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Unique mechanical properties of Cu/(NbMoTaW) nanolaminates

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ABSTRACT

Nanostructured face-center-cubic/body-center-cubic Cu/(NbMoTaW) multilayers were prepared with equal layer thickness (h) spanning from 5 to 100 nm. The hardness was found to increase with reducing h to ~50 nm, following the Hall–Petch relation. Below this critical thickness, a hardness plateau emerged indicative of an interface barrier strengthening mechanism. The high density of misfit dislocations at interfaces facilitates the yielding of high entropy alloy NbMoTaW layers at stresses far less than the strength of Cu/(NbMoTaW) estimated by rule-of-mixture. Compared with reported multilayers, the present Cu/(NbMoTaW) samples show the size-independent hardness at a larger size-range $h < 50$ nm.

Nanostructured metallic multilayers (NMMs) with individual layer thickness (h) <100 nm are widely used in practical applications due to their novel properties such as superior strength, high toughness and great radiation tolerance, which stem from their tunable interfacial structure [1–3]. Extensive studies have conducted on the mechanical properties of the metallic multilayers, including FCC/FCC [4–8] and FCC/BCC [9–11] NMMs, often uncovering a fashion of smaller is stronger. Accordingly, the underlying strengthening mechanisms have been proposed to quantify the size-dependent strength/hardness [9,12–14]. In fact, some NMMs exhibit the hardness plateau (H_P) [3,15] or softening [5,16] as layer thickness h to several nanometers, implying ultra-high strength/hardness can be realized at large h. Since Misra et al. [9] proposed that the hardness plateau H_P can be estimated through the Hall–Petch (H-P) slope (K_{HP}) based on the dislocation pile-up theory, some studies have been done to correlated the slope K_{HP} with the hardness H_P [11,17–20]. Previous studies [18,19] revealed that K_{HP} actually determines the strengthening rate with decreasing h, i.e., larger K_{HP} represents that the material can reach the saturation strength even the ideal strength at a larger intrinsic size h. However, few studies have been focused on the critical layer thickness (h_P) for the beginning of hardness plateau in NMMs. Also, some researchers [11,17] tried to connect the hardness H_P with physical parameters of constituents, including the difference in stacking fault energy $\Delta\gamma_{sf}$, modulus mismatch $\Delta\mu$, and enthalpy of mixing ΔH_{mix}. Recently, Zeng et al. [20] proposed a parameter in terms of the coupling effects of the lattice mismatch and modulus mismatch to calculate the critical stress required to transmit a perfect dislocation across the bimetal A-B interface, which accounts for the hardness plateau H_P.

Unlike the pure metals as the constituents of NMMs, high entropy alloys (HEAs) are currently receiving extensive attentions from the materials science community due to their metastability associated with unique microstructure and outstanding mechanical properties [21–23]. In particular, the refractory NbMoTaW HEA thin films with the BCC structure manifest ultra-high hardness ~16 GPa at the nanoscale and great thermal stability [24,25]. Such high hardness of the NbMoTaW HEA is much higher than previously studied pure refractory metals, e.g., Nb ~3 GPa [26], Mo ~6 GPa [26], Ta ~10 GPa [27], W ~8 GPa [28]. It is natural that one may expected the introduction of hard NbMoTaW HEA nanolayers into the soft Cu matrix in the form of nanolaminates can create ultrastrong Cu/HEA nanostructured composites. Therefore, motivated by above issues, we selected the Cu/(NbMoTaW) NMMs with layer thickness h spanning from 5–100 nm as the model materials to investigate their size-dependent hardness and the mutual constraining effects between Cu and NbMoTaW HEA nanolayers.

Cu/HEA (HEA = NbMoTaW) NMMs with total thickness of 1.5 μm were deposited on Si-(111) substrates by direct current magnetron sputtering at room temperature. The Cu layer was first deposited on the substrates followed by NbMoTaW layer with the 0.5 Pa working pressure during the deposition process. Modulation ratio, defined as the layer thickness ratio of Cu (h_{Cu}) to HEA (h_{HEA}) was kept constant of ~1, and the layer thickness h varied from 5 to 100 nm. To examine the phase structure and crystallographic texture, X-ray diffraction (XRD) experiments were performed on the Cu/HEA NMMs, as shown in Fig.1. It indicates that the NbMoTaW HEA layers are single phase BCC solid solution associated with strong (110) peak and the Cu layers exhibit strong (111) peak at small h < 50 nm. Weak Cu (200) and

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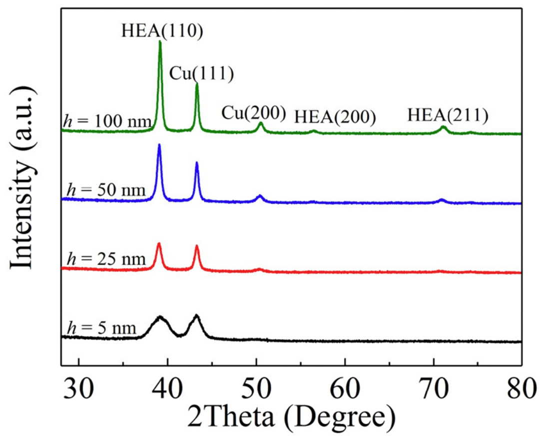

Fig. 1. XRD patterns of the Cu/HEA NMMs with different thickness.

NbMoTaW (211) peaks appear with increasing $h \geq 50$ nm. For comparison reasons, the monolithic Cu and NbMoTaW HEA thin films with thickness of ~100 nm were also prepared under the same deposition condition.

Atomic force microscopy (AFM) was applied to examine the film surface roughness and morphology using a Bruker Dimension Icon. The representative surface images of Cu/HEA NMMs with $h = 5$ nm and $h = 100$ nm are displayed in Fig.2 (a) and (b), respectively. The surface morphologies are individual sphere-like grains, associated with small roughness in the range of 2 to 4 nm. High-resolution transmission electron microscopy (HRTEM) observations were employed to determine internal microstructure of Cu/HEA NMMs. It is found that the grain size of Cu scales with the layer thickness, while that of HEA layers is almost constant of ~5 nm. The typical cross-sectional TEM images of Cu/HEA NMMs with $h = 10$ nm are displayed in Fig. 2(c) and (d), showing clear modulation structure and sharp interfaces. Columnar nanosized grains in Cu layers and ultrafine nanocrystals in NbMoTaW layers can be observed, and the specific grain size of Cu layer and HEA layer is 9.2 nm and 4.8 nm, respectively. The selected area diffraction pattern (SADP), as the inset in Fig. 2(c), definitely demonstrates Cu (111) and NbMoTaW (110) textures, which is in good agreement with XRD patterns.

Mechanical properties of the Si substrate-supported Cu/HEA NMMs were measured using a TI950 TriboIndenter (Hysitron, Minneapolis, MN) with a standard Berkovich tip at room temperature. The hardness test was performed in the load-controlled mode for all multilayers (5500 μN) at the strain rate of 0.1 s^{-1}. A minimum of nine indentations were performed on each sample to obtain the average hardness (H) and standard deviations. To eliminate substrate effects, the nanoindentation data were collected within a maximum indentation depth of 10%–15% of the entire thickness for each sample. Given the average surface roughness is quite small relative to the indentation depth, thus we neglect its effect on the hardness. The load-depth curves are shown in Fig. 3(a), indicating that indentation depth decreases when the layer thickness h decreases from 100 to 50 nm and then nearly remains constant with further reducing h. Fig. 3(b) presents the indentation hardness H of Cu/HEA NMMs as a function of h. It appears that the hardness of Cu/HEA NMMs drastically increases as h reduces from 100 to 50 nm, then reaches a plateau of ~5.9 GPa. The measured hardness (in the range of ~5.1 to 5.9 GPa) of Cu/HEA NMMs is in-between the values of ~1.7 GPa for Cu and ~12.6 GPa for NbMoTaW HEA.

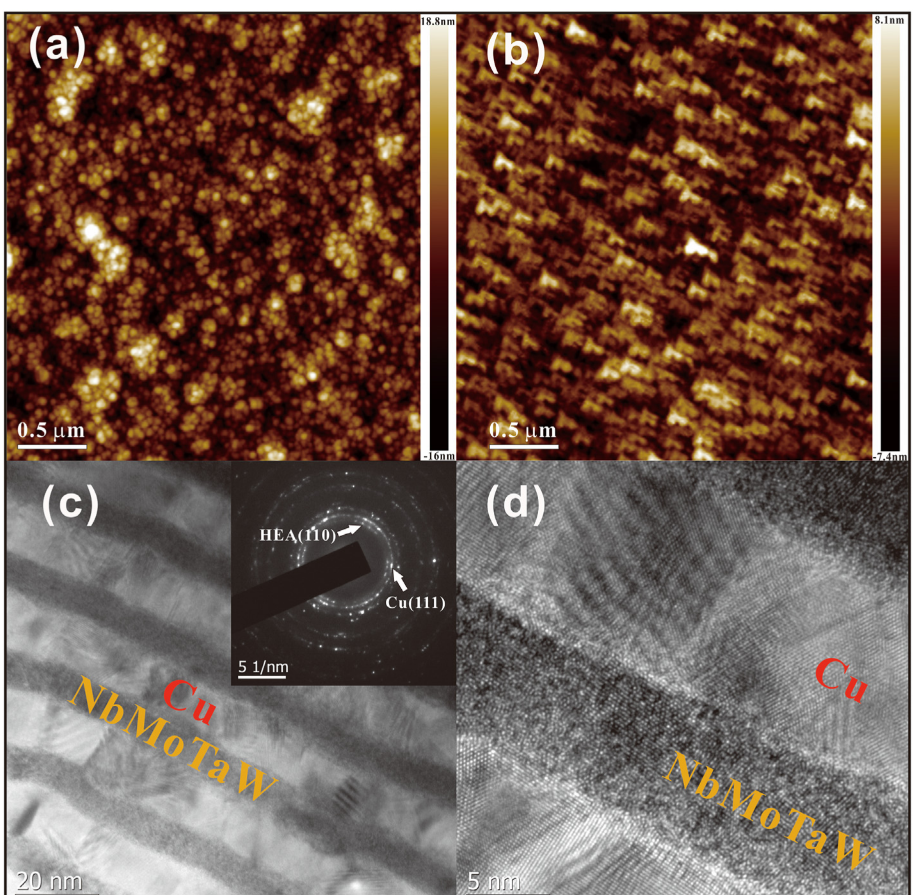

Fig. 2. AFM images of the surface of Cu/HEA NMMs with different layer thickness h (a) $h = 5$ nm, (b) $h = 100$ nm. Representative (c) TEM and (d) HRTEM images of the as-deposited Cu/HEA NMMs with $h = 10$ nm. Inset in (c) is the corresponding selected area diffraction (SDAP), showing strong Cu (111) and NbMoTaW (110) textures.