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Alloying effects on the microstructure and mechanical properties of nanocrystalline Cu-based alloyed thin films: Miscible Cu-Ti *vs* immiscible Cu-Mo

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Tuning the microstructure to optimize the mechanical performance of nanocrystalline Cu thin films via the alloying strategy is quite important for their application in microdevices. In this work, we prepared nanocrystalline miscible Cu-Ti and immiscible Cu-Mo alloyed thin films to investigate alloying effects on the microstructure and mechanical properties of Cu thin films in terms of mixing enthalpies. It is found that the dopants of both Ti and Mo can notably refine the grains, and in particular promote the formation of nanotwins below a critical content of solute, beyond which the formation of nanotwins is notably suppressed. The nonmonotonic solute concentration-dependent twinning behavior observed in Cu-Ti and Cu-Mo alloyed thin films is explained by the coupling effects between grain size and grain boundary segregated dopants that affects the stimulated slip process of partials. The increased hardness of both Cu-Ti and Cu-Mo systems with increasing the solute contents are quantitatively explained by combining several strengthening mechanisms, including solid solution strengthening, grain/twin boundary (GB/TB) strengthening, solute segregation-induced strengthening. It unexpectedly appears that with increasing the solute contents, the Cu-Ti system exhibits monotonically reduced positive strain rate sensitivity (SRS, *m*), whereas the Cu-Mo system manifests almost constant negative SRS. The fundamental difference in SRS *m* between Cu-Ti and Cu-Mo is rationalized in terms of the interactions between solute atomic clusters and dislocations based on the cross-core diffusion mechanism.

1. Introduction

The metallic copper (Cu) thin films at micro- and nano-scales (including grain size *d* and film thickness *h*) manifest the size effects with the fashion that "smaller is stronger and smaller is less ductile" [1–4], attracting much attention for both the scientific interests and the reliability of microdevices [5–7]. To overcome the drawbacks of pure Cu thin films, such as low strength and weak oxidation resistance, tremendous studies have been conducted to design superior Cu-based binary alloys, in particular the immiscible Cu-W [8], Cu-Ta [9] and Cu/Cr [10] ones. The non-equilibrium deposition technique offers great possibilities to grow nano-structured, e.g. nanocrystalline (NC) and nanotwinned (NT) alloyed thin films with unique mechanical properties [11–14]. A representative example is given by the miscible Cu-Zr alloyed films to which remarkable ductility and high strength were conferred through a hierarchical structure [15]. The multi-hierarchical microstructures enable their outstanding mechanical properties can be tuned by embedding atoms/clusters or nano-particles in grain interiors to increase the resistance for dislocation motion and thus enhance the capability of dislocation accumulation on the one hand, and embedding atoms/clusters or nano-particles at grain boundaries (GBs) to prevent grain growth by reducing GB energy and mobility on the other [16–20]. Another example is that, Vüllers and Spolenak [8] prepared the NC "immiscible" Cu-W alloyed films by magnetron sputtering deposition, which have superior strength but undergo a transformation into a more stable, partially phase separated structure upon annealing.

Previous studies have unambiguously verified that the initial microstructures of binary alloyed films as well as their evolution are significantly affected by interatomic interactions between solvent A and solute B [11–15], which can be characterized by the mixing

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enthalpy (ΔH_{Mix}) [21] and the elastic (moduli) misfit between solvent and solution [22] to a great extent. The strong atomic repulsive interaction, e.g. in the “immiscible” Cu-W system [8], significantly accelerates GB segregation, thereby facilitates grain refinement. By contrast, the strong atomic attractive interaction generally hinders nanoscaled GB-segregation in NC alloys, e.g. the “miscible” Ni-P system [23], whereas they often suffer another problem with the microstructural stability — precipitation of a second phase, which disrupts the segregation state necessary for stability and thus induces grain coarsening. Therefore, a binary system of weak segregation tendency associated with the medium attractive interaction likely manifests high microstructural stability against coarsening, such as Cu-Ti and Ni-W. This is because higher activation energy for diffusion induces the (metastable) dissolved solute atoms diffuse over smaller distances. Also, alloying can cause the variation of the generalized planar fault energy (GPFE) of a bulk material [24–26]. Atomistic simulations showed that alloying in general enhances the twinnability of the miscible system [24,25], whereas it lowers the twinablity of the immiscible system (e.g. Cu-Ta) [26]. These simulation results were further verified by experimental findings [15,26]. Thus, these soluble atoms can influence the nucleation/motion of dislocations, thus in principle allow certain material properties to be finely tailored. However, much less attention has been paid to such a miscible alloyed system, e.g. Cu-Ti. Although the present authors preliminarily investigated the correlation between mechanical properties (*i.e*., hardness/strength, ductility) and microstructure in Cu-Al [12] and Cu-Zr [15] alloyed thin films, the fundamental differences in alloying Cu by these two elements with different ΔH_{Mix} are still unclear. It is thus very important to elucidate the doping effects of different alloying elements (e.g. Mo, Al, Ti, Zr) on tuning the microstructures of Cu thin films under the same/similar deposition conditions for a complete tunability of microstructural length scales for material design.

On the other hand, the diatomic interaction between solute A and solvent B determines the dopant-dislocation interaction (to a great extent), which in turn notably influences the mechanical response of alloys [27–29]. For example, the dynamic strain aging (DSA) effect [30–32] caused by dynamical atom-dislocation interactions via repeated pinning-unpinning of dislocations occurred in the binary Al-Mg ($\Delta H_{Mix} \sim -2$ kJ mol^{-1}) [33] and Cu-Zn ($\Delta H_{Mix} \sim +1$ kJ mol^{-1}) [34] alloys, both of which have medium, even weak diatomic interactions. Aboulfadl and coworkers [35] have unveiled that an asymmetrical Mg distribution along dislocations and that depletion of Mg in a tail-like form behind fast-moving dislocations in Al-Mg alloys undergoing DSA. Therefore, it is reasonable to surmise the strain rate sensitivity (SRS, m) of binary alloyed systems with strong repulsive diatomic interactions (e.g. Cu-Mo) would be significantly different from the systems with strong attractive diatomic interactions (e.g. Cu-Ti). Prior studies mainly focused on the size-dependent mechanical properties and deformation mechanisms of Cu nanostructures [1–4], uncovering their positive SRS m [36–42]. However, it is still unclear that how these alloyed thin films, *i.e*., “miscible” Cu-Ti and “immiscible” Cu-Mo, response under different external loading rates and the underlying mechanism(s).

Motivated by the above issues, the present work focuses on the internal features and strain rate sensitivity (SRS, m) of nanostructured Cu films respectively doping with a series of atomic fraction of solute Ti and Mo spanning from 0.5 at.% to 15.0 at.%. It is found that both Ti and Mo doping first promote formation of nanotwins at low Ti and Mo contents and then suppress their formation at high Ti and Mo contents above a critical concentration threshold. Compared with Ti, Mo dopants refine grains of Cu thin films to much smaller sizes associated with lower propensity of twinning. In sharp contrast to the miscible Cu-Ti system with positive SRS m, the immiscible Cu-Mo samples exhibit negative SRS m. These results are rationalized in terms of the interatomic interactions, which strongly influence the GB segregation and the DSA in these two binary alloyed thin films.

2. Experimental procedures

2.1. Materials preparation

The Cu-X (X = Ti, Mo) alloyed thin films with different X contents spanning from 0.5 at.% to 15.0 at.% were prepared on SiO_2/(111)-Si substrate by direct current (DC) magnetron sputtering deposition technique at room temperature. Note that in this work, the used materials for sputtering deposition have the purity of ~99.995%. With a constant power for Cu target, the power setting of the X target was varied from 0 to 84 W to change the compositions of alloyed thin films. The sputtering chamber was evacuated to a base pressure of 3.0×10^{-7} Torr, and a 7.5×10^{-3} Torr Ar pressure was maintained during the deposition process. The substrate was neither heated nor cooled during the deposition process. All the alloyed thin films have the same total thickness of ~1.5 μm. For comparison purpose, the monolithic Cu, Mo and Ti thin films with thickness of ~1.5 μm were also prepared.

2.2. Microstructure characterization

X-ray diffraction (XRD) experiments were carried out using a Bruker D8 Discover powder X-ray diffractometer with Cu K_α radiation at room temperature to determine the crystallographic orientations of these two kinds of Cu-based alloyed films. Microstructures were examined by using transmission electron microscopy (TEM) on a JEOL JEM-2100F TEM with an accelerating voltage of 200 kV. The average size of grains (d), thickness (λ) and fraction (f) of nanotwins were statistically evaluated following the procedures in Ref. [43]. At least 300 grains were examined in each sample. The statistical grain size distribution and the twin thickness distribution of Cu-Ti and Cu-Mo samples are fitted by the lognormal distribution function with the potential error of ~5% [44]. The number fraction of the twinned grains is defined as the number of twinned grains per unit area divided by the total number of grains per unit area. Still, one has to keep in mind that not all twins are visible in a (plane-view) TEM image. The scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) capabilities of the JEOL JEM-2100F TEM were used for diffraction- and atomic-contrast imaging, and also for elemental mapping of the as-deposited alloyed thin films. The chemical distributions of Cu and X were examined using the STEM-EDS technique. To investigate the microstructural evolution during plastic deformation, postmortem TEM observations were carried out on the indented Cu-Ti and Cu-Mo alloyed thin films. These TEM foils were prepared using a FEI HELIOS NanoLab 600i with an in-situ Omniprobe lift-out micromanipulator, and were subsequently analyzed in a FEI Tecnai G2 F20 microscope operating at an accelerating voltage of 200 kV.

2.3. Hardness test

The hardness of the miscible Cu-Ti and immiscible Cu-Mo alloyed thin films as well as the monolithic pure Cu, Ti and Mo films was measured using a TI950 TriboIndenter (Hysitron, Minneapolis, MN) with a standard Berkovich tip at room temperature, following the Oliver-Pharr method adopted in our previous work [45]. The hardness test was conducted on the load-controlled mode (~2600 μN for Cu-Ti thin films and ~3500 μN for Cu-Mo thin films, respectively) under different loading time spanning from 5 to 100 s