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Moving grain boundary as a "comb" for surface particles

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ABSTRACT

Ordering of surface particles by the moving grain boundary was detected in this study. This beautiful effect was revealed in the previously studied Cu[Co] system. The ordering involves lining up of particles to form chains oriented along the direction of grain boundary motion. The process takes place in the range of temperatures and compositions corresponding to the surface phase transition. The morphology of thermally etched grooves allows one to estimate the speed of grain boundary ordering the surface particles.

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1. Introduction

The chemical and phase compositions of the surface of a solid body often differ from those in the bulk [1–3]. Most typically, an increase in concentration of the second component in the bulk results in surface impurity segregation, i.e., formation of the solution with higher concentration on the surface (McLean adsorption [4]). Further increase in bulk concentration leads to phase transitions that involve formation of mono-, bi-, and multilayers [5]. Eventually, the crystallites turn out to be coated with a stable liquid film [6]. All these processes apparently reduce the surface energy. We detected the systems where no classical segregation is observed and the surface energy rises after concentration of the second component was increased. These systems are the iron-copper [7] and cobalt-copper [8] solid solutions. Stable particles were formed on the outer surfaces of cobalt-copper and iron-copper solid solutions at high temperatures [9,10]. An abrupt decrease in surface energy was observed in these solutions at some concentrations; this decrease can be interpreted as a surface phase transition. Indeed, the phase transition is, by definition, a jump in the concentration or temperature curves of the state functions, in particular, of Gibbs free or Helmholtz energies [11]. Surface energy is the excess Helmholtz surface energy [12]. In the Cu[Co] system, the phase transition is observed in the range of high temperatures at bulk concentration of ~2 at.% [8] (Fig. 1). The phase transition

corresponds to particles formation at high temperatures [13] and apparently change in their structure or (and) grain boundary faceting [14]. Forming particles are crystallographically oriented and faceted at concentrations higher than ~2 at.% (Fig. 1b). Small-angle X-ray scattering showed that these particles belong to the cobalt-based fcc phase (a solid solution of copper in fcc cobalt). The surface energy isotherms (Fig. 1a) show the range of bulk concentrations where the surface phase transition occurred, from ~1.5 at.% to 2.2 at.% Co (Fig. 1a). This concentration range is caused by the difference in crystallographic orientations of the outer and inner surfaces and, therefore, difference in surface energies [15]. According to the electron microscopy studies (Fig. 1b), grain boundaries move intensively for reach a new mechanical equilibrium altered by the phase transition. Fig. 1b demonstrates that the upper portion of the boundary was shifted leftward. The line going into the top right hand corner used to be a thermally etched groove, i.e., it is its trace. A certain ordering of surface particles and nanorods is observed in the direction of grain boundary motion.

We aimed to verified the observation by studying the free surface of Cu[Co] alloy with Co concentration from 1.5 to 2.2 at.% Co range after high temperature annealing.

2. Experimental

The Cu + 1.7 at.% Co alloy was melted and homogenized for 2 days at 1323 K. The ingot was cut, mechanically ground and pol-

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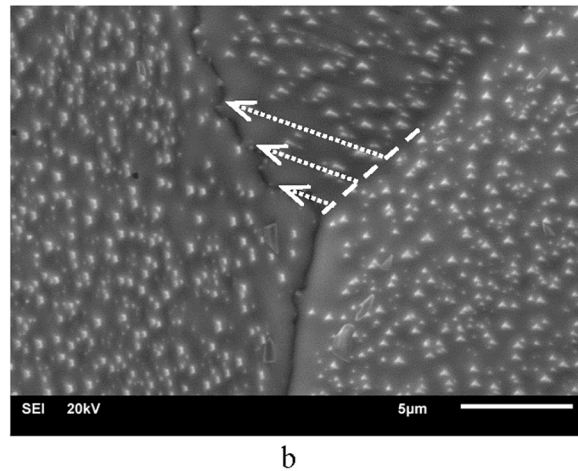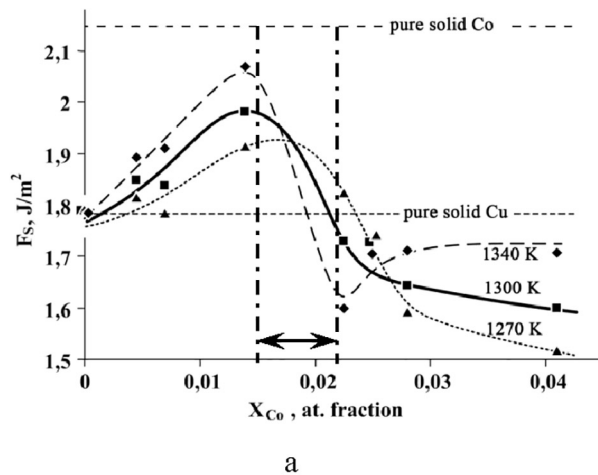
Fig. 1. Isotherms of the surface energy of Cu[Co] solid solutions at different temperatures (a) and (b) SEM image of the Co + 2.25 at.% Co sample [8]. Dot-dash lines on (a) indicate the concentration interval where the surface phase transition occurs. (b) a trace from the groove of the thermal etching of the grain boundary (right, top) and a new position of the groove and the boundary after moving (left, top) after annealing. Arrows show the direction of movement of grain boundary.

ished. These samples were subjected to long-term preannealing for ~100 h in the Ar + 10% H$_2$ atmosphere and electrochemical polishing in a 60% H$_3$PO$_4$ solution. After cleaning and drying the samples were annealed 5 and 12.5 h at 1323 K in the Ar + 10% H$_2$ atmosphere.

The free surfaces of the samples were studied by Scanning Force Microscopy. We used the SmartSPM 1000 Scanning Probe Microscope from AIST-NT company. We worked in semicontact mode using Atomic Force Microscopy (AFM) with 10 nm Si tip curvature radius, resonant frequency from 250 to 380 kHz and Magnetic Force Microscopy (MFM) with 40 nm tip curvature radius. Tip side coating is CoCr, resonant frequency from 100 to 230 kHz. Scan speed was 0.5 Hz with 1024 * 1024 scan size.

3. Results and discussion

After the main annealing at 1323 K for 5 (Fig. 2a, c) and 12 h (Fig. 2b, d), nanowires were found to be formed in the direction of boundary shift by atomic force microscopy. The more detailed AFM studies demonstrated that nanowires were composite; i.e., a single line was formed by a set of particles arranged in special manner (Fig. 2f). The MFM studies have additionally confirmed that the particles had a composite structure (Fig. 3). It is clear that the nanorods have a multi-domain structure [16]. Hence, particles overgrow each other to form a straight line as the grain boundary moves. The grain boundary probably plays a dual role. First, the moving grain boundary mechanically pulls particles in the direction of motion due to the energy of bonding between a particles and the grain boundary [17–19]. Second, the moving boundary is a plane where fast diffusion processes take place [20,21]; these processes ensure migration of the substance (Co) to a growing nanorod.

Fig. 4a, b show the difference between the thermally etched groove and its trace. The groove, whose entrance contains a grain boundary, is sharp; the derivative of its profile is discontinued (Fig. 4a). In its trace, the entrance is gradually closed due to capillary force so it has a rounded shape (Fig. 4b). In order to estimate the speed of particles ordering by grain boundary motion, we studied the kinetics of propagation of thermally etched grooves in the Cu + 1.7 at.% Co alloy [22,23]. The samples were consecutively pol-

ished electrochemically and annealed at 1323 K for different time periods. The propagation rate of the grooves was assessed with respect to their depth and width. Depth was determined as the distance between the groove peaks (the maxima in Fig. 4a) and entrance (the lowest point in the profile); width, as the distance between two peaks. Averaging was performed over 15 grooves. In addition to the alloy, we studied groove propagation in pure copper (99.999 wt% Cu). The results for the alloy and pure copper were consistent within an experimental error (30%). The kinetic curves of the averaged groove depth and width are shown in Fig. 4c and d, respectively. These curves can be used to make an attempt to estimate the time during which the boundaries shown in Fig. 2a, b were shifted. For this purpose, we compared the dimensions of the grooves with the boundaries (the final position of the grain boundary) and their trace (the initial boundary position).

Taking into account the appreciably high error, time of groove motion was less than 20 min in both cases. Hence, the nanorod growth rate is equal to (distance travelled by the boundary)/(time of boundary motion) ~ 6 μm/1200 s = 0.005 μm/s; i.e., is at least 5 nm/s.

4. Conclusion

We believe that we have discovered a new mechanism for the formation of nanostructures, which can be attributed to self-assembly on the surface assisted by a moving boundary. This occurs under conditions of a surface phase transition at high temperatures in Cu[Co] solid solutions. The shape of the grooves of thermal etching and their traces makes it possible to estimate the kinetics of the formation process of nanorods. Detailed selection of conditions for the stable growth of nanorods is the task of great future work.