere.
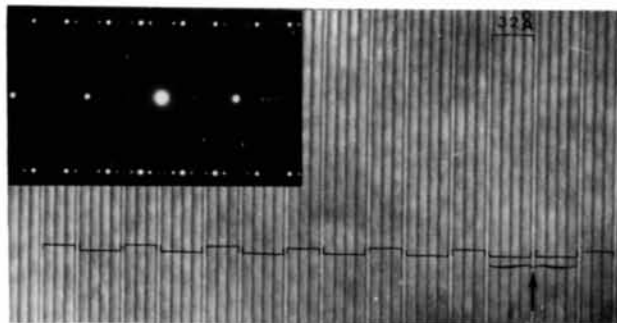

Fig. 7. Lattice image and corresponding diffraction pattern of the ordered syntaxy $(2\bar{2}2\bar{1}2\bar{2}2\bar{2}1)_2$ ($b = c = 4$ Å; $a = 128$ Å). Note the existence of stacking disorder (arrowed).
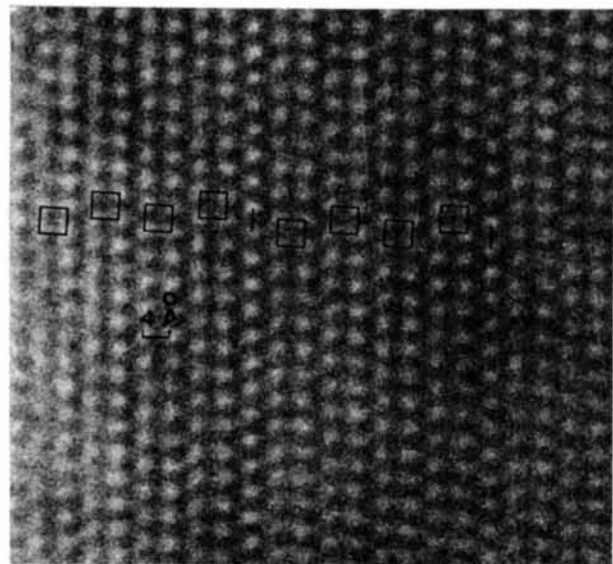

Fig. 8. High-resolution image of the $(2\bar{2}2\bar{2}1)_2$ structure.

4. Discussion

The high-resolution images of ordered Ag_3Mg show that disorder fluctuations are accommodated in the stacking sequence and that the thinness of the boundaries (true reticular planes) is not affected. Moreover, all observed structures may be derived from a periodic step function corresponding to a 'uniform mixing' as expected by Fujiwara. The degree of disturbance in the arrangement may be estimated from the micrographs by a normal statistical distribution with a root-mean-square deviation of about 10^{-3}. It is interesting to compare these images with those obtained by similar means from AuCu II alloys (Mikama, 1971; Watanabe & Takashima, 1975). In this case, the antiphase boundaries appear as sinuous, blurred equispaced regions more indicative of Jehanno & Pério's model. We also have obtained such images, in bulk materials, thus confirming the observations of the above authors (Guymont, Portier & Gratias, 1980). The normal statistical distribution of disorder along **a** for the boundary itself may also be crudely estimated by measuring its thickness. One obtains a root-mean-square deviation σ of about 10^{-1} for $M \simeq 5$. The ratio σ/M for AuCu II is much larger than that for Ag_3Mg. Obviously a comparison may be meaningful for PAP alloys epitomizing both classes only with comparable $\bar{M}$ values.

References

ANDERSON, J. S. (1977). *J. Phys. (Paris) Colloq.* **38**(C7), 17–27.
FUJIWARA, K. (1957). *J. Phys. Soc. Jpn*, **12**, 7–13.
FUJIWARA, K., HIRABAYASHI, M., WATANABE, D. & OGAWA, S. (1958). *J. Phys. Soc. Jpn*, **13**. 167–174.
GUINIER, A. (1964). *Théorie et Technique de la Radiocristallographie.* Paris: Dunod.
GUYMONT, M. & GRATIAS, D. (1978). *J. Phys. (Paris) Lett.* **39**, 437–439.
GUYMONT, M. & GRATIAS, D. (1979). *Acta Cryst.* A**35**, 181–188.
GUYMONT, M., PORTIER, R. & GRATIAS, D. (1980). *Acta Cryst.* A**36**. Submitted.
HÄHNIS, K. MÄKI, J. & PAALASSALO, P. (1971). *Acta Metall.* **19**, 15–20.
JEHANNO, G. (1965). *Structures et Longues Périodes dans les Alliages Or–Cuivre.* Thèse, rapport CEA R2812, Univ. D'Orsay.
JEHANNO, G. & PÉRIO, P. (1964). *J. Phys. (Paris)*, **25**, 966–974.
MIKAMA, K. (1971). *J. Phys. Soc. Jpn*, **31**, 1677–1682.
SCHUBERT, K., KIEFER, B., WILKENS, M. & HAUFLER, R. (1955). *Z. Metallkd.* **46**, 692–715.
VAN TENDELOO, G. & AMELINCKX, S. (1977). *Phys. Status Solidi A*, **43**, 533–564.
WATANABE, D. & TAKASHIMA, K. (1975). *J. Appl. Cryst.* **8**, 598–602.