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THE STRUCTURE AND MECHANICAL PROPERTIES OF Ru-Cu AND Ru-Ti NANOLAYER COMPOSITES

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ABSTRACT

Multilayers of Ru-Cu and Ru-Ti have been prepared by electron beam evaporation technique. One set of composites has Ru thickness varying from 250 to 2500Å alternating with Cu or Ti of 15Å. The other set has 250Å of Ru and the Cu or Ti layer varies between 15 and 200Å. Nanoindentation measurements show that there is no significant change in hardness as either Ru or Cu/Ti thickness varies. However, the Ru-Cu multilayer has twice the hardness of the Ru-Ti system. High resolution transmission electron microscopy discloses that there is an epitaxial orientation relationship between Ru and Ti in Ru-Ti while no such relationship exists in Ru-Cu.

The strengthening mechanism proposed by Koehler [1] predicts that Ru-Ti composites should have a higher strength than Ru-Cu due to the larger modulus difference between Ru and Ti. The discrepancy between the prediction and the experimental results suggests that other strengthening mechanism(s) may be operating. We have proposed two models based on a "shear" mechanism to explain the differences observed between these two systems. The effects of these mechanisms in controlling the deformation process in nanolayer composites are discussed.

INTRODUCTION

Thin film nanolayer composites composed of alternating layers of two metals have been shown to possess high strengths. These strengthening effects were predicted by Koehler [1] and confirmed experimentally for Al-Cu and Al-Ag nanolayers by Lehoczy [2,3]. An example from the work of Lehoczy on Al-Cu [2] of thickness t is given in Fig. 1. These data show that the tensile yield strength increases with $1/t$ until a maximum value is reached at a critical thickness of 70nm; the tensile fracture strength also peaks at this critical thickness. In fine scale structures, we need to consider both scale and elastic modulus mismatch constituents. According to Koehler's theory, the strengthening phenomena comes from the significant differences in elastic constants between the two components and also the thin layer thickness, which result in the large applied force needed to drive dislocations from the material with a low modulus into the high one. Using Koehler's model, Lehoczy showed that for a dislocation moving on a glide plane in a softer metal, A, into a stiffer metal, B, the minimum stress required for yield is given by:

$$\sigma_y \geq (V_A + V_B) \frac{Y_B}{Y_A} \frac{\mu_A}{8\pi} \left(\frac{\mu_B - \mu_A}{\mu_B + \mu_A} \right) \quad (1)$$

where V_A and V_B are the volume fractions, Y_A and Y_B are the Young's moduli, and μ_A and μ_B are the shear moduli of the softer and stiffer materials respectively. Taking into account both of the strengthening constraints discussed above, Kelly [4] predicted that Frank-Read sources will be restricted from operating and Koehler strengthening will be observed when the layer thickness t_K is such that:

$$t_K \leq 32\pi b_A \left(\frac{\mu_B + \mu_A}{\mu_B - \mu_A} \right) \quad (2)$$

where b is the Burgers vector of the Frank-Read dislocation source in A.

In very fine scale structures (as we reach the plateau region in Fig. 1), the achievable strength levels are so high that we need to consider the basic aspects of plastic deformation. The fine scale may make it very difficult or even prohibitive for mechanisms such as dislocation pile-ups or dislocation bowing to operate. It will be extremely difficult to bow dislocations to very small radii, especially when the scale is approaching the core dimensions of the dislocations or the separation distance of the partials. Since the stresses are so high (close to the theoretical strength),

it is possible to create dislocations or directly shear the lattice and it will no longer be limited by the crystallographic orientation of the dislocations. In this study we have selected two multilayer systems, both with large modulus differences between the components (Ru-Cu and Ru-Ti), with very thin layer thickness to investigate the mechanical properties, microstructure and the strengthening mechanism(s) operating in these composites.

Fig. 1 The tensile yield stress as a function of $1/t$ for Al-Cu nanolayers. The solid horizontal line at maximum stress is given by Eq. 1. The vertical line at 70nm is predicted by Eq. 2. (From the work of Lehoczy [2])

EXPERIMENTAL PROCEDURE

Alternating layers of Ru and Cu or Ti were prepared by electron beam evaporation onto Si(100) and sapphire substrates. In order to assure good adhesion between the Ru and substrate, a thin layer (100Å) of Ti was first deposited onto the substrate. The chamber was cryo- and turbo-pumped to a base pressure of 2×10^{-8} torr, and a pressure between 1×10^{-7} to 5×10^{-8} torr was maintained during the evaporation process. Table 1 lists the layer type, nominal layer thickness and the total thickness of the specimens examined in this study.

Investigations of the surface hardness were performed using an indentation load-depth sensing apparatus, commercially available as a Nanoindenter™ [5,6]. This instrument directly measures the load on a triangular pyramid diamond indenter tip as a function of displacement from the surface. Hardness is determined from the load data using the relation:

$$H = L(h)/A(h),$$

where $L(h)$ is the measured load, and $A(h)$ is the projected area of the indent as a function of the plastic depth h . The area function is determined by an iterative process involving indents into materials of known and isotropic properties [7]. Measurements were made under a constant load rate of $20 \text{ mN} \cdot \text{sec}^{-1}$ to a nominal depth of 70nm. Typically nine indents were made on each sample and the data averaged. The depth of the indents was chosen to be less than 10% of the total thickness of the nanolayered composites [8]. As discussed by Doerner and Nix [9], the actual depth of the indent includes the plastic depth as well as the elastic recovery of the material as the indenter is removed. Following their analysis, we used the unloading portion of the curve to estimate the elastic contribution to the total displacement. This analysis assumes a homogeneous material, rather than a layered surface structure, but the limitation on the depth of the indentation should validate this assumption.

The as-deposited multilayers were made into cross-sectional transmission electron microscopy (XTEM) specimens and were examined using conventional and high resolution transmission electron microscopy (HRTEM) on a Phillips CM30ST microscope operating at 300kV. Optical diffractograms were taken from the lattice images, the patterns were then analyzed to identify the phase and orientation of each pattern.

Table 1 Layer type, thickness, total thickness and hardness of Ru-M composites.

Specimen No.	Ru (Å)	Metal type (Å)	Total (Å)	Hardness (GPa)
1	250	Cu 15	7500	19.2±2.7
2	1000	Cu 15	8100	18.7±1.7
3	2500	Cu 15	7500	17.8±0.8
4	250	Cu 50	7800	24.1±1.0
5	250	Cu 100	7700	19.2±0.7
6	250	Cu 200	7600	18.3±0.7
7	250	Ti 15	7500	11.2±0.1
8	1000	Ti 15	8100	11.5±1.0
9	2500	Ti 15	7500	13.2±0.2
10	250	Ti 50	4800	8.3±0.3
11	250	Ti 100	7700	8.2±0.3
12	250	Ti 200	7600	7.4±0.2

RESULTS

Nanoindentation Measurements

The hardnesses of the Ru-Cu and Ru-Ti composites determined by nanoindentation are listed in Table 1. All indents, except one, have a penetration depth less than 10% of the total thickness. By keeping the Cu or Ti layer thickness constant and varying the Ru layer between 250 to 2500Å, no significant changes in hardness were observed. The dependence of hardness on the inverse of Ru layer thickness (t_{Ru}^{-1}) is shown in Fig. 2(a). The Ru-Cu composites have hardness values as high as ~20 GPa, which is almost twice as high as the Ru-Ti composites throughout the layer thickness range studied. If the Ru layer thickness is kept at 250Å and the Cu/Ti layer varies from 50 to 200Å, a difference of ~200% in hardness is observed in these two systems and the hardness does not change significantly with metal layer thickness (Fig. 2(b)).

Fig. 2(a) Hardness variation with Ru thickness in Ru-Cu(15Å) and Ru-Ti(15Å) multilayers; Fig. 2(b) Hardness variation with Cu or Ti thickness in Ru(250Å)-Cu and Ru(250Å)-Ti multilayers.

Microstructural Characterization

Fig. 3(a) shows the typical microstructure of a Ru-Cu composite, when the layer thickness of Ru and Cu is 250Å and 50Å respectively. The layers exhibit more waviness as the deposition proceeds which can be seen by the gradual change in layer morphology from planar to wavy away from the substrate. The Ru(250Å)-Ti(100Å) composites possess a more planar layer geometry as is shown in Fig. 3(b). In addition to the difference in layer morphology, the Ru-Ti composites

seem to have a higher percentage of voids, as indicated by arrows in Fig. 3(b). A comparison of the selected area diffraction (SAD) patterns of these two composites is shown in Fig. 4(a,b). Even though both patterns exhibit the polycrystalline nature in the structure of the composites, the Ru-Ti multilayer shows a slight preferential (textured) growth with respect to the substrate. HRTEM has disclosed an epitaxial relationship between the Ru and Ti layer as is shown in Fig. 5. Both of the Ru and Ti grains have the $\langle 1210 \rangle$ orientation, as was determined by the optical diffractogram patterns taken respectively in the two regions adjacent to the interface. No such relationship was found in the Ru-Cu composites.

Fig. 3 TEM micrographs showing typical microstructure in (a) Ru(250Å)-Cu(50Å) multilayer composites and (b) Ru(250Å)-Ti(100Å) multilayer composites.

Fig. 4 SAD patterns taken from (a) Ru(1000Å)-Cu(15Å) and (b) Ru(1000Å)-Ti(15Å) multilayers.

DISCUSSION

According to Koehler's model, the strength ratio between Ru-Cu and Ru-Ti can be determined using Eq. 1. Table 2 lists the Young's modulus, Poisson's ratio and shear modulus of Ru, Cu and Ti. [10] The critical thickness, below which Koehler strengthening is expected to occur, was calculated based upon Eq. 2. The t_K for Ru-Cu and Ru-Ti was determined to be 460Å and 489Å, respectively. The almost constant hardness values observed with respect to the layer thickness changes seem to be consistent with the t_K values calculated, which indicates that both sets of composites are in the plateau regime shown in Fig. 1. On the other hand, the strength ratio between the two sets of composites as predicted by Eq. 1 is inverted and significantly different from the experimental results, as is shown in Table 3. The discrepancy indicates the breakdown of

the Koehler model in cases where the thickness of the softer material is extremely small; other mechanisms may be operating in such cases.

Fig. 5 (a) HRTEM image of a Ru-Ti interface region showing an epitaxial relationship between Ru and Ti grains. Optical diffractograms taken from the two regions adjacent to the interface which show the Ru in $\langle 1120 \rangle$ orientation (b) and Ti also in $\langle 1120 \rangle$ orientation (c).

Table 2 Young's moduli, Poisson's ratios and shear moduli of Ru, Cu and Ti.

Modulus	Ru	Cu	Ti
Y (GPa)	412	123	106
ν	0.286	0.345	0.345
μ (GPa)	159	45	39

Table 3 Observed hardness ratio, predicted strength ratio from Eq. 1 for Ru-Cu and Ru-Ti composites and shear modulus ratio between Cu and Ti.

Ru ($\text{\AA}$)	Cu or Ti ($\text{\AA}$)	Observed H Ratio (Cu/Ti)	Predicted σ Ratio (Cu/Ti)	μ Ratio (Cu/Ti)
250	15	1.7	0.91	1.2
1000	15	1.6	0.91	
2500	15	1.3	0.91	
250	50	2.9	0.92	
250	100	2.3	0.92	
250	200	2.5	0.94	

To understand other possible strengthening mechanisms that may be operating in these multilayers, we first examine the indentation process. A typical 70nm in depth indent will penetrate from 1 to 3 bilayers of these composites. If the softer material is thin enough to inhibit dislocation motion to contribute to (or be a major part of) the deformation process, then the deformation will have to be accommodated by "shearing" of the softer layer. There are two possible ways to shear the Cu (or Ti) layer. One possibility (Fig. 6(a)) is to have dislocation plasticity in the thick Ru layer and then the dislocation will have to propagate through the softer

layer by a shearing mechanism. The thin softer layer will then serve as a barrier for dislocation motion as in the case of grain boundary or precipitation hardening. In this case, the existence of an epitaxial relationship between the layers will lessen the effectiveness of the interface as a dislocation barrier and will therefore decrease the strengthening effect. Another possibility requires fracture in the Ru layer to accommodate the shear of the Cu or Ti. (Fig. 6 (b)) An example of such mechanism was demonstrated in GaAs/AlAs superlattices by Castell et al. [11]. In either cases, the strength or hardness of the composites will be limited by the shear strength of the softer layer. Since the Cu (or Ti) is under constraint between the two adjacent stiff Ru layers, a much higher shear strength (should be approaching the theoretical strength, $\sim \mu/15$) of Cu (or Ti) is expected. A similar situation can be found in the work of Ashby and coworkers [12] where a six times increase in yield strength was observed in Pb wire when it was constrained by a glass matrix.

In summary, the hardness of the layer composites in either case will both be proportional to the shear modulus of the softer layer or some magnitude of the modulus if taking into account the texture orientation relationship between the layers. The current results seem to be in good agreement with the trend predicted by both mechanisms, and we can not disprove either mechanism at this stage. Future work is planned in characterizing the true deformation process which is expected to benefit our understanding on the process-structure-property relationship in these nanolayer composites.

Fig. 6 Schematic diagrams showing two different mechanisms to accommodate indent in layer composites. (a) Dislocation plasticity in the Ru layer causing shearing of the Cu layer. (b) Fracture of the Ru layer followed by the shearing of the Cu layer.

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