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Formation of 4H-closely packed structure in thin films of metastable nanocrystalline $Co_{13}Cu_{87}$ alloy

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Abstract

The crystal structure of the thin films of metastable $Co_{13}Cu_{87}$ alloy prepared by magnetron sputtering was investigated by transmission electron microscope. As-deposited films have a nanocrystal structure with an fcc lattice. As a result of the prolonged ion polishing with a beam of Ar ions with the energy of 4.7 keV, the four-layer 4H dhcp structure was formed.

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1. Introduction

The CoCu alloys are immiscible at the equilibrium state and characterized by positive heat of formation. The phase diagram permits only small solubility ($<1\%$) at each end of the composition range. Due to this fact, the CoCu system is widely used for the development of such practically important structures as multilayer films [1] and granular alloys [2], where the GMR effect is revealed.

Otherwise, many different approaches have been used to prepare supersaturated CoCu solid solutions. In recent years, a number of papers have been published where technique of the mechanical milling [3] and magnetron sputtering [4] were used to obtain CoCu metastable alloys. The interest to this problem is caused by fundamental importance of study of the structural and the other physical properties of aforesaid alloys, which can develop the basic knowledge in the field of solid-state physics. In particular, in the metastable $Co_{34}Cu_{66}$ alloy the new quasi-crystal phase has been found by Z.F. Li and B.X. Liu [5]. This phase with the twelfth-order crystal symmetry axis identified by transmission electron microscope (TEM) diffraction has been obtained by high-energy (200 keV) Xe ion irradiation and thermal treatment of as-deposited fcc Co/Cu multilayer films.

In this paper, we report the structural transformation in thin films of nanocrystalline $Co_{13}Cu_{87}$ alloy resulted from energy treatment. After Ar ion irradiation, the initial fcc structure has changed to the double hexagonal close packed (dhcp) 4H structure.

2. Experimental procedure

Nanocrystalline $Co_{13}Cu_{87}$ film was prepared by the magnetron sputtering on glass substrate at room temperature in Ar atmosphere. The portions of Co and Cu atoms were sputtered successively with the deposition rates of 3.5 and 20 Å/s, respectively; the total number of Co–Cu deposition cycles was equal to 120. The complete thickness of the film was 2500 Å. Basic pressure was 5×10^{-6} Torr, the pressure during sputtering—2×10^{-4} Torr. The compositions of

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as-deposited and modified films were controlled by methods of X-ray fluorescent and energy-dispersive spectrum (EDS) analyses. Microstructure of the films was examined by TEM. TEM images were performed with JEM-2010 microscope operating at 200 kV. The TEM specimens were prepared by ion milling technique using Gatan 691 PIPS ion polishing system at the ion beam energy of 4.7 keV, background pressure of about 10^{-7} Torr, gun current of 3 μA, tilt angel of 10 degrees. For the cross-section specimen, the time of ion beam treatment was 1.5 h. The preparation of films was carried out at the Kirensky Institute of Physics; structural investigations were performed at the Department of Metallurgical and Material Science of Hanyang University.

3. Experimental results

Fig. 1 shows the TEM image and selected area diffraction (SAD) pattern of as-deposited $Co_{13}Cu_{87}$ film. From the SAD pattern, one can see the diffraction rings corresponding to fcc structure with parameter $a = 3.64$ Å. Also the weak rings are discerned that apparently correspond to oxides. They should be Cu_2O or CoO or both of them, but it is difficult to distinguish Cu_2O from CoO oxide because of coincidence of the most important diffractions rings. EDS data confirm the presence of some amount of oxygen in the film.

The characteristic grain size of as-deposited nanocrystal film was of about 100 Å (Fig. 1(a,b)). However, the TEM images of cross-section specimen were quite different from that of as-deposited film. Impact of prolonged ion polishing on nanocrystalline metastable CoCu alloy has resulted in re-crystallization of as-deposited film: the characteristic grain size has increased to 1500 ÷ 2500 Å. Fig. 2 shows the microstructure TEM image of the modified specimen and the SAD pattern corresponding to one of grains. From the pattern, it can be seen that instead of diffraction rings some spots have arisen, indicating formation of a new phase. To identify this diffraction pattern, it should be mentioned that there exists the combination of two sets of spots: more intensive one corresponds to the fcc metallic lattice, the other with lower intensity corresponds to oxides. One can easily see that oxide lattices identified from Fig. 2(b) are partly coherently oriented with the lattice of metallic alloy: position of some oxide spots corresponds to the coincidence of the orientations of cubic oxide lattice and fcc alloy lattice; other spots reveal the 45-degree turn of oxide lattice in the (100) plane with regard to alloy lattice. The presence of oxides in the investigated films can be connected with not high background vacuum and the possibility of oxidation process during the time period between the sample preparation and structural investigations. The

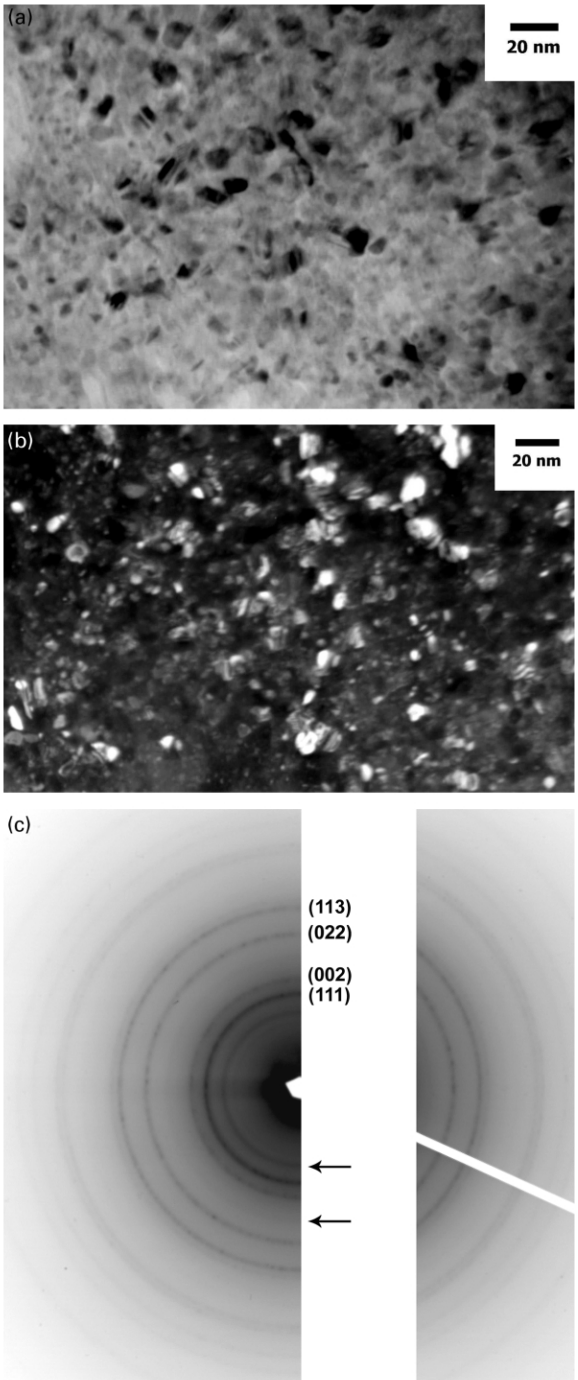

Fig. 1. Bright-field TEM image (a), dark-field TEM image (b) and electronic diffraction pattern (c) of as-deposited $Co_{13}Cu_{87}$ film.

tendency to epitaxy of metal and metallic oxide was partly realized by the re-crystallization of nanocrystal metal-metallic oxide structure.

Fig. 3 shows the SAD pattern taken from another grain of the same specimen. The set of spots of this pattern can be

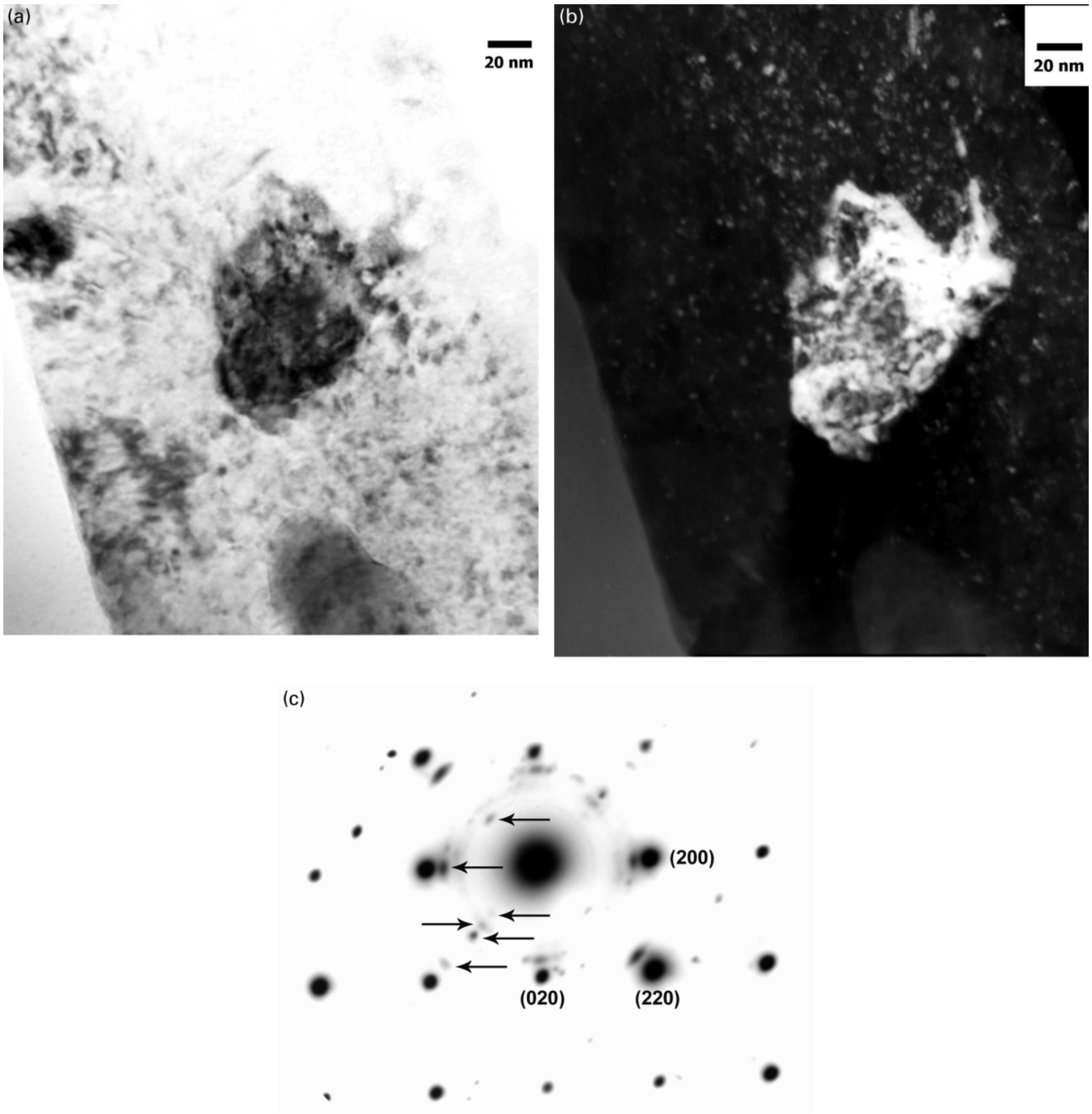

Fig. 2. Bright-field TEM image (a), dark-field TEM image (b) and corresponding electronic diffraction pattern (c) of ion polished $Co_{13}Cu_{87}$ film. The axis of reflection zone is [001]. Spots corresponding to oxides are marked by arrows.

easy identified by using the hcp coordinates. The axis of reflection zone is $[01.\bar{1}]$. For ideal hcp-lattice ($c/a = 1.63$), the angle between the wave vectors $(\bar{1}101)$ and $(01\bar{1}1)$ is 52.5 degrees. It can be seen from the SAD pattern that the corresponding angle for this structure is about 57 degrees. It conforms to the hcp* lattice with $c^*/a = 3.3$. The determined parameters of this structure are $a = 2.5$ Å and $c^* = 6.2$ Å. It should be taken into account that c^*/a ratio is twice more than that of the ideal hcp-lattice. We suppose that this crystal phase is double hexagonal close packed 4H structure (4H dhcp) with the atomic layers packed in ABACABAC… order [6,7].

4. Discussion

Now the ion milling technique is widely used for TEM specimen preparation. In most of the cases, the time of treatment and the ion energy of 1.5 ÷ 6 keV are sufficiently small to produce any specimen structure modification. However, it was shown by L.V. Tereshko et al. [8] that under the low-energy (0.5 ÷ 5 keV) ions bombardment, the modification of material occurs. In particular, such a treatment of samples of different metals and alloys leads to an increase of dislocation density up to a depth of 10 mm from the irradiated surface.

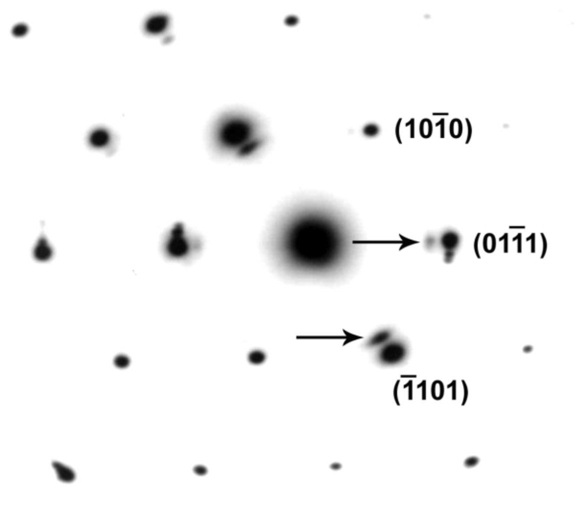

Fig. 3. Electronic diffraction pattern of another grain of ion polished $Co_{13}Cu_{87}$ film. Spots corresponding to oxides are marked by arrows.

In our case, the ion beam polishing process of cross-section specimen preparation results not only in removing some part of material but also in modification of the specimen. At first, the diffusion process takes place leading to mixing of atoms and formation of metastable super-saturated CoCu solid solution. Besides, the process of re-crystallization occurs, which results in considerable increasing of the grain size. It can be assumed that the observed SAD patterns (Figs. 2 and 3) are connected with the initial chemical heterogeneity of as-deposited CoCu films.

The observed SAD patterns can be interpreted in the following way. After ion beam treatment, the grain size has been increased to 1500 ÷ 2500 Å. The CoCu alloy with fcc lattice has been formed in initially depleted with Co atoms area of as-deposited film. In comparison with Fig. 2(c), it is assumed that the SAD pattern confirming the presence of 4H structure (Fig. 3) corresponds to the part of re-crystallized CoCu specimen with the considerably higher concentration of Co atoms c(Co). The diffusion processes stimulated by Ar ions bombardment result in formation of supersaturated CoCu solid solution. It leads to increasing of free energy of investigated alloy because of positive heat of formation. We consider that the formation of dhcp 4H structure is the way to reduce the thermodynamic potential G of the super-saturated solid solution: $G(\text{fcc}) > G(\text{dhcp})$. It should be noticed that both Co- and Cu-based alloys are characterized by low energy of stacking faults [9]. That is the reason why these alloys have tendency to form multilayer lattices. For example, in bulk CoCu alloy (8 at.% Cu) the phase with 126-layer rhombohedral lattice (126R) has been observed [10].

5. Summary

On the base of undertaken structural investigations of modification processes resulting from ion beam treatment the chemical heterogeneity of $Co_{13}Cu_{87}$ alloy has been determined. The as-deposited CoCu films with grain size of about 100 Å have fcc structure. As a result of impact of Ar ions with the energy of 4.7 keV, the supersaturated CoCu solid solution with four-layer 4H structure is formed. In the areas with lower concentration of Co atoms the formation of CoCu solid solution on the base of fcc-Cu matrix takes place.

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