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Initiation of ordering in an AuCu alloy

MICHIO OHTA, MASAHARU NAKAGAWA
Department of Dental Materials Engineering, Faculty of Dentistry, Kyushu University, Fukuoka 812, Japan
KATSUHIRO YASUDA
Department of Dental Materials Science, School of Dentistry, Nagasaki University, Nagasaki 852, Japan

Planar misfit between fcc and fct and elastic anisotropy in a cubic crystal were examined to understand the crystallographic relationship between the ordered domain and the matrix in the ordering of an AuCu alloy. The results of these calculations did not indicate any definite conjugate plane between the ordered phase and surrounding matrix. A model modified from the crystallization phenomena in amorphous alloys was proposed to understand the ordering in the AuCu alloy. According to the model, the degree of order can be varied from the surface of the ordered domain to the matrix with some area of transitional region, i.e. without any defined interface. This leads to the conclusion that the idea of a specific habit plane is meaningless for understanding the initiation of the AuCu ordering. The validity of the model was supported by the direct observation of the initial stage of precipitation in an Al–Li alloy.

1. Introduction

Disorder–order transformation which involves a change in the crystal symmetry is accompanied by an elastic distortion of the matrix. This elastic strain causes hardening of the alloy as an analogy with precipitation hardening. Because of age-hardenability, much attention has been given to the ordering of such alloys and many works have been reported.

An equiatomic AuCu alloy has a disordered face centred cubic (fcc) structure above 683 K. Below 658 K, an AuCuI type ($L1_0$, face centred tetragonal, fct) ordered structure forms, which consists of alternate (0 0 2) planes of all gold and all copper atoms. Between 658 and 683 K, an AuCuII type ($L1_{0\text{-s}}$, orthorhombic) structure with periodic anti-phase domain boundaries forms. A fully ordered structure is characterized by a twinned structure with twin boundaries of (1 0 1) type.

Ordering in the AuCu alloy was believed to be initiated by the nucleation of ordered domains on the plane parallel to the (1 0 1) type of the disordered matrix. Most of the predictions arise from the basis of lattice misfit between the ordered and the disordered structure. However, observations on the initiation of ordering have not yet been carried out in detail.

Hirabayashi and Weissmann [1] observed the structure of equiatomic AuCu alloy aged at 373 K for 7.2 ksec, using a transmission electron microscope. They concluded, from the analysis of directions of striae in a bright-field image and streaks in a selected-area diffraction pattern, that thin platelets of ordered domain were formed on the plane parallel to (1 0 1) of the matrix.

Kuczynski *et al.* [2] and Syutkin *et al.* [3] predicted that the elastic strain would be minimum if a (1 0 1) type plane was chosen as the habit plane of the AuCuI ordering. But their prediction arose only from observations of a fully ordered twin or twin-needle structure.

According to the reports so far, the ordering process in the AuCuI may be summarized as follows.

1. A thin platelet of ordered domain is formed coherently on the plane parallel to some definite crystallographic plane (supposed to be (1 0 1) type) in the matrix [1].
2. Elastic coherent strain increases with the growth of the domain.
3. Because of the elastic anisotropy, a disordered matrix will have relatively low resistance to shear on (1 0 1) to $[10\bar{1}]$ [4]. Order twins are generated by the movement of $\frac{1}{2}[10\bar{1}]$ dislocations on successive (1 0 1) planes [5].

Among the above items, no direct evidence is available on the crystallographic orientation relationship between the ordered domain and the matrix. Observations of twinned structure or dark-field image by superlattice reflection do not give us any useful information relating to the habit plane of the AuCu ordering. The former does not correspond to the initial stage of ordering and the latter shows only the arrangement of ordered domains.

In this study, some factors which concern the above problem are discussed and a mechanism for the initiation of ordering in the AuCu alloy is proposed.

2. Factors playing a part in the conformity between ordered and disordered structure

2.1. Misfit between fcc and fct

A difference in the crystal structure between the matrix and precipitates (ordered phase in this case) causes misfit on the conjugate plane of these phases. The amount of misfit depends, apparently, on the crystal

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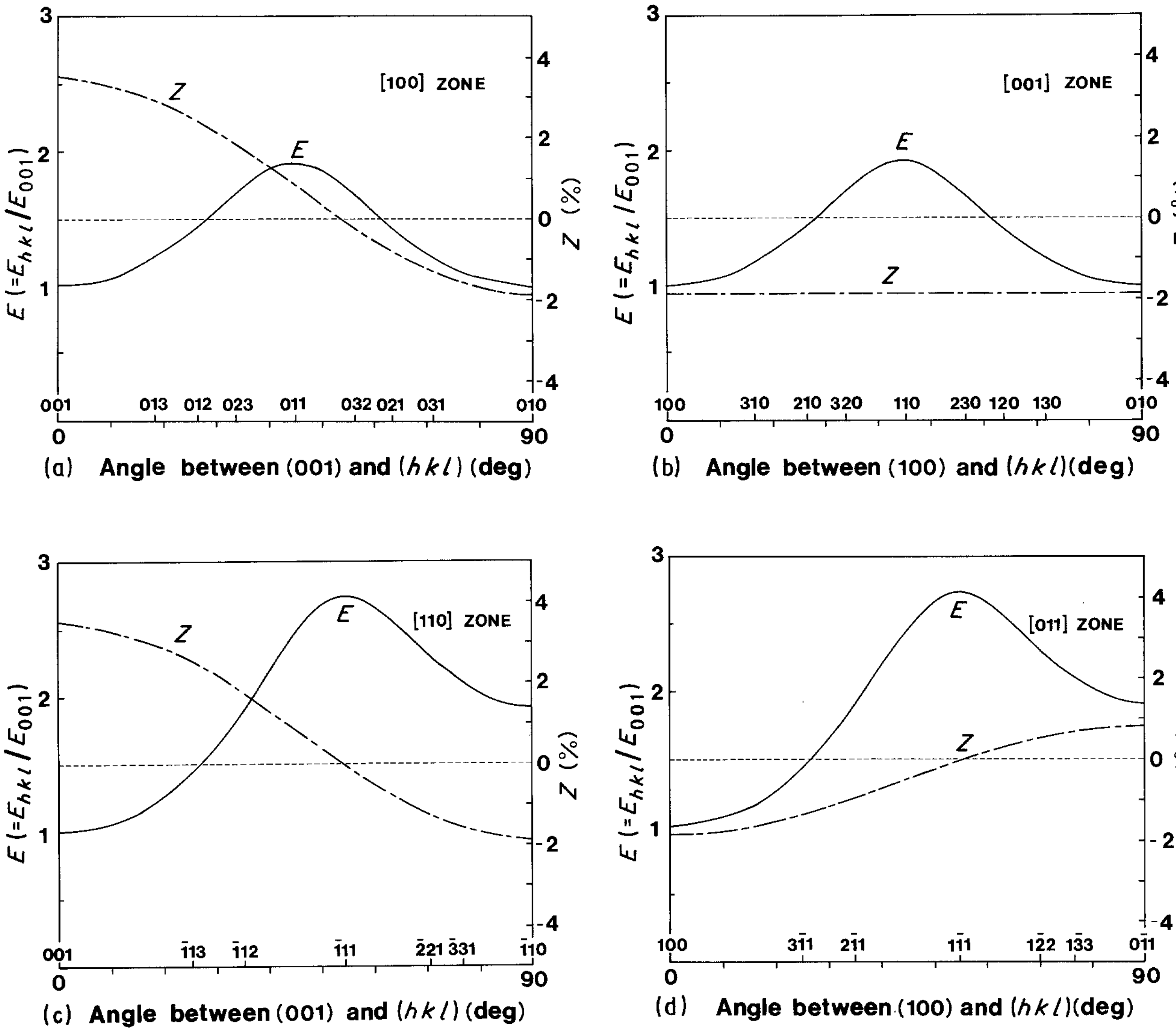

Figure 1 Planar misfit parameter, Z, elastic anisotropy, E, of (a) [1 0 0], (b) [0 0 1], (c) [1 1 0] and (d) [0 1 1] zonal planes.

structures of these two phases and varies with lattice constants and the indices of the conjugate plane.

Planar misfit parameter, Z, is expressed by

$$Z = (A'_{hkl} - A_{hkl})/A_{hkl} \qquad (1)$$

where A_{hkl} and A'_{hkl} are the area of the hkl plane in the unit cell of the matrix and ordered fct phase, respectively.

The misfit parameter, Z, of the hkl zonal plane are plotted in Figs 1a to d the zone axes of which are [1 0 0], [0 0 1], [1 1 0] and [0 1 1], respectively. In the estimation of Z, a lattice parameter of $a_0 = 0.3872$ nm for the matrix (aged at 573 K for 120 sec), $a' = 0.3939$ nm and $c = 0.3735$ nm for the ordered tetragonal (at 573 K for 300 sec) were employed.

Among the low-index planes, Z becomes large in the order $\{1\,1\,1\}$, $\{1\,1\,0\}$, (1 0 0) (0 1 0) (planes parallel to the c-axis) and (0 0 1) (plane perpendicular to the c-axis). If the amount of misfit only is concerned, $\{1\,1\,1\}$ must be the most favourable habit plane of ordering, as suggested by Harker [6].

2.2. Elastic anisotropy of the matrix

Anisotropy of the elastic modulus of a crystal affects the ease of growth and the resulting shape of coherent precipitates. Anisotropy of Young's modulus is expressed by

$$\frac{1}{E_{\alpha\beta\gamma}} = \frac{C_{11} + C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})} + \left(\frac{1}{C_{44}} - \frac{2}{C_{11} - C_{12}}\right)(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2) \qquad (2)$$

where C_{11}, C_{12}, C_{44} are elastic constants and direction cosines α, β, γ are related to the Miller index h, k and l.

The values of elastic constants of disordered AuCu alloy are not available. Although the elastic constants of gold and copper are different, the parameter $E = E_{hkl}/E_{001}$ which represents the elastic anisotropy, are concordant between them. The parameter E for [1 0 0], [0 0 1], [1 1 0] and [0 1 1] zonal planes was calculated using elastic constants of gold ($C_{11} = 1.92 \times 10^{12}$ dyn cm^{-2}, $C_{12} = 1.63 \times 10^{12}$ dyn cm^{-2}, $C_{44} = 0.42 \times 10^{12}$ dyn cm^{-2}), and are shown in Figs 1a to d. Young's modulus is minimum along the $\langle 1\,0\,0\rangle$ direction and maximum along the $\langle 1\,1\,1\rangle$ direction.

In the cubic crystal, a (G.P.) zone is frequently formed on the plane parallel to (0 0 1). On ageing Cu-2% Be [7] and dental Ag-Pd-Cu-Au [8, 9] alloys, a G.P. zone of one atomic layer is formed on every

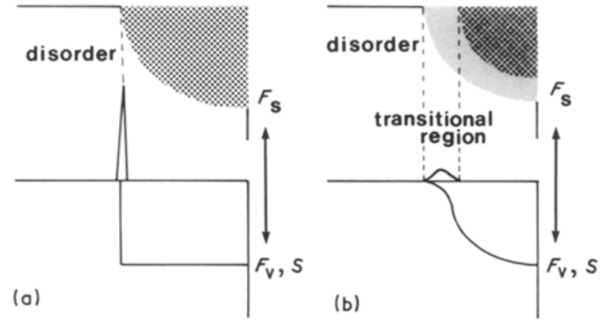

Figure 2 A model for nucleation of an ordered domain and corresponding volume (F_v) and surface (F_s) free energy. (a) CuPd with clear interface and (b) AuCu with transitional region.

two layers of (0 0 2) plane, which yield an $L1_0$ platelet parallel to the (0 0 1) plane of the matrix. This seems to be pertinent to the fact that the fcc matrix is elastically softest along the ⟨0 0 1⟩ direction.

In the case of ordering of stoichiometric AuCu alloy, fct ordered phase is formed in the fcc matrix and the situation is the same as in the alloy systems mentioned above in this regard. It is supposed, therefore, that (0 0 1) is more favourable as the habit plane of AuCu ordering than (1 0 1).

As described above, no clear evidence is available for the definite ordering habit plane of the AuCu alloy. The high resolution lattice image technique seems to be useful to reveal the crystallographic orientation relationship between ordered domain and disordered matrix. However, the ordering reaction is too fast to catch the morphology of the very initial stage of ordering [10].

3. Supposed mechanism of ordering

Ordering behaviour of the stoichiometric AuCu is different from that of CuPd. Ordering in CuPd is accompanied by a change in the crystal structure from fcc to $L2_0$ (body centred cubic), whereas the ordered structure of the AuCu (fct) is fundamentally the same as that of the disordered structure (fcc).

Ordering in the CuPd alloy starts with short-range ordering in all the crystal grains. With a sufficient length of incubation period, long-range ordered domains start to appear at the grain boundaries with clear interfaces [11, 12]. As ageing continues, the interface moves towards the grain interior, which accompanies the increase in the volume fraction of the ordered phase; in other words, increase in the degree of order.

Ordering in the AuCu alloy also accompanies a structural change (from fcc to fct). Both structures, however, have four atomic sites at $0\,0\,0$, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$ in the unit cell. In the ordered state, gold atoms occupy the lattice points of $0\,0\,0$, $\frac{1}{2}\frac{1}{2}0$ and copper atoms occupy the remainder. In a stoichiometric alloy, ordering can be easily attained by short-range diffusion of atoms, probably by exchanging atomic sites between nearest or second nearest neighbours. Because of the ease of ordering, some amount of long-range ordering is accomplished during quenching, as evinced by the increase in hardness and decrease in electrical resistivity [13].

Such an easy start of the phase transformation can be seen in the crystallization of amorphous alloys which also entails a decrease in the free energy of the system analogous to the ordering phenomena. Fujita *et al.* [14] observed the crystallization processes of amorphous Fe–B and Ni–B alloys by high-resolution electron microscopy and proposed a model for crystallization. According to their observations, crystallization occurs through the formation of microcrystals which consist of fine crystallites without sharp interfaces with the matrix. The interface gradually changes to a sharp one before further growth of the microcrystals. This model can be applied to the ordering of the stoichiometric AuCu alloy.

Some amount of excess vacancies migrate to the crystal surfaces, dislocations or grain boundaries during quenching from a temperature higher than the critical temperature of ordering (T_c), because of low migration energy of a vacancy in this alloy system [15]. This causes the exchange of atoms, and this exchange invariably increases the number of correct atoms which occupy correct atomic sites in the unit cell of the ordered structure. This region, in which the density of correct atoms is high, has a high degree of order (S) and low volume free energy (F_v), and is thought to be the nucleus of the ordered domain. If a clear interface is introduced between this region and the matrix, free energy increases with increasing interface energy (F_s). In the case of AuCu, however, both the ordered phase and the matrix have fundamentally the same structure and a clear interface is not required; that is, the density of correct atoms (or degree of order) can vary gradually from the surface of the ordered domain to the matrix, as schematically illustrated in Fig. 2b. If the transitional region ($1 > S > 0$) has some width, misfit between the ordered domain and the matrix should be relaxed. This leads to the conclusion that the idea of a specific habit plane is meaningless for understanding the initiation of the AuCu ordering.

Because of the fast reaction of ordering in the AuCu alloy, no direct evidence can be obtained from the transmission electron microscopy to support the above-mentioned ordering mechanism, as mentioned before. However, observation of the structure formed in the

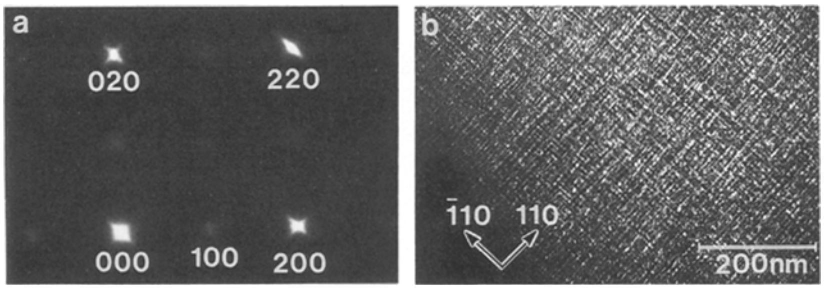

Figure 3 (a) Selected-area diffraction pattern and (b) (1 0 0) dark-field electron micrograph of a stoichiometric AuCu alloy quenched from 773 K.

initial stage of precipitation in an alloy of Al–9.7 at % Li [16] showed that small ordered domains of $L1_2$ structure were distributed homogeneously in the disordered f c c matrix, and the interface or boundary of these domains have a characteristic vague and complicated morphology. This fact supports the validity of the model proposed in this study.

Fig. 3 shows an electron diffraction pattern (a) and a (1 0 0) dark field electron micrograph (b) of stoichiometric AuCu alloy quenched from 773 K into iced brine. The ordered domains aligned along [1 1 0] and $[\bar{1}\,1\,0]$ directions of the matrix. Streaks along ⟨1 1 0⟩ were also seen in the diffraction pattern. These results seemingly indicate the preferential nucleation of thin ordered domains on {1 1 0} planes. However, elastic interaction between domains must be considered in the explanation of the morphology. Wen *et al.* [17] carried out a computer simulation experiment for a precipitate rearrangement process in a simple two-dimensional solid. In the model, coherent rectangular particles are randomly distributed over a square lattice, and are permitted to undergo a step-wise reconfiguration so as to decrease the elastic energy. The computer-generated picture and a simulated diffraction pattern are in good agreement with the dark-field image and the diffraction pattern which are shown in Figs 3a and b, respectively. The results suggest that preferential growth of the domain after nucleation is allowed only for the domains which exist along the ⟨1 1 0⟩ direction of the matrix.

4. Conclusions

Planar misfit between f c c and f c t and elastic anisotropy in a cubic crystal were considered to understand the crystallographic orientation relationship between the ordered domain and the matrix in the ordering of an alloy AuCu.

Principal results obtained were as follows.

1. Among the low-index planes, planar misfit parameter, Z, becomes large in the order {1 1 1}, {1 1 0}, (1 0 0) and (0 1 0) (planes parallel to c-axis) and (0 0 1) (plane perpendicular to c-axis). If only the amount of misfit is concerned, {1 1 1} must be the most favourable habit plane of ordering.

2. The matrix with f c c structure is elastically softest along the ⟨0 0 1⟩ direction, and (0 0 1) seems more favourable as the habit plane than (1 0 1).

3. The results of the calculation did not indicate any specific conjugate plane between disordered and ordered structure.

4. A model for the crystallization in amorphous alloys was applied to the ordering in the AuCu alloy, in which a transitional region between ordered domain and disordered matrix exists and relaxes the misfit. This leads to the conclusion that the idea of a specific habit plane is meaningless for understanding the initiation of the AuCu ordering. The validity of the model was supported by the direct observation of the initial stage of precipitation in an Al–Li alloy.

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