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Experimental study on solid solution strengthening in nanocrystalline alloys using multilayered films

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ABSTRACT

In nanocrystalline alloys, some microstructural factors are usually tied to grain interior composition, including grain size, grain boundary composition, and grain boundary width. Due to the coupling of these factors, it is challenging to reveal the individual effect of solid solution strengthening. In this paper, sputtered Cu–Ti alloy multilayered films were designed to isolate the effect of solid solution strengthening in nanocrystalline alloys. Two series of nano-multilayered films were synthesized consisting of different low-alloy-content crystalline layers (6–188 nm thick) and same high-alloy-content amorphous layers (~5 nm thick). The columnar crystals in crystalline layers with two different compositions both have the same diameters. The comparison of the two series of multilayered films show that the increase of Ti content from 0.3 to 5.3 at% results in a constant hardness enhancement of 1.5 ± 0.2 GPa, as the height of columnar crystals in diameter of 10 nm decreases from 188 nm to 6 nm. This indicates that the solid solution strengthening effect of nanocrystalline alloys is independent of grain size not only when the deformation behavior is dominated by intragranular dislocation mechanism as coarse-grained ones, but also, more importantly, when it becomes dominated by grain boundaries.

1. Introduction

As one of the main strengthening mechanisms for alloys, solid solution strengthening has been widely and deeply studied for a long time. There are a lot of models and formulas based on obstacles of solute atoms to dislocation motion, including the classical Fleischer model [1], the Labusch model [2] and the Suzuki model [3]. In recent years, with the development of computational materials science, more sophisticated models have appeared using first-principles calculations [4,5] or molecular dynamics simulations [6] based on the stress field in crystal lattices created by solute atoms. These models are effective to explain the effect of solid solution strengthening in coarse grains.

However, these theories are not necessarily suitable for nanocrystalline metals. There are still controversies over whether solid solution strengthening exists in nanocrystalline alloys and how large the effect is. Some researches believed that nanocrystalline grains can accommodate more solute atoms [7], and the strengthening effect might be more significant than in coarse grains [8,9]. Others reported that in some alloy systems, the effect of solid solution strengthening in nanocrystals will weaken along with the decrease of grain size, and the strength may even decrease, which is so-called solid solution softening phenomenon [10,11].

Actually, these controversies mainly result from variable coupling. Some microstructural factors including grain size, grain boundary composition, and grain boundary width are usually tied to grain interior composition. The coupling of these factors makes it difficult to separate and reveal each individual effect. Although theoretical studies have been adopted by improving strengthening models of each microstructural factor for nanocrystalline alloys, due to the lack of corresponding experimental support, the reliability of results is not convincing enough.

Therefore, isolating the effects of various microstructural factors is vital to studying the strengthening mechanisms of nanocrystalline alloys. For this purpose, we designed a structure of multilayered films to separate composition and other factors. Through this method, this paper revealed the effect of solid solution strengthening in nanocrystalline alloys and the effect variation with the change of nanocrystal size.

2. Experimental methods

Utilizing the characteristic of columnar crystal diameter insensitive to composition when alloy films grow on heterogeneous

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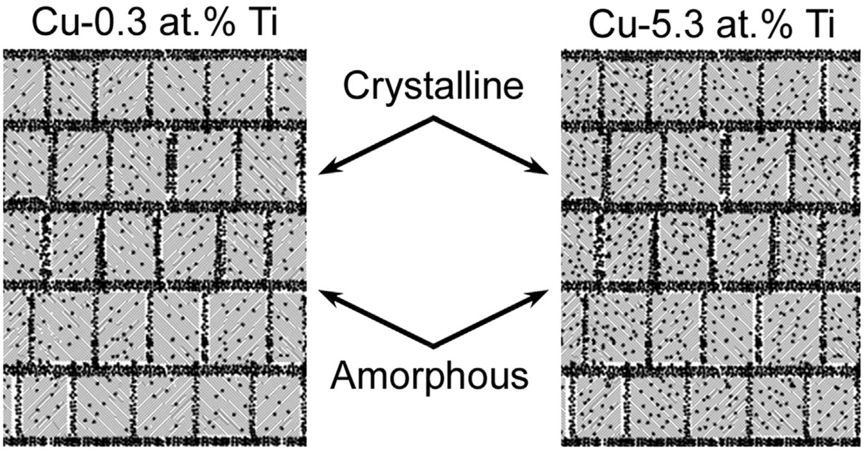

Fig. 1. Illustration of nano-mutilayered films consisting of different low-alloy-content crystalline layers and same high-alloy-content amorphous layers.

surface at initial stage [8], we designed two series of nano-multilayered films consisting of different low-alloy-content crystalline layers and same high-alloy-content amorphous layers, as shown in Fig. 1. In such multilayered films, due to the interruption of amorphous layers, the heights of columnar crystals in crystalline layers were limited to the layer thicknesses. Through the comparison of the two series of multilayers, we can reveal the effect of solid solution strengthening in nanocrystalline alloys.

The films were deposited by co-sputtering using a multi-target magnetron sputtering system. The polished 304 stainless steel substrates were ultrasonically cleaned in acetone and ethanol successively before deposition. After base pressure of chamber reached 10^{-4} Pa, high-purity Ar was backfilled and the pressure was maintained 0.6 Pa throughout deposition. A copper target (99.99%) was controlled by a D.C. cathode and two titanium targets (99.99%) were controlled by R.F. cathodes respectively. Through the control of target powers, copper alloy films with different Ti content were conveniently obtained. In the experiment, single-layer films with 0.3, 5.3 and 27.4 at% Ti were first deposited. Composition of each film was measured through energy dispersive spectroscopy (EDS, Oxford Inca). X-ray diffraction (XRD, Rigaku D/max-2550/PC) showed that alloy films with 0.3 and 5.3 at% Ti were single-phase Cu–Ti solid solution while the film with 27.4 at% Ti was amorphous. By controlling the powers and shutters of Ti targets, we synthesized two series of 2-μm-thick multilayered films consisting of low-alloy-content crystalline layers (6–188 nm thick) and high-alloy-content amorphous layers (~5 nm thick).

The grain sizes of films were observed by JEM-2100F transmission electron microscope (TEM) from cross-sectional and in-plane views. The hardness of films was tested in a nanoindentor (Fischerscope H100VP) using a diamond Vicker indenter. Through Martens hardness selection method [12], 15 mN was selected as the maximum load to avoid the influence of substrate on film hardness. More than 20 indentations were performed for each sample.

3. Results and discussion

Before the design and preparation of multilayered films, we observed the growth structure of Cu-0.3 at% Ti film through cross-sectional TEM. As shown in Fig. 2, the film growing on the amorphous buffer layer with high Ti content presented a growth structure of columnar crystals. It is notable that the columnar crystals are of small diameters at initial stage, and the diameters gradually increase as the thickness exceeds ~200 nm. Actually, this is a typical structural characteristic of vapor-deposited crystalline films growing on heterogeneous surface. To eliminate the possible negative effects of columnar crystal coarsening, we adopted a design of multilayered films: using high-Ti-content amorphous layers to periodically interrupt the growth of columnar crystals, thus keeping columnar crystals of small diameters.

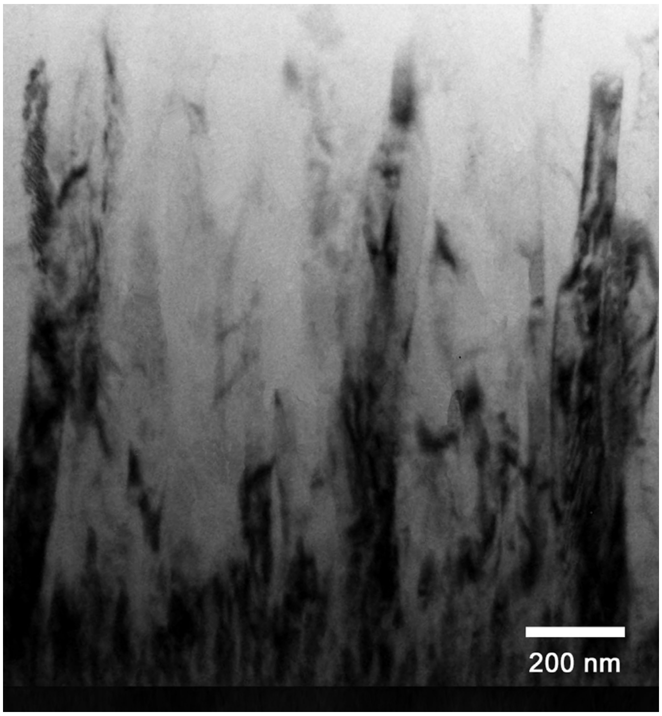

Fig. 2. Cross-sectional TEM image of the growth structure of the Cu-0.3 at% Ti film.

Fig. 3 shows XRD patterns of two series of multilayers in which crystalline layers contain 0.3 and 5.3 at% Ti respectively. From the figures, a weak and broad Cu (1 1 1) peak is found for the single-layer amorphous film. All the patterns of multilayers in two series exhibit a Cu (1 1 1) preferred oriented peak, which mainly comes from crystalline layers. For Fig. 3(b), the Ti content of 5.3 at% in crystalline layers exceeds the solubility limit, but only single-phase Cu supersaturated solid solution exists due to highly non-equilibrium process of sputtering. These crystalline layers have the same Cu (1 1 1) orientation with those containing 0.3 at% Ti (Fig. 3(a)) and the peaks only differ in intensity and position ($\Delta 2\theta \approx 0.25°$). For both series of multilayers, as the thickness of crystalline layers decrease, the volume fractions and grain sizes of them also