***In situ* TEM observation of long range ordering via short range order in Cu₃Pt**

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Abstract. The thermoequilibrium state of short range order (SRO) and the ordering process to the long range order (LRO) phase in Cu₃Pt have been studied by the *in situ* transmission electron microscope (TEM) observation method. It is confirmed that the alloy has the SRO state in thermoequilibrium within the temperature region for the disordered fcc phase (designated as A1). The SRO state can be interpreted in the 'microdomain model'. The degree of order fluctuates temporally as well as spatially at higher temperature, but freezes at a lower temperature in the A1 region. In the temperature region of (A1 + LRO), some of the microdomains in the SRO grow up to large domains of LRO. This indicates that the transformation process to LRO via SRO proceeds without a process of nucleation even though the transformation is of a first order. Division of A1 into subregions and physical meaning of the phase boundary between (A1 + LRO) and A1 are discussed.

Keywords. *In situ* TEM observation; short range order; ordering kinetics; first order transformation; phase diagram; copper based alloy.

1. Introduction

Many Cu-based alloys quenched from a high temperature region for an fcc (A1) phase show characteristic diffuse scatterings in their diffraction patterns. The origin of the diffuse scatterings is explained by the Fermi-surface imaging (Krivoglaz 1969; Moss 1969; Ohshima and Watanabe 1973). It has been reported that dark-field image taken by using the diffuse scattering frequently indicates a fine dot-contrast (Torfs *et al* 1974, 1975; Chevalier and Stobbs 1979; Kuwano *et al* 1987; Lee *et al* 1990). The diffuse scattering is attributed to the presence of short range order (SRO) and the fine dot-contrast is considered to be an evidence for 'microdomains'. In this connection, Aubauer (1972) proposed that microdomains dispersed in the disordered matrix are stabilized by the elastic energy between the ordered microdomains and the disordered matrix. However, the possibility that the microdomains observed in the dark field image might have been actually formed during quenching cannot be completely excluded if the experiment is carried out for quenched specimens. In this study, we carried out *in situ* transmission electron microscopic (TEM) observations in order to clarify if the microdomains are stabilized in A1-phase of Cu₃Pt and to analyze the early stage of ordering process from SRO. The phase diagram including the SRO state and the physical meaning of phase boundary of A1/(A1 + LRO) are discussed.

2. Experimental

An alloy ingot was made from pure metals of copper (99.99% pure) and platinum (99.95% pure) in an arc-furnace under an atmosphere of argon. Disk specimens 3 mm in diameter for TEM observation and powder specimen for X-ray diffraction experiment were prepared from the ingot after annealing for homogenization. The chemical composition of the alloy was estimated to be 25.1 at % Pt from its lattice parameter. The disk specimens were annealed in evacuated quartz capsules at 1000 K for 10.8 ks to promote disordering, followed by fast quenching into iced brine. They were electropolished to electron transparency in an electrolyte of HCL : HNO₃ : C₂H₅OH = 4 : 1 : 5 by the Ballmann method. *In situ* observation was carried out with an electron microscope JEM-200CX equipped with a heating stage. The specimen was heated in the microscope once up to 950 K which is within the temperature region for the A1-phase, and then cooled down to the intended temperature. Since TEM images drifted quickly, they were recorded on imaging plates (IP) and/or video tapes. The dark field images were processed with digitalization of signals in order to improve the quality of image contrast.

3. Results

Figure 1a shows an electron diffraction (ED) pattern taken at 950 K, where one can apparently see diffuse scattering. The scattering is almost the same in intensity

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Figure 1. *In situ* observation of diffuse scattering in electron diffraction pattern and dot-contrast in dark field image (950 K).

distribution as observed for the quenched specimen of this alloy (Ohshima and Watanabe 1973; Kuwano *et al* 1987). Figure 1b shows a dark field (DF) image taken by using the diffuse scattering around $hkl=110$. In the DF image a fine dot-contrast is observed. These results indicate that the alloy has an SRO state in thermoequilibrium in the temperature region of A1-phase and that the SRO structure is essentially the same as observed in the quenched alloy (Kuwano *et al* 1987).

Figure 2 shows series of DF images taken at certain intervals at particular temperatures. It is seen in the series (a) 949 K, that a bright dot appears in circle A, but in turn, another dot disappears from circle B within

Figure 2. Series of dark field images taken *in situ* at certain intervals (a) 949 K, (b) 929 K and (c) 833 K.

about 0.6 s: the dot-contrast is flickering very quickly. In series (b) for 929 K, the rate of flickering is lowered so that a dot disappears from circle C in 1.2 s, and at last a dot remains in circle D after 6.6 s in (c) 833 K. The bright dots in DF images formed by diffuse scattering do not always correspond to 'microdomains' one by one. However, the rather sharp dot-contrast is thought to indicate an inhomogeneity in the degree of order in the alloy: The degree of order is not constant over the alloy, but has a fluctuation spatially. 'Microdomains' correspond to particular parts where the degree of order happens to be high compared with that in the matrix. The origin of flickering dot-contrast is controversial. Contamination on the specimen surface gives diffuse scattering, and white noise contrast due to the contamination is sometimes flickering in dark field image. If it were the case, the dot-contrast would continue flickering at 833 K which is still the high temperature and would not grow to an LRO-domain at a lower temperature as shown in figure 3. Bending of the specimen and small variation in observation conditions change the brightness of the dots. But the characteristics of the flickering suggest that the flickering is due to thermal fluctuation inside the specimen (Chiwata *et al* 1998), i.e. the degree of order has also a temporal fluctuation. The rate of temporal fluctuation decreases with falling temperature, and finally freezes even in the temperature region of A1.

Figure 3 shows a series of DF images taken to 813 K, indicating the development of a microdomain to a precipitate of the LRO phase of $L1_{2-s}$ which has a long

Figure 3. A series of dark field images taken *in situ* at 813 K: (a) 4.2 ks, (b) 7.8 ks, (c) 11.0 ks and (d) 18.7 ks. A microdomain (arrowed) grows to a precipitate of $L1_{2-s}$.

period superstructure derived from $L1_2$. The specimen was heated once up to a high temperature to promote disordering in the electron microscope and then held at 813 K. In (a), bright dots are dispersed randomly, but later, some of them (arrowed) grow to larger domains which contain periodic antiphase boundaries.

4. Discussion

Figure 4 shows a partial phase diagram for the Cu-Pt alloy system based on previous reports (Ogawa *et al* 1973; Kuwano *et al* 1987). The $Cu_{1-x}Pt_x$ alloy with $x \sim 0.25$ has thermoequilibrium phases of A1 at high temperatures and of the LRO phases ($L1_2$ and $L1_{2-s}$) at low temperatures. There is a region of mixed phase of $(A1 + L1_{2-s})$. With a consideration of the present experimental results, the region of A1 is divided into some subregions. At very high temperatures in the A1-region, the alloy has an almost completely disordered state, A1 (CD), where the degree of order is, in this case, defined only statistically and naturally is very small in magnitude. In an intermediate temperature region, A1 (SRO-T), the SRO is developed in a fashion of 'microdomains'. The degree of order is not constant, but fluctuates spatially and temporally in the alloy. At a lower temperature in A1 (SRO-S), however, the degree of order fluctuates just spatially. The phase boundaries between A1 (CD) and A1 (SRO-T) and between A1 (SRO-T) and A1 (SRO-S) have a certain width since the state is altered gradually and continuously to the other. These subregions do not always exist in A1 region of another alloy system. The alloy of $\alpha-Cu_{1-x}Al_x$ with $x \sim 0.19$ has the phase relation similar to that of the present Cu-Pt alloy; it has the states of A1 and A1 + LRO,

Figure 4. Partial phase diagram for Cu-Pt. The A1 region is divided into subregions.

and the A1-phase also has SRO. The LRO phase has a long period antiphase structure derived from $L1_2$ (Gaudig and Warlimont 1969; Kuwano *et al* 1977). However, the ordering temperature is lower than ~ 635 K and then at high temperature the degree of order decreases vanishingly before it starts to have temporal fluctuation; the A1-phase of Cu-A1 does not have a subregion of A1 (SRO-T). The results for Cu-A1 alloy will be described separately.

Thermodynamically, the transformation of $L1_{2-s} \rightleftharpoons A1$ is of a first order, and therefore the formation of $L1_{2-s}$ in A1 was thought to proceed by the nucleation and growth process. But actually, there are already microdomains in the matrix of A1-phase as the thermoequilibrium state, and some of the microdomains play a role of nucleates of the LRO phase. The formation of LRO phase therefore proceeds almost continuously via the SRO state without a process of nucleation. Conventionally, the phase boundary between (LRO + A1) and A1 is defined as a border-line for the LRO phase to exist stably with assumption of coexistence of large domains of LRO and the matrix of A1. It should be noted that in the present case of transformation from A1 to (A1 + LRO), the boundary of (A1 + LRO)/A1 is regarded as the border for the microdomains in A1 (SRO) to start growing infinitely. In this case, additional effects such as elastic energy between microdomains and the matrix are expected to have significant influences on the stability of phases. Then the location of the boundary of (A1 + LRO)/A1 in the phase diagram depends on the manner of transformation and on the microstructure in the alloy.

5. Conclusions

From the *in situ* observation of the SRO state and of the ordering process to LRO phase in Cu_3Pt , the following results were obtained.

- (I) The SRO state in Cu_3Pt can be interpreted with a microdomain model. The SRO is stable at a high temperature.
- (II) At high temperatures, the degree of order fluctuates

temporally as well as spatially. The temporal fluctuation in degree of order stops at a lower temperature.

(III) Since some of microdomains can become seeds of the LRO phase, the transformation to LRO proceeds almost continuously without a process of nucleation in spite of which the transformation is of a first order.

(IV) The region of A1 in the phase diagram is divided into three subregions depending on the existence of temporal fluctuation and spatial one in the degree of SRO.

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