Materials Letters 65 (2011) 119–121

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Theoretical explanation of Ag/Cu and Cu/Ni nanoscale multilayers softening

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ARTICLE INFO

Article history:
Received 3 August 2010
Accepted 22 September 2010
Available online 29 September 2010

Keywords:
Multilayer structure
Hardness
Mechanical properties
Metals and alloys
Thin films

ABSTRACT

Relationship between metallic multilayers hardness and monolayer thickness has been investigated and explained for electroplated Ag/Cu and Cu/Ni multilayers using a modified Thomas–Fermi–Dirac electron theory. Experiments reveal that the peak hardness of Ag/Cu multilayers occurs at the monolayer thickness of about 25 nm, while the peak hardness of Cu/Ni multilayers occurs at about 50 nm. Critical monolayer thickness corresponding to the peak hardness is approximated by the grain size limit of stable dislocations in Ag crystals for the Ag/Cu multilayers and in Cu crystals for Cu/Ni multilayers. Grains size limits are calculated based on a modified Thomas–Fermi–Dirac electron theory. Developed relationship between the critical monolayer thickness and the grains size limit helps understand nanoscale metallic multilayers softening.

1. Introduction

Metallic multilayers, such as Cu/Nd [1–4], Cu/Cr [1,4], Cu/V [1,4] and Al/Nb [1] either get softer or hold their strength when each layer thickness decreases below a certain value. For nanostructured materials no apparent dislocations activity is observed during or after straining [5]. Thus there exists a size limit for grains with stable dislocations (the size limit hereafter).

Gryaznov et al. [6,7], Nieh et al. [8] and Wang et al. [9] analyzed the stress field around dislocations, and provided the size limit for some metals and compounds. Cheng et al. [10] calculated the size limits of fifteen metals according to the modified Thomas–Fermi–Dirac electron theory (TFDC). However, the size limits calculated by Cheng et al. are larger in magnitude than the actual measured grain sizes.

In present work the effects of the monolayer thickness on hardness of electrodeposited Ag/Cu and Cu/Ni multilayers were investigated. Cheng's method was complemented with dislocation core energy, and a model for the size limit was derived based on the TFDC electron theory. The model explains the monolayer thickness corresponding to the peak hardness (the critical monolayer thickness hereafter).

2. Experimental procedure

Ag/Cu and Cu/Ni multilayers were prepared by electrodeposition in a dual bath. Each multilayer structure consists of the same thickness multiple monolayers. Each monolayer thickness was controlled by electroplating duration and the current density of the cathode substrate. Monolayer thickness was measured using scanning electron microscopy (SEM).

Ag/Cu and Cu/Ni multilayers hardness was measured using a microhardness tester. The mean value of six hardness measurements per sample was taken. The indentation depth was less than one-tenth of the total thickness of the multilayer but no less than seven periodic thicknesses.

3. Size limit model

Prevailing driving force for generating a dislocation arises from external stress and the pressure exerted by Fermi electrons, which supports electron shells expansion at the expense of decreasing internal energy. Such a counterbalance generates a relatively stable state [10].

The strain energy E_L (the sum of the elastic strain energy and the dislocation core energy) of an edge dislocation per unit length can be approximately expressed as [11]

$$E_L = \frac{\mu b^2}{4\pi(1-\nu)} \ln \frac{4R}{b} \tag{1}$$

where μ is the shear modulus, b is the Burgers vector, ν is the Poisson's ratio and R is the radius of the edge dislocation elastic stress field.

The electron pressure P at the atomic boundary in solid materials is equal to $(1/3)(2K + V_{ex})$ [10], where K is the kinetic energy density of the electrons at the atomic boundary and V_{ex} is the exchange energy density at the atomic boundary. The electron pressure P can be written as

$$P = \frac{h^2}{5m}\left(\frac{3}{8\pi}\right)^{2/3} n^{5/3} - \frac{e^2}{16\pi\varepsilon_0}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3} \tag{2}$$

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doi:10.1016/j.matlet.2010.09.063

where n is the electron density at the atomic boundary, m is electron mass, h is the Plank's constant, ε_0 is the permittivity of vacuum and e is the electron charge.

It can be assumed that in every crystal plane perpendicular to the dislocation line of an edge dislocation, there is a cavity directly below the extra half plane of atoms. The work E_P, done by the electron pressure P to create dislocation cavities per unit length, can be written as $E_P = -PV/d$, where V is the volume of electrons driven into a cavity by the environment, and d is the distance between adjacent cavities [10].

$V \cdot n = z$, where z is the number of valence electrons. For a close-packed structure, $d = 2r(2/3)^{1/2}$, where r is the atomic radius. The total energy ε used to create a dislocation per unit length is the sum of E_L and E_P. Since dislocation is in a relatively stable state, ε must be positive. When $\varepsilon = 0$, dislocation is in the critical state between stability and instability. Corresponding elastic stress field diameter, D ($=2R$), is the limit size of a grain with stable dislocations, D_c. Thus the size limit (limit diameter of a grain with stable dislocations) is

$$D_c = 2(b/4)e^{\eta} \tag{3}$$

where $\eta = 96.9(1-\nu)zr^{*-3}n^{*2/3}(1-0.523n^{*-1/3})/\mu^*$, $n^* = n \cdot 10^{-29}$, $r^* = r \cdot 10^{10}$, $b \approx 2r$ and $\mu^* = \mu \cdot 10^{-10}$. Here, SI units are used.

4. Results

Fig. 1 shows a cross−section SEM micrograph of 250 nm/250 nm Cu/Ni multilayers. In Fig. 2 the multilayer hardness is plotted against the inverse square root of the monolayer thickness h. The hardness of both multilayers vary linearly with $h^{-1/2}$ for $h > 150$ nm. The peaks in hardness and the softening appear for $h < 150$ nm. The peak hardness is 1.48 GPa at the thickness $h = 25$ nm for Ag/Cu multilayers, and the peak hardness is 3.19 GPa at the thickness $h = 50$ nm for Cu/Ni multilayers.

5. Discussion

It is clear that for Ag/Cu and Cu/Ni multilayers with $h > 150$ nm hardness behavior is consistent with the Hall–Petch relation. In this paper the critical monolayer thickness is a focus of the discussion.

For metallic films prepared by electrodepositing the grains are roughly columnar [12]. Each layer in the multilayer structure contains one layer of grains, 1–2 times the layer thickness in diameter [12,13]. For nanoscale metallic multilayers, the monolayer thickness is approximately the height of the columnar grains.

Using Eq. (3), for Ag crystal, $z = 1$, $n^* = 2.026\ \mathrm{m}^{-3}$, $r^* = 1.597$ m, $\mu^* = 2.7$ Pa and $\nu = 0.38$ [10] one gets $D_c = 27$ nm; for Cu crystal, $z = 1$, $n^* = 2.934\ \mathrm{m}^{-3}$, $r^* = 1.413$ m, $\mu^* = 4.79$ Pa [10] and $\nu = 0.31$ one gets $D_c = 88$ nm; and for Ni crystal, $z = 2$, $n^* = 3.195\ \mathrm{m}^{-3}$, $r^* = 1.382$ m, $\mu^* = 8$ Pa and $\nu = 0.34$ [10], thus $D_c = 663$ nm. According to the calculated size limits of Ag and Cu, for Ag/Cu multilayers, dislocations in Cu layers will disappear when the monolayer thickness is reduced to 88 nm, roughly consistent with prior observations [13]. No dislocations in Ag layers will appear if the monolayer thickness is below 27 nm. Similarly, for Cu/Ni multilayers, dislocations in Ni layers will disappear when the monolayer thickness is reduced to 663 nm, while dislocations in Cu layers continue to monolayer thickness of 88 nm. In Fig. 2 the critical monolayer thicknesses are respectively 25 nm and 50 nm in Ag/Cu and Cu/Ni multilayers, which is roughly consistent with the critical grain size of Ag and Cu crystals.

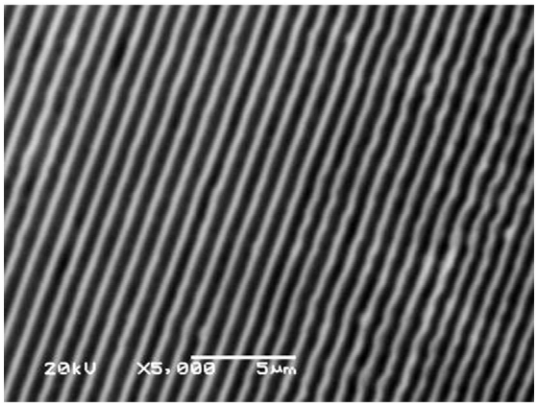

Fig. 1. SEM micrograph of 250 nm/250 nm Cu/Ni multilayers.

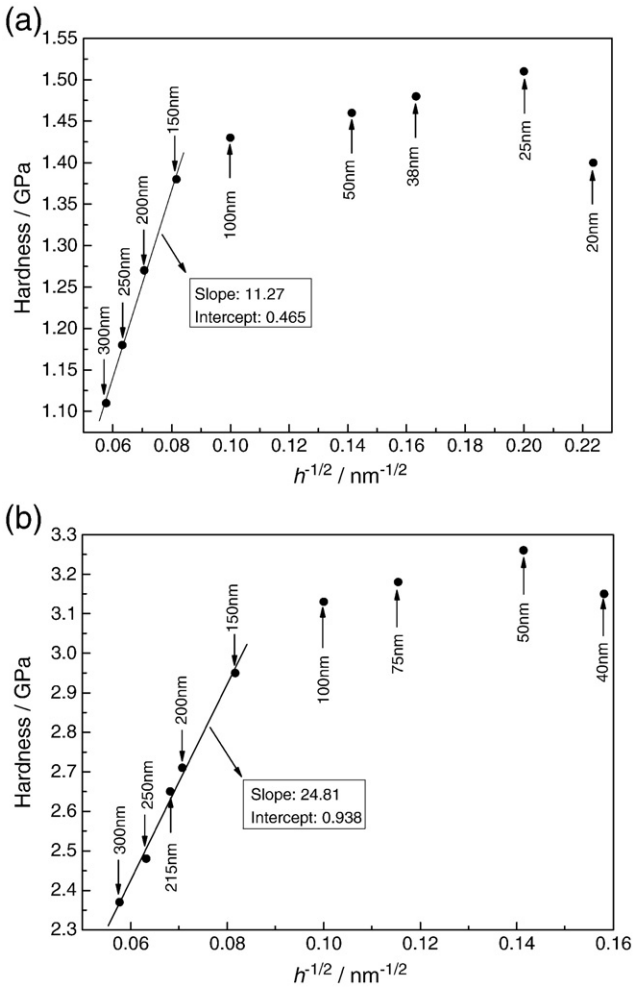

Fig. 2. Hardness versus $h^{-1/2}$; (a) Ag/Cu multilayer, (b) Cu/Ni multilayer.

When the monolayer thickness in both multilayers decreases from 150 nm to the size limit, dislocations adjacent to the grain boundaries of Ag and Cu crystals would disappear because the strain energy cannot counterbalance the electron pressure work and dislocations in the center of every grain can exist until the monolayer thickness is equal to the size limit. At this scale of the monolayer thickness, there are only a few dislocations present in every grain, thus the work hardening effect weakens and the Hall–Petch relation based on the dislocations pileup theory breaks down. When the number of dislocations (q) in a pileup is small ($q \leq 6$ for a single-ended pileup, and $q \leq 3$ for a double-ended pileup), deviations from the Hall–Petch relation are predicted [14].

The critical monolayer thicknesses of electroplated multilayers in this paper are larger than reported in other publications, where multilayers are prepared by physical vapor deposition [15] (the critical monolayer thickness is about 4 nm for Cu/Ni) or e-beam evaporation [16] (the critical monolayer thickness is about 1.2 nm for Ag/Cu). Compared with physical vapor deposition and e-beam

evaporation, electroplating can reduce inter-diffusion across the interface due to the lower deposition temperature and coherent interface, since semi-coherent interfaces and epitaxial growth are less likely [17]. The constraint effect of the interface in electroplated multilayers is reduced. An experimental study of Oberle et al. [18] showed that the interfacial diffusion affects the multilayer hardness. For Cu/Ni multilayer prepared by physical vapor deposition microstructure analysis shows that inter-diffusion of Cu and Ni takes place over several atomic layers [15]. Dislocation elastic stress field will be affected by the interfacial diffusion, coherent and semi-coherent interfaces. Dislocation elastic stress field can be transmitted across coherent and semi-coherent interfaces. Thus dislocations stability in multilayers prepared by physical vapor deposition and e-beam evaporation increases, and the critical monolayer thickness is reduced.

6. Conclusions

The critical monolayer thicknesses of electrodeposited Ag/Cu and Cu/Ni multilayers are 25 and 50 nm, respectively. Theoretical size limits for Ag, Cu and Ni crystals are 27, 88 and 265 nm, respectively. These estimations are based on the model of the grain size limit that includes elastic strain energy and dislocation core energy. The critical monolayer thickness is roughly consistent with the lower grain size limit of the multilayer crystals.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (No. 50771042) and the program for Basic and Frontier Technologies Research in Henan Province (092300410064) for the financial support. Alex Volinsky would like to acknowledge support from the National Science Foundation.

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