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FIELD ION MICROSCOPIC OBSERVATION OF ORDERING PROCESS IN A CuPt ALLOY

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Abstract. Change in microstructure of CuPt alloy was studied by field ion microscopy. It was found that in a quenched alloy small spherical ordered domains with a low degree of order are dispersed in a disordered matrix. The size of the domains was estimated to be about 1 - 2 nm. Upon aging at an appropriate temperature, the size of the ordered domains preferentially increases, and then the degree of order inside the domains increases by a significant extent to reach the equilibrium value. The kinetic behavior of the ordered domains was analyzed with thermodynamics, and it was concluded that excess increases in strain energy and surface energy of the ordered domains suppress the development of degree of order in the early stage of aging.

I. Introduction

A CuPt alloy with an equiatomic composition is known to have an order-disorder transformation of the first order at $T_c=1088$ K. The order structure is of Ll1 type which has a rhombohedral symmetry. The transformation of the alloy was intensively studied by means of electrical resistivity measurement [1-3], electron microscopy [1,2,4], X-ray diffraction [5,6] and so on. However, the ordering process in the alloy still remains obscure in terms of the kinetic behavior which is correlated with the microstructure. In the present study, the change in microstructure of the alloy with ordering was observed using a field ion microscope (FIM). The changes in size of the ordered domains and degree of order inside the domains obtained were analyzed with thermodynamics where the effects of strain energy and surface energy of the order domains were taken into account.

II. Experimental

Alloy ingots of CuPt were made in an induction furnace or an arc furnace in vacuum. The alloy compositions of the ingots were chemically analyzed or estimated from the values for the lattice parameters to be 50.3 - 50.6 at%Pt. The ingots were swaged and drawn to wires 0.3 mm in diameter. The wires sealed in a quartz capsule were annealed at 1173 K and then quenched into iced brine. At the moment of quenching, the quartz capsule was broken in order to get a fast quench. The wires were

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subsequently aged for various lengths of time to promote ordering. The heat-treated wires were electropolished to tips in an electrolyte of \((\text{CaCl}_2 + \text{HClO}_4 + \text{HCl})\) or aqua KCN. Field ion micrographs were taken at the temperature of liquid nitrogen using He as an imaging gas.

III. Results

(i) Ordered alloys

CuPt alloys well ordered were observed in order to examine the visibility of the ordered structure. Figure 1 shows an example of the micrographs of the specimen annealed at 873 K for 0.85 Ms. One can see some white dots are missing (indicated by arrows in (a)) and extra ones have appeared between the concentric white rings (in (b)). These indicate the existence of wrong occupations of atoms in the alloy, as the white dots are thought to correspond to Pt atoms. According to Walker’s results [5], the equilibrium value for the degree of order in CuPt at 873 K is about \(S = 0.96\) in Bragg and Williams’ sense, so that a few wrong occupations are naturally expected. Actually, such irregularities of the white-dot-arrangement were scarcely recognized in the FIM photographs of the alloy annealed at 623 K, where the equilibrium value for \(S\) is almost equal to unity. The observation confirms a good visibility with the FIM apparatus used in the present work.

(ii) Partially ordered alloys

Figure 2 shows FIM photographs of the alloy which was quenched from 1173 K and subsequently aged at 923 K. In Fig. 2(a) for the as quenched alloy, one can see numerous white dots arranged almost randomly and also small ring patterns locally (indicated by a circle). Even if the alloy is completely disordered, ring patterns can be observed around poles with low indices. In such a case, however, the ring pattern is expected to be more irregular and the difference in radius is much small between the adjacent rings. Therefore, the regions with the ring pattern in Fig. 2(a) are considered as "locally ordered regions" or "ordered domains". The diameter of the ordered domains and the interdomain distance are roughly estimated to be 1 nm and several nanometers, respectively.

Upon aging, as shown in Figs. 2(b) to (d), the ordered domains grow up gradually and the alloy becomes to have a homogeneous state of order. It is noted that the ring pattern in the ordered domains is not so clear at the early stage of aging as that in the well ordered alloy, whereas the domains have grown up to be as large as 2 - 4 nm in diameter. This indicates that the ordered domains increase their size first, keeping the degree of order \(S\) at a relatively small value. In this connection, Chevalier et al.[4] reported \(S = 0.5\) inside ordered domains in a quenched CuPt. It is interesting that the numerical value is smaller than 0.77, the minimum value for the equilibrium degree of order [5].

Many models for ordering process have been proposed, some of these being schematically drawn in Fig. 3. The ordering process can be essentially described by the evolution of the degree of order and the size of the ordered regions, and the evolution has a different fashion among the models. There is not a disordered matrix in models (a) and (b), but in (c) and (d). The degree of order changes in a different way between (a) and (b), as well as (c) and (d). The present FIM observation strongly suggests that the ordering process in the quenched CuPt is in the category of model (d).

IV. Discussion

The kinetic behavior of ordering in CuPt is analyzed in terms of free energy. Figure 4 shows the structure model under consideration, where we presume as follows: ordered domains are embedded in a disordered matrix; the degree of order is homogeneously equal to \(S\) inside the ordered domains; the radius of the ordered domains and the interdomain distance have unique values \((r \ and \ 2R)\); there are no Ostwald ripening and no new precipitating during the process. The total free energy of the alloy per unit volume, \(F\), can be presented by

\[ F = 4\pi r^3 n f(S)/3q + n \varepsilon(S,r,R) + 4\pi r^2 n \sigma(S), \]

(1)

where \(f(S)\) is the configurational free energy for the ordered state with \(S\) per atom, \(q\) the averaged volume of an atom, \(n(=3/4\pi R^3)\) the number of ordered domains in a unit volume, \(\varepsilon(S,r,n)\) the strain energy around an ordered domain and \(\sigma(S)\) the surface energy. \(f(S)\) is expressed by Landau’s expansion:
where \( a, b \) and \( c \) are temperature dependent parameters:
\[
a = -a_1 + a_2 T, \quad b = b_1 + b_2 T, \quad c = c_1 + c_2 T.
\]
The values for the parameters are determined using the data in the literature \([5,6]\):
\[
S = 0.93 \text{ at } T = 923 \text{ K}, \quad S = 0.77 \text{ at } T = 1088 \text{ K}, \quad f(S=1)_{T=0} = -3w/2,
\]
where \( w \) is the ordering energy \((-5\times10^{-14} \text{ erg/atom})\);
\[
a_1 = 1.13\times10^{-13} \text{ erg}, \quad a_2/a_1 = 9.474\times10^{-4} \text{ K}^{-1},
\]
\[
b_1 = 0, \quad b_2/a_1 = -9.446\times10^{-5} \text{ K}^{-1},
\]
\[
c_1/a_1 = 1, \quad c_2/a_1 = -6.825\times10^{-4} \text{ K}^{-1}.
\]
Using the numerical values for the parameters, the equilibrium degree of order can be calculated for CuPt of a homogeneous state. The results are plotted in Fig. 5, together with Walker's experimental data \([5]\).

The dimension of the unit cell of CuPt actually little changes with ordering, but the axial angles vary by 0.0175 rad \([5]\). Therefore, the strain energy stored is due to the shear strains. However, we content ourselves to use the equation for homogeneous strains for simplicity:
\[
e(S, r, R) = \frac{8\pi r^3 (R^3 - r^3)}{3R^3} \left\{ \frac{E}{(1-\nu)} \right\} \Delta^2,
\]
where \( E \) is Young's modulus, \( \nu \) Poisson's ratio, \( \Delta \) the amount of the strains. The term \( (R^3 - r^3)/R^3 \) is included in Eq. (3), because there are no strains for \( r = R \). The amount of shear strains at \( S = 1 \) is estimated to be approximately \( 3\times10^{-3} \), and \( \Delta \) is thought to be proportional to \( S^2 \). Therefore, \( \Delta^2 \) in Eq. (3) can be substituted by \( S^4\times10^{-5} \). There is no available datum for the surface energy of CuPt ordered domains in a disordered matrix. We adopt \( \sigma = 10\times S^2 \text{ erg/cm}^2 \), as 10 erg/cm\(^2\) is reported for Ni\(_3\)Al \([8,9]\). Figure 6 shows the changes in the total free energy vs. \( S \) and \( r/R \) at \( T = 923 \text{ K} \) for various values for \( R \). One can see that \( F \) has a maximum for large \( S \) when \( R \) is small. This strongly suggests that if a large number of small domains are formed (that is, \( R \) and \( r/R \) are both small) and if the domains happen to be highly ordered (\( S \) is large), they cannot grow up keeping the large value for \( S \). Ordered domains with relatively small \( S \), on the contrary, are expected to increase preferentially \( r \) and \( S \) to reach the state of the minimum energy. The process is in a good agreement with the one observed in the present experiment. The mobilities of \( r \) and \( S \) should be taken into account in order to analyze the kinetics quantitatively, but the above discussion is thought to be essentially valid.

Fig. 1 Field ion micrographs of CuPt annealed at 873 K for 0.85 Ms.
Wrong occupations, excess Cu atoms in (a) and excess Pt atoms in (b) are recognized (indicated by arrows).
Fig. 2 Field ion micrographs of CuPt aged at 923 K for various durations. 
(a) as quenched (b) 0.2 ks (c) 1 ks (d) 100 ks. 
Dominant ordered domains are marked by a circle in (a) and (b).

Fig. 3 Models for ordering process.

Fig. 4 Structure model for CuPt.

Fig. 5 Calculated change in the equilibrium degree of order for CuPt.
$R = 1.5 \text{ nm}$

Fig. 6 Changes in total free energy $F$ with $S$ and $r/R$ for various values for $R$ at 923 K.

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