Microstructure and Mechanical Properties of Nanostructured Co-Cu Alloy Films Processed by Electrodeposition

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Abstract. Two kinds of nanostructured Co-Cu alloy films: a nanolamellar Co-Cu alloy film and an ultrafine-grained two-phase Co-Cu alloy film were processed by electrodeposition, and their microstructures and mechanical properties were investigated. These nanostructured Co-Cu alloy films showed the high hardness and the low activation volume. The mechanical properties of the nanostructured Co-Cu alloy films strongly depended on the grain boundary characteristics. Molecular dynamics simulations were performed in the two-phase Co-Cu alloy film to investigate the dislocation emission at the Co/Cu interface. The molecular dynamics simulations showed that the stacking faults, which are generated by the intense geometrical strain at the Co/Cu interface, play an important role in the dislocation emission.

1. Introduction

Ferromagnetic thin films are widely used as computer components, magnetic sensors and so on. Co alloy films are one of promising ferromagnetic thin films. For various applications, it is desirable to improve the mechanical properties of Co alloy films. Nanocrystallization can give rise to a significant enhancement of mechanical properties in metallic materials. However, nanocrystalline metals tend to be very brittle with a ductility of less than a few percent in tensile tests [1-3], as the result of the absence of dislocation activity [4]. It is accepted that nanocrystalline metals show the high hardness (high strength) and the low activation volume [5-9]. These features of nanocrystalline metals are attributed to emission of dislocations at the grain boundaries, and the grain boundaries play a critical role in deformation of nanocrystalline metals. Hence, it is required to develop nanocrystalline Co alloys with unique grain boundaries for enhancement of the mechanical properties.

In the present work, two kinds of nanostructured Co-Cu alloy films with unique grain boundaries are processed by electrodeposition, and their microstructures and mechanical properties are investigated. In addition, molecular dynamics (MD) simulations are performed in the ultrafine-grained two-phase Co-Cu alloy to investigate the dislocation emission at the Co/Cu interface.

2. Experimental

Two kinds of nanostructured Co-Cu alloy films, that is, a nanolamellar Co-Cu alloy film and an ultrafine-grained two-phase Co-Cu alloy film were processed by electrodeposition [10,11].
electrolyte composition was CoSO$_4$·7H$_2$O (0.4-1 M) and CuSO$_4$·5H$_2$O (0.025-0.1 M). Microstructure of the Co-Cu alloy films was investigated by transmission electron microscopy (TEM). A TEM observation was carried out with a JEOL JEM-2100 at an operating voltage of 200 kV. A high-resolution TEM image was observed with a JEOL JEM-3100F operating at 300 kV with a spherical aberration of $C_s$=1.0 nm. Energy dispersive X-ray (EDX) analysis was carried out at 200kV using the TEM with EDX equipment (Noran Instruments Vantage) to investigate the chemical composition of the Co-Cu alloy films. Mechanical properties of the Co-Cu alloy films were investigated by the hardness tests at room temperature. The hardness tests were performed with a diamond Berkovich tip at constant loading rates of 13.24, 1.324 and 0.378 mN/s.

3. Results and discussion

3.1. Nanolamellar Co-Cu alloy film

3.1.1. Microstructures
A TEM image of a nanolamellar Co-Cu alloy film is shown in figure 1. The grain size of the Co-Cu alloy film was 110 nm. Note that most of the grains contained a high-density fine nanoscale lamellar structure. In previous studies [12,13], the nanocrystalline Cu with nanoscale twins with a spacing of tens of nanometers was fabricated by electrodeposition. On the other hand, the Co-Cu alloy developed in the present work contained nanoscale lamellar structure with a much smaller spacing of 3 nm. The EDX analysis showed that the Co content was 93 wt.% and the Cu content was 7 wt.%. The solid solubility limit of Cu in Co at room temperature is almost 0% in the equilibrium state. It is therefore suggested that the Cu is forced to dissolve into the Co because electrodeposition tends to cause the nonequilibrium state. Figure 2 shows a selected area diffraction (SAED) pattern and a high-resolution TEM image in the nanolamellar Co-Cu alloy film. The SAED pattern shows strong streaks between the reflections along the [111] directions, which means the stacking disorder along the [111] direction. The high-resolution TEM image also shows that the microstructure of the nanolamellar Co-Cu alloy film exhibits many stacking disorder composed of various stacking sequences, such as ABCABACB..., along the [111] direction of the fcc structure, as shown in figure 2.

Figure 1. A TEM image of the nanolamellar Co-Cu alloy film.

Figure 2. An SAED pattern (a) and a high-resolution TEM image (b) of the nanolamellar Co-Cu alloy film
3.1.2. Mechanical properties

Load-displacement curves obtained from the hardness tests at the three loading rates are shown in figure 3(a). The hardness of the nanolamellar Co-Cu alloy film was 4.12-5.02 GPa. As shown in figure 3(a), a higher load was required at a higher loading rate to impose the same displacement. The variation in hardness as a function of loading rate is shown in figure 3(b). From the results in figure 3, the strain rate sensitivity and activation volume were 0.055 and $3.3b^3$ for the nanolamellar Co-Cu alloy film, respectively. It is reported that the presence of nanotwins leads to a reduction in activation volume [13,14], and the reduction is attributed to the emission of partial dislocations at twin boundaries. In the present study, the activation volume for the nanolamellar Co-Cu alloy film is much lower than those for the nanotwin Cu [14]. Clearly, the low activation volume for the nanolamellar Co-Cu alloy film is attributed to the nanoscale lamellar structure of 3 nm.

![Load-displacement curves and hardness variation](image)

**Figure 3.** The results of hardness tests for the nanolamellar Co-Cu alloy film, (a) load-displacement curves at three different loading rates and (b) variation in hardness as a function of loading rate.

3.2. Ultrafine-grained two-phase Co-Cu alloy film

3.2.1. Microstructures

A TEM image of an ultrafine-grained two-phase Co-Cu alloy film is shown in figure 4. From the X-ray diffraction spectrum and EDX measurements, the Co-Cu alloy film consisted of two phases with Co grains and Cu grains. The average concentration of Cu was 38 wt.%. The grain sizes were 141 nm for Co phase and 181 nm for Cu phase, respectively. No (Co, Cu) intermetallic compounds were observed in the Co-Cu alloy.

![TEM image of ultrafine-grained Co-Cu alloy](image)

**Figure 4.** A TEM image of the ultrafine-grained two-phase Co-Cu alloy film.

3.2.2. Mechanical properties

The variation in hardness as a function of loading rate is shown in figure 5 for the ultrafine-grained two-phase Co-Cu alloy film, the ultrafine-grained single phase Co and the ultrafine-grained single phase Cu. From the results, the activation volume was $3.1b^3$ for the ultrafine-grained two-phase Co-Cu alloy film, $13.1b^3$ for the ultrafine-grained single phase Co and $32.8b^3$ for the ultrafine-grained single
phase Cu, respectively. Note that the strain rate dependence of the two-phase Co-Cu alloys was much larger than those of single phase Co and Cu despite the almost same grain sizes. The rate controlling process of inelastic deformation in ultrafine-grained and nanocrystalline metals is the emission of dislocations from the grain boundaries [5,8,9], and the grain boundary characteristics affect the deformation behaviour [15].

**Figure 5.** The variation in hardness as a function of loading rate for the ultrafine-grained two-phase Co-Cu alloy film, the ultrafine-grained single phase Co and the ultrafine-grained single phase Cu.

### 3.2.3. Molecular dynamics simulations

It is accepted that nanocrystalline metals exhibit the low activation volume, resulting from the emission of dislocations at the grain boundaries. In the present work, the nanostructured Co-Cu alloy films with the characteristic grain boundaries: the nanolamellar Co-Cu alloy film and the ultrafine-grained two-phase Co-Cu alloy film showed much lower activation volumes of about $3b^3$, compared with the nanocrystalline pure metals. The much lower activation volumes of the nanostructured Co-Cu alloy films with the characteristic grain boundaries cannot be explained only by the refinement of grains. Therefore, it is suggested that the unique grain boundary characteristics in the Co-Cu alloy films affect the emission of dislocations at the grain boundaries.

MD simulations were performed in the ultrafine-grained two-phase Co-Cu alloy film to investigate the dislocation emission at Co/Cu interface. Figure 6 shows atomic configuration in Co/Cu (554) grain boundary before and after dislocation emission. Note that the stacking faults were generated before the tensile testing, as shown in figure 6 (a). This results from the intense geometrical strain at the Co/Cu interface. Partial dislocations were emitted to the Cu grain from the stacking faults. Dislocations were not emitted under an applied tensile stress of 1.7 GPa, but dislocations were emitted under an applied tensile stress of 2.0 GPa, as shown in figure 6 (b). Thus, a large stress was needed to emit the dislocations at the interface.

**Figure 6.** Atomic configuration in Co/Cu (554) grain boundary during the tensile tests under an applied stress of 2.0 GPa, (a) before dislocation emission ($t=0$ ps) and (b) after dislocation emission ($t=5$ ps).
4. Conclusions
Two kinds of nanostructured Co-Cu alloy films: a nanolamellar Co-Cu alloy film and an ultrafine-grained two-phase Co-Cu alloy film were processed by electrodeposition, and their microstructures and mechanical properties were investigated. These nanostructured Co-Cu alloy films showed the high hardness and the low activation volume. The mechanical properties of the nanostructured Co-Cu alloy films strongly depended on the grain boundary characteristics.

MD simulations revealed that the stacking faults, which are generated by the intense geometrical strain at the Co/Cu interface, play an important role in the dislocation emission at the interface.

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