**Unusual size dependent strengthening mechanisms in helium ion irradiated immiscible
coherent Cu/Co nanolayers**

Y. Chen^a, Y. Liu^a, E.G. Fu^b, C. Sun^c, K.Y. Yu^d, M. Song^a, Jin Li^a, Y.Q. Wang^c, H. Wang^{a,e}, and
X. Zhang^{a,f*}

^a Department of Materials Science and Engineering, Texas A&M University, College Station,
TX 77843

^b State Key Laboratory of Nuclear Physics and Technology, School of Physics, Peking
University, Beijing 100871, PR China

^c Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos,
NM 87545

^d Department of Materials Science and Engineering, China University of Petroleum-Beijing,
Beijing 102249, PR China.

^e Department of Electrical and Computer Engineering, Texas A&M University, College Station,
TX 77843

^f Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843

* Corresponding author: X. Zhang, zhangx@tamu.edu, Tel: (979) 845-2143

Abstract

He ion irradiation induced damage in several immiscible metallic nanolayer systems with incoherent interfaces has been investigated recently and a prominent size effect on mitigation of radiation damage has been observed. In general the magnitude of radiation hardening and defect cluster density are both less at smaller individual layer thickness (h) than those with larger h , as

interfaces can effectively reduce density of radiation induced defect clusters. Here we show, however, an opposite size dependent strengthening behavior in He ion irradiated immiscible coherent Cu/Co multilayers, that is films with smaller h have greater radiation hardening. Such unusual size dependent strengthening could be explained via a transition from partial dislocation transmission (before radiation) to full dislocation transmission (after radiation) dictated strengthening mechanisms due to formation of He bubbles at layer interface. Furthermore we show that, similar to incoherent immiscible systems, coherent interface in immiscible system can also effectively reduce the population of radiation induced defect clusters.

Key words: He ion irradiation, immiscible multilayers, size effect, radiation hardening, He bubbles, strengthening mechanisms, partial dislocations

1. Introduction

Neutron radiation on structural materials in nuclear reactors creates abundant vacancies and interstitials, which could form defect clusters, primarily in the form of dislocation loops and voids/bubbles [1]. The nucleation and growth of voids/bubbles are enhanced by Helium (He), a byproduct of (n,α) nuclear transmutation. He can swiftly migrate into and combine with vacancies to accelerate the nucleation of bubbles and stabilize them [2-4]. Recent study shows that He atoms can be trapped and stored at defect sinks such as grain boundaries (GB) [5, 6] and interphase boundaries [7-11]. The storage of He at interfaces can delay bubble growth significantly and thus alleviate radiation hardening, void swelling and blistering. GB and interphase boundaries also provide effective annihilation sites for radiation induced interstitials and vacancies [12, 13]. Increasing efforts have been devoted to investigate the radiation

tolerances of nanostructured materials, including ODS alloys with abundant metal/oxide interfaces [14-18], nanocrystalline (nc) metals[6, 19] and multilayers [8, 9, 20]. Experimentally, Singh and Foreman [21, 22] have observed significant grain size dependence of void swelling in stainless steel decades ago. Sun *et al.*[19] have reported the first *in situ* evidence of defect absorption by grain boundaries (GBs) in nanocrystalline nickel subjected to Kr ion radiation. Theoretically, molecular dynamics (MD) simulations have shown that GBs can emit interstitials into grain interior to annihilate vacancies [23]. Chen *et al.* [24] have also shown defect-GB interactions by formation and annealing of chain-like defects. Yu *et al.* [25, 26] reported that twin boundaries can effectively interact with and remove radiation induced defect clusters, such as stacking fault tetrahedra. Besides these internal defect sinks, free surfaces in nanoporous (np) metals were also reported to significantly reduce defect density during irradiation [27-29]. Furthermore *in situ* radiation studies on np Ag also revealed that both global and instantaneous diffusivity of defect clusters in np Ag is much lower than those in coarse grained Ag, quite different from general perception [29].

Radiation damage in metallic multilayer systems with various types of interfaces has been investigated, including face-centered cubic (FCC)/ body-centered cubic (BCC) interfaces (e.g. Cu/Nb [8, 9], Cu/V [30-32], Cu/Mo [33], Cu/W [34], Al/Nb [35], Ag/V[36, 37]), FCC/FCC interfaces (e.g. Cu/Ni [38], Ag/Ni [39, 40]), BCC/BCC interfaces (Fe/W [41]) and FCC/hexagonal close-packed (HCP) interfaces (Al/Ti [42]). In general clear size dependent enhancement of radiation tolerance was observed in immiscible systems, that is the density of defect clusters (dislocation loops or He bubbles) declines with decreasing individual layer thickness h . Meanwhile the magnitude of radiation hardening typically decreases at smaller h . The rationale behind these phenomena is that immiscible layer interfaces appear to be effective

sinks that absorb and remove radiation induced defect clusters [7, 20]. Yu *et al.* [40] have provided the first *in situ* observation where layer interface in immiscible Ag/Ni nanolayers can effectively capture and annihilate radiation induced defect clusters.

Size dependent radiation hardening has also been quantitatively analyzed in several He ion irradiated metallic multilayer systems. The peak strength of irradiated multilayers is determined by the inherent resistance of layer interfaces to the transmission of single dislocations and the interaction of dislocations with radiation induced obstacles, such as dislocation loops, stacking fault tetrahedra, and He bubbles. The models developed by comparing the characteristic dimension (average separation distance between He bubbles) and layer thickness were able to capture the major trend of size dependent strengthening in He ion irradiated nanolayers [8, 36, 39, 43]. Interestingly Yu *et al.* also noticed that in contrast to size dependent strengthening in He ion irradiated Ag/Ni nanolayers, there is not a strong size dependence in proton irradiated Ag/Ni systems, implying the significance of He bubbles on radiation hardening [39].

Recently, we reported that as-deposited immiscible Cu/Co (FCC) (100) multilayer system has a peculiar size dependent strengthening behavior [44]. In general we anticipate that Cu/Co (100) [44] and Cu/Ni (100) [45] multilayer systems should have similar size dependent strengthening. This is because both systems have comparable Koehler stress (due to the same magnitude of modulus mismatch) and coherency stress (arising from lattice mismatch). However nanoindentation experiment reveals three drastic differences between strengthening behaviors of the two systems. (1) When individual layer thickness (h) is several nm, the peak hardness of Cu/Co is significantly lower, by ~ 1 GPa, than that of Cu/Ni. (2) When h is 50-200 nm, the hardness of Cu/Co is greater than that of Cu/Ni nanolayers. (3) Cu/Co (100) system has a much smaller Hall-Petch slope than that of Cu/Ni (100) system. The lower peak strength of Cu/Co is

ascribed to the transmission of partial dislocations across the interface, in comparison to full dislocation transmission across Cu/Ni interface, as Cu and Co both have low stacking fault energy (SFE) ($\gamma_{SF}^{Co} = 24 \text{ mJ/m}^2$, $\gamma_{SF}^{Cu} = 41 \text{ mJ/m}^2$), whereas Ni has inherently high SFE ($\gamma_{SF}^{Ni} = 125 \text{ mJ/m}^2$). At large h , Co has high-density stacking faults, with an average spacing of several nm, and hence contributes significantly to the high strength of Cu/Co nanolayers.

The motivations of the study on radiation damage in Cu/Co (100) system include the followings. (1) To date there is only one study on radiation damage in immiscible FCC/FCC system, Ag/Ni, which has incoherent interfaces (due to large lattice mismatch between Ag and Ni). In comparison the immiscible Cu/Co has coherent FCC/FCC layer interfaces, permitting us to probe the influence of coherency on radiation tolerance of immiscible FCC/FCC multilayers. (2) Size dependent strengthening mechanisms in irradiated Cu/Co with coherent interface may not be identical to immiscible multilayers with incoherent interface. (3) To examine size dependent variation of defect density in a system with immiscible coherent interfaces. (4) The stability of FCC Co could be varied during radiation.

2. Experimental

Cu/Co multilayers with identical h , varying from 1 to 200 nm, were magnetron sputtered at room temperature on HF etched Si (100) substrates. The chamber was evacuated to a base pressure less than 8×10^{-8} torr prior to deposition. Before the deposition of Cu/Co multilayers, a 100 nm thick Cu seed layer was deposited. The total thickness of multilayers was $\sim 1 \text{ }\mu\text{m}$ when $h \leq 10 \text{ nm}$, $\sim 1.5 \text{ }\mu\text{m}$ when $10 \text{ nm} < h < 100 \text{ nm}$, and $\sim 4 \text{ }\mu\text{m}$ when $h \geq 100 \text{ nm}$. The total film thickness was designed so that indentation experiment will probe at least one bilayer, but the

maximum indentation depth is limited to 10-20% of total film thickness to avoid substrate effect. The deposition rate of Cu and Co is ~ 0.5 nm/s for all layer thicknesses. The films with various h were irradiated at room temperature using 100 keV He ions with a total fluence of 6×10^{20} ions/m². The temperature rise of the sample stage was $\sim 50^\circ\text{C}$ during implantation. Calibration studies show that the sample temperature is close to sample stage temperature, within 10°C as there were conducting copper tapes connected between stage and sample. The sample temperature difference among irradiated multilayers of various layer thicknesses is very small, $\pm 10^\circ\text{C}$. The base pressure in the ion implantation system was 4×10^{-5} Pa. X-ray diffraction (XRD) experiments were performed on a Brukers D8 Discover X-ray powder diffractometer at room temperature. The plan-view samples were examined by conventional out-of-plane method, in reflection mode, with energy of 20 keV. Transmission electron microscopy (TEM) experiment was carried out on a JEOL 2010 transmission electron microscope operated at 200 kV and an FEI Tecnai G2 F20 microscope operated at 200 kV with a Fischione ultra-high resolution high-angle annular dark field (HAADF) detector. Film hardness was measured from an average of 12 - 15 indents at different indentation depths by using instrumented nanoindentation technique on a Fisherscope HM 2000XYp micro/nanoindenter with a Vickers diamond indenter tip, using instrumented indentation technique [46]. One typical load-displacement curve is provided in Fig. 8a, which can be used to calculate indentation hardness at a specific indentation depth. The average indentation hardness is determined when hardness value reaches a plateau, nearly independent of indentation depth [45] and one example is displayed in Fig. 8b. Cross-sectional TEM (XTEM) samples were prepared by dimpling and low energy (3.5 keV) Ar ion milling and subsequent ion polishing. The average TEM foil thickness was measured by using convergent beam electron diffraction (CBED) technique. The thickness of TEM foils is measured to be $\sim$

100 ± 20 nm throughout the irradiated regions in multilayer films. The CBED method can reach an accuracy of ~ 5% in determining foil thickness [47]. The detailed procedure of thickness measurement is shown in reference [14]. In addition, this method has been employed in our previous studies [25, 30-33, 35, 39-41].

Depth-dependent damage and defect concentration profiles were calculated by the Stopping and Range of Ions [48] in Matter (SRIM)-2008 using the Kinchin-Pease option in the SRIM software [49]. The Kinchin-Pease option for SRIM calculation has recently been adopted by the community as a new routine to reliably estimate radiation damage for irradiated materials [50].

3. Results

Fig.1. shows the depth profile of He ion radiation damage in unit of displacements per atom (dpa) and helium concentration obtained from SRIM simulation of Cu₅₀Co₅₀ compound subjected to He ion radiation at 100 keV with a total fluence of 6×10^{20} ions/m². The peak damage approaches ~ 2.5 dpa at a depth of ~ 300 nm and the projected ion penetration depth is ~ 500 nm. He concentration approaches a maximum of ~ 3% at a depth of ~ 350 nm.

XRD patterns were collected to investigate radiation induced structural evolution. For as-deposited films, when $h \geq 10$ nm (Fig. 2a), only Cu (200) and FCC Co (200) peaks were detected. Superlattice peaks were observed in Cu 10 nm/Co 10 nm (referred to as Cu/Co 10 nm hereafter) nanolayers. Radiation led to diminished peak intensity with insignificant peak shift. Further decrease of h (1-5 nm) led to a fully coherent peak located between Cu (200) and Co (200) in the as-deposited films (Fig. 2b). The position of satellite peaks is consistent with bilayer thickness in these fine nanolayers. After radiation, the intensity of all diffraction peaks decreased, and the

central peak became broader. No hexagonal closely packed (HCP) Co peaks were detected after radiation.

Extensive TEM experiments were performed to examine the microstructure of irradiated Cu/Co nanolayers. As-deposited Cu/Co 100 nm multilayer contained high density of stacking faults (SFs) in Co layers. The density of SFs in Co decreased rapidly at smaller h . No bubbles and little dislocation loops were detected in as-deposited Cu/Co multilayers without He ion irradiation, as shown in Fig. 3. Fig. 4a shows the cross-section TEM (XTEM) overview of He ion irradiated Cu/Co 100 nm nanolayer along $\langle 001 \rangle$ zone axis. The superimposed solid curve shows the depth profile of He concentration calculated by SRIM. The layered structure can be clearly discerned and the embedded selected area diffraction (SAD) pattern of the irradiated region confirms the retention of single-crystal like Cu and FCC Co. Boxes b-e at different penetration depth are shown at higher magnification in succeeding figures. In the surface region (Fig. 4b), He bubbles were randomly distributed. In the peak damage region, high-density bubbles were observed in both Cu (Fig.4c) and Co (Fig.4d) layers. Fewer He bubbles were observed in Co layer near the end of projected ion range (Fig. 4e).

Fig. 5 displays XTEM images of irradiated Cu/Co 5 nm multilayer. In the peak damage region, 400 nm from surface (Fig. 5a), He bubbles were distributed both within the layers and along layer interfaces as indicated by arrays of dash lines. In a region (600-700 nm from surface) beyond the peak radiation damage (Fig. 5b), we observed clear alignment of bubbles along layer interfaces (indicated by dash lines). The embedded SAD pattern of irradiated Cu/Co multilayer shows the film retained epitaxial structure with fully coherent Cu/FCC Co interface. A typical region captured at underfocus (Fig. 5c1) and overfocus (Fig. 5c2) conditions confirmed the alignment of He bubbles, appearing as white and dark dots, along interfaces.

Similarly the microstructure of He ion irradiated Cu/Co 1 nm multilayer was also examined by XTEM. Fig. 6a exhibits a panoramic view of the irradiated specimen incorporating the SRIM simulated depth dependent profile of He concentration. The embedded SAD pattern of the irradiated region confirmed the retention of epitaxial FCC Cu/FCC Co structure. Boxes b-d captured at different penetration depth are shown at higher magnifications. The surface region of irradiated specimens (Fig. 6b) contained randomly distributed He bubbles with barely discernable layer interfaces. High-density bubbles were observed (Fig. 6c) around peak damage region in absence of layer structures. However, layered structure can be distinguished with few He bubbles at the end of the irradiated region, as shown in Fig. 6d.

Comparisons of depth dependent He bubble density in several irradiated Cu/Co multilayers were made in Fig. 7, based on XTEM results. We selected 3 boxes with dimensions of $50 \times 50 \text{ nm}^2$ at one specific depth to measure the bubble density at that depth, and analyzed bubble density at various depths along the projected ion path. This method has been successfully applied to investigate depth dependent bubble density distribution in other He ion irradiated nanolayers [25, 30-33, 35, 39-41]. Several features are noteworthy. First, the peak He bubble density in Cu/Co 5 and 1 nm is similar, $\sim 60\%$ of that in Cu/Co 100 and 50 nm counterparts. Second, the locations of peak bubble density in irradiated Cu/Co 100 and 50 nm multilayers coincide with that of the calculated He concentration profile (the dash line), while the positions of peak maxima in irradiated Cu/Co 5 and 1 nm multilayers are slightly deeper. Third, the range of He bubble profiles in irradiated multilayers exceeds that of the calculated He profiles.

The method to determine indentation hardness was discussed in experimental section (Fig. 8a,b). Hardnesses of as-deposited and irradiated Cu/Co multilayers as a function of $h^{-1/2}$ are compared to that of as-deposited Cu/Ni (100) [45] in Fig. 8c,d. The comparisons reveal the

following characteristics. (1) In general radiation induced hardening in Cu/Co across all h. (2) Compared to as-deposited Cu/Co, the peak hardness of irradiated Cu/Co multilayer increased substantially from ~3.8 to 5 GPa. (3) When $h = 2.5 - 10$ nm, the hardnesses (including peak hardness) of irradiated Cu/Co overlapped with that of as-deposited Cu/Ni with the same h. (4) When $h = 50 - 200$ nm, the Hall-Petch slope of irradiated Cu/Co is much greater than that of as-deposited Cu/Co, but close to that of as-deposited Cu/Ni (100).

4. Discussion

4.1. Comparisons of radiation induced microstructure evolution in multilayers with immiscible coherent and incoherent layer interfaces

Metallic multilayers are attractive systems to study radiation damage as they possess abundant layer interfaces which could be effective defect sinks [9]. In general, in comparison to miscible multilayers, immiscible multilayer systems are more effective to alleviate radiation damage as layer interfaces are more stable against radiation induced intermixing [7, 20, 31, 35, 41]. Among immiscible systems, multilayers with FCC/BCC incoherent interfaces have been extensively investigated [7-9, 20]. The driving force behind the frequent selections of incoherent FCC/BCC multilayers for radiation studies may be attributed to the general perception that incoherent interfaces may be more effective in eliminating radiation induced defects than their coherent siblings. Among FCC/FCC metallic multilayer systems, few have immiscibility. Ag/Ni is one such system that has been investigated after He, proton and heavy ion (Kr) irradiations [39, 40]. Indeed Ag/Ni multilayer with smaller h has lower He bubble density after radiation [40].

Foregoing discussions focus on systems with immiscibility and incoherency. A question follows naturally: what is the radiation response of a coherent immiscible system?

The challenge in the design of such a system is that coherency typically exists in metallic materials with the same crystal structure and nearly identical lattice parameters, such as Cu/Ni [45], Ag/Au[51], Ag/Al [52, 53], or Fe/Cr [54]. However metallic materials with these similarities typically have significant solid solubility, in other words, the immiscibility criterion cannot be satisfied. Interestingly we have recently discovered that Cu/Co (100) multilayers can be fabricated, where Co has FCC phase, stabilized by FCC Cu. Furthermore FCC Co has lattice parameter of 3.709 Å, nearly identical to Cu, 3.615 Å, and is immiscible in Cu. Hence opportunity arises to compare radiation tolerance of a coherent immiscible system to the incoherent immiscible systems.

Examination of microstructures of irradiated Cu/Co reveals several important phenomena. First when reducing h from 200 to 5 nm, there is a prominent reduction of average and peak He bubble density, that is size dependent alleviation of radiation damage is also observed in immiscible FCC/FCC system with coherent layer interfaces. *In situ* radiation of immiscible Ag/Ni multilayers showed that interfaces can effectively capture radiation induced defect clusters [40], and hence reduce the defect density in irradiated metallic multilayers. Similarly coherent Cu/Co layer interface may be as effective as incoherent interfaces.

Second, when $h = 5$ nm, clear alignment of He bubbles along interfaces was observed. Similar phenomena have been reported in He ion irradiated FCC/BCC systems, such as Cu/Nb and Cu/Mo [9, 33, 43]. The Cu/Co interfaces clearly trap He efficiently and lead to the alignment of He bubbles along interfaces.

Third, further decrease of h from 5 to 1 nm does not lead to prominent benefit in reducing defect density. Similarly in immiscible incoherent metallic multilayers, size dependent reduction of He bubble density is insignificant when h is the range of several nm [31, 36, 39]. Radiation of immiscible incoherent multilayers, such as Cu/V [31] and Ag/Ni [39] to similar dose did not lead to destruction of layer interfaces when h is 2.5 nm or greater. Although layer interfaces in peak damage zone of irradiated Cu/Co 1 nm was invisible, this could be related to contrast variation compromised by He bubbles. Similar phenomena (disrupted layer interfaces) have been observed in other immiscible incoherent systems with h of 2.5 nm [30, 37]. Meanwhile we notice that the SAD of peak damage zone in irradiated Cu/Co reveals single crystal like diffraction pattern (Fig. 6a). Furthermore XRD studies show the retention of single diffraction peak after radiation of Cu/Co 1 nm nanolayers, implying that coherency survived after such radiation (instead of forming semi-coherent interfaces). The survival of coherency implies that Cu and Co remain rigidly connected with corrugated coherent interface, which may continuously absorb radiation induced point defects. Finally, both XRD and TEM studies show no evidence of HCP Co after radiation, implying that fcc Co remains stable again He ion irradiation. This is an important observation as it simplifies our discussions on the influence of radiation on variation of strengthening mechanisms in irradiated Cu/Co nanolayers.

The position of peak He bubble density in irradiated Cu/Co 5 nm and Cu/Co 1 nm multilayers appears deeper (from surface) than that in irradiated Cu/Co 50 nm film. Such disparity may arise from ion channeling effect. During ion implantation of single crystals, channeling effect can occur, which may result in a deeper ion range than what is predicted by SRIM simulations [1, 55, 56]. In FCC/FCC Cu/Co multilayers, the system becomes increasingly

coherent, when h is 5 nm or less, and hence the channeling effect may have become more prominent during ion irradiation.

4.2 Size dependent strengthening mechanisms in irradiated Cu/Co multilayers

Prior studies on immiscible multilayer systems, including Cu/V [31], Ag/V [36] and Ag/Ni [39], typically showed less radiation hardening at smaller h as shown in Fig. 8d. However, in Cu/Co multilayers, radiation hardening escalated with decreasing h , in drastic contrast to general trend in previous studies. The mechanisms behind such deviation will be discussed below.

(a) Strengthening mechanisms at small h ($h < 10$ nm)

In as-deposited Cu/Ni (100) and Cu/Co (100) systems, the peak strength was determined by interface barrier strength of layer interfaces, and can be estimated by [44]

$$\tau_{barrier}^* = \tau_k^* + \tau_{ch}^* = \frac{\mu_1(\mu_2 - \mu_1)}{4\pi(\mu_2 + \mu_1)} \frac{b}{l} + \frac{\gamma_2 - \gamma_1}{b} \quad (1)$$

where τ_k^* is Koehler stress originating from modulus mismatch ($\mu_2 - \mu_1$), τ_{ch}^* is chemical interaction term related to SFE difference ($\gamma_2 - \gamma_1$) between layer constituents, b is Burgers vector. l is dislocation core size. τ_k^* for Cu/Co and Cu/Ni is close as they have similar magnitude of shear modulus mismatch ($\mu_{Co} = 82$ GPa and $\mu_{Ni} = 76$ GPa [44]). Thus, the major discrepancy of interface strength between Cu/Ni and Cu/Co ($\tau_{Cu/Ni}^* - \tau_{Cu/Co}^*$) mainly arises from the SFE difference. Given $\gamma_{SF}^{Co} = 24$ mJ/m², $\gamma_{SF}^{Cu} = 41$ mJ/m², and $\gamma_{SF}^{Ni} = 125$ mJ/m², their difference in τ_{ch}^*

amounts to ~ 0.19 GPa, corresponding to a hardness discrepancy by ~ 1.5 GPa (by estimating $H = 2.7\sigma$ [57, 58], where σ is the flow stress, and $\sigma = 3\tau^*$), close to the experimentally determined hardness difference, ~ 1.2 GPa. Physically this means that in Cu/Co multilayers, the peak strength is dominated by the interface barrier strength to transmission of partial dislocations, whereas in Cu/Ni system, it is the transmission of full dislocations that dictates the maximum strength of multilayers [44].

Fig. 9 schematically illustrates strengthening mechanisms in as-deposited and irradiated Cu/Co (100) multilayers at small h (using h of 5 nm as an example). The transmission of partial dislocations (Fig. 9a) dominates the strengthening mechanism in as-deposited Cu/Co system, as discussed previously [44]. However, after radiation, He bubbles at layer interfaces (as observed experimentally) significantly interfere with the transmission of partials, as He bubbles are typically over pressurized (at the current high He concentration) and are strong obstacles [30-32, 39], as shown in Fig. 9b. Consequently these partials may have to constrict to full dislocations (in Cu) before proceeding to the adjacent Co layers. In other words, He bubble decorated interface might become as strong as Cu/Ni interfaces, and only permit the transmission of full dislocations. Hence the interface barrier strength of irradiated Cu/Co should include constriction stress $\tau_{constriction}^*$, and friction stress due to the bubble-dislocation interaction τ_{bubble}^* , in addition to τ_k^* and τ_{ch}^* , as described in the following equation

$$\tau_{barrier}^* = \tau_k^* + \tau_{ch}^* + \tau_{constriction}^* + \tau_{bubble}^* \quad (2)$$

First we estimate constriction stress arising from high-pressure He bubbles decorated layer interfaces. The equilibrium separation distance r_e between partials dissociated from a full dislocation inclined at an angle β to its Burgers vector can be estimated as [59]

$$r_e = \frac{\mu b^2}{8\pi\gamma} \frac{2-\nu}{1-\nu} \left(1 - \frac{2\nu \cos 2\beta}{2-\nu} \right) \quad (3)$$

where ν is Poisson's ratio. Taking a full screw dislocation as an example, r_e can be estimated to be $9b$ (~ 2.2 nm for Cu). To avoid the cut-off problem in dislocation core in linear elasticity, MD simulation [60] was performed to investigate the dependence of constriction stress on partial separation distance in Cu, and the study showed a rapid increase of constriction stress with the decrease of partial separation distance. The equilibrium separation without stress from the simulation fits well to the value calculated by Eq. 3. With the increase of external applied stress to $0.0025\text{--}0.005\mu$, the partial separation distance reaches a separation of $\sim 5b$ (~ 1 nm for Cu, referring to Fig. 2 in [60]), below which the partials could act as full dislocations. Using a lower bound estimation, the constriction stress could reach 0.0025μ , corresponding to hardening by ~ 1 GPa, comparable to the magnitude of radiation hardening observed in irradiated Cu/Co when $h = 1 - 2.5$ nm.

Next, besides the constriction, we also consider strengthening due to He bubble-dislocation interactions. The contribution of He bubbles to radiation hardening is negligible at low He concentration ($< \sim 1\%$) and becomes significant with the increase of He concentration [61]. He bubbles are generally treated as weak obstacles for dislocation migration [31]. Friedel–Kroupa–Hirsch (FKH) model is widely used to describe weak obstacle induced strengthening ($\Delta\sigma$) [31, 62] by using

$$\Delta\sigma = \frac{1}{8} M \mu b d N^{2/3} \quad (4)$$

where M is the Taylor factor (~ 3.06), μ is the shear modulus (48 GPa for Cu), b is Burgers vector, d is the average bubble diameter (~ 1.2 nm), N is bubble density that can be obtained from TEM studies. **Note that the average diameter of He bubbles has little dependence on irradiation depth for various irradiated Cu/Co multilayers.** Using Eq. (4), we estimate the magnitude of He bubble induced yield strength increase to be ~ 0.05 GPa, corresponding to a hardness increase by ~ 0.15 GPa. Thus the magnitude of radiation hardening from partial constriction and He bubbles becomes ~ 1.2 GPa. Since the peak strength of as-deposited Cu/Ni is also controlled by constriction of dislocations (due to large SFE difference between Cu and Ni), the interface barrier strength of as-deposited Cu/Ni and irradiated Cu/Co becomes comparable.

(b) Strengthening mechanisms at large h ($h = 50 - 200$ nm)

Fig. 10 schematically illustrates different strengthening mechanisms in as-deposited and irradiated Cu/Co (100) multilayers at large h (50-200 nm). In as-deposited state, as interface is a weak barrier to partial dislocation transmission, the mechanical strength of multilayers is determined primarily by high-density SFs in Co (with an average spacing of a few nm). The inset dark field TEM micrograph shows a typical Co layer with high-density SFs.

After radiation, high-density He bubbles are distributed both along layer interfaces and within the layers **as evidenced by extensive TEM studies. Furthermore XRD studies show that He bubbles clearly distorted crystal structures of irradiated multilayers as indicated by prominent reduction of peak intensity.** The average bubble spacing (L) for Cu/Co 100 nm multilayer is ~ 9 nm ($L = 1/N^{1/3}$, where N is bubble density), larger than the average spacing between SFs. Hence

SFs in Co remain the primary defects that determine the peak strength of multilayers. It follows that the magnitude of radiation hardening in Cu/Co 200 nm multilayers is insignificant. Our previous studies show that when h reduces to tens of nm or less, the density of SFs also reduces significantly [44]. The magnitude of radiation hardening in Cu/Co 50 nm film is greater than that of Cu/Co 200 nm nanolayers, although the bubble density in Cu/Co 50 nm films is comparable to that of Cu/Co 200 nm. It is likely that He bubbles play increasing role in determining the strength of multilayers as the density of SFs reduces at smaller h . Consequently the magnitude of radiation hardening becomes prominent at smaller h .

Finally we notice that the Hall-Petch (H-P) slope (K_{HP}) of irradiated Cu/Co is similar to that of Cu/Ni, as He bubble decorated Cu/Co interfaces can effectively resist the pile-up of full dislocations. The H-P slope is related to the interface barrier strength (τ^*) via [63]:

$$K_{HP} = \sqrt{\tau^* \mu b / [\pi(1-\nu)]} \quad (5)$$

For Cu, using $\mu = 48$ GPa, $b = 0.25$ nm, and $\nu = 0.33$, we obtain τ^* of 0.6 GPa. Correspondingly the peak hardness (H) can be estimated as ~ 4.9 GPa for both as-deposited Cu/Ni and irradiated Cu/Co, which is very close to the experimentally measured values of ~ 5 GPa for both systems.

It is worth emphasizing that the radiation hardening phenomenon in Cu/Co is very different from what have been reported before. Although radiation hardening increases at smaller h , it does not necessarily indicate a dramatic degradation of mechanical properties. The large hardening at smaller layer thickness is mainly a consequence of the surprisingly low initial hardness of as-deposited films, due to the partial dislocation dominated deformation mechanism.

The layer interface in immiscible coherent Cu/Co system remain significant on alleviation of radiation damage as manifested by progressive reduction of He bubble density at smaller h .

Finally our previous dose dependent study on He ion irradiated incoherent Cu/V multilayers up to 18 dpa [32] shows superior stability of Cu/V interfaces and saturated radiation hardening at higher dose. The structural stability of interfaces and strengthening mechanisms in immiscible coherent Cu/Co multilayers subjected to much greater doses remain unclear and are interesting subjects for future studies.

Conclusions

We investigated He ion radiation response of immiscible coherent Cu/Co multilayer systems. Similar to incoherent interfaces in immiscible systems, the coherent interfaces can also effectively mitigate radiation damage in terms of reducing He bubble density in nanolayers with smaller h . Layer interfaces in Cu/Co are in general resistant to radiation induced intermixing.

In contrast to the major reported trend of reduced radiation hardening at smaller h in immiscible incoherent multilayers, the size dependent strengthening behavior in Cu/Co system is just the opposite, although the density of He bubble density is indeed lower at smaller h . Such a surprising observation was explained by a transition from partial transmission dominated strengthening mechanisms (before radiation) to full dislocation transmission dictated deformation behavior in immiscible Cu/Co nanolayers due to decoration of pressurized He bubbles at layer interface in irradiated multilayers.

Acknowledgement

XZ acknowledge financial support by NSF DMR-1304101. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Los Alamos National Laboratory, an affirmative action equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. Access to microscopy and imaging center (MIC) at Texas A&M University is also acknowledged.

References

- [1] Was GS. Springer Verlag, 2007.
- [2] Reed D. Radiation Effects (1977) 31:129.
- [3] Thomas G. Radiation Effects (1983) 78:37.
- [4] Lucas AA. Physica B+C (1984) 127:225.
- [5] Han WZ, Demkowicz MJ, Fu EG, Wang YQ, Misra A. Acta Mater. (2012) 60:6341.
- [6] Yu KY, Liu Y, Sun C, Wang H, Shao L, Fu EG, Zhang X. J. Nucl. Mater. (2012) 425:140.
- [7] Zhang X, Fu EG, Misra A, Demkowicz MJ. JOM (2010) 62:75.
- [8] Demkowicz MJ, Misra A, Caro A. Curr. Opin. Solid State Mater. Sci. (2012) 16:101.
- [9] Misra A, Demkowicz MJ, Zhang X, Hoagland RG. JOM (2007) 59:62.
- [10] Zhernenkova M, Jablin MS, Misra A, Nastasi M, Wang Y, Demkowicz MJ, Baldwin JK, Majewski J. Appl. Phys. Lett. (2011) 98:241913.
- [11] Kashinath A, Misra A, Demkowicz M. Phys. Rev. Lett. (2013) 110:086101.
- [12] Shao S, Wang J, Misra A, Hoagland RG. Sci. Rep. (2013) 3:2448.
- [13] Di Z, Bai X-M, Wei Q, Won J, Hoagland RG, Wang Y, Misra A, Uberuaga BP, Nastasi M. Phys. Rev. B (2011) 85:052101.
- [14] Klueh RL, Gelles DS, Jitsukawa S, Kimura A, Odette GR, van der Schaaf B, Victoria M. J. Nucl. Mater. (2002) 307–311:455.
- [15] Murty KL, Charit I. J. Nucl. Mater. (2008) 383:189.
- [16] Odette GR, Alinger MJ, Wirth BD. Annu. Rev. Mater. Res. (2008) 38:471.
- [17] Schaublin R, Ramar A, Baluc N, de Castro V, Monge MA, Leguey T, Schmid N, Bonjour C. J. Nucl. Mater. (2006) 351:247.
- [18] Ukai S, Fujiwara M. J. Nucl. Mater. (2002) 307–311:749.
- [19] Sun C, Song M, Yu KY, Chen Y, Kirk M, Li M, Wang H, Zhang X. Metall. Mater. Trans. A (2013) 44:1966.

- [20] Zhang X, Fu EG, Li N, Misra A, Wang Y-Q, Shao L, Wang H. J. Eng. Mater. Technol. (2012) 134:041010.
- [21] Singh BN. Philos. Mag. (1974) 29:25.
- [22] Singh BN, Foreman AJE. Philos. Mag. (1974) 29:847.
- [23] Bai X-M, Voter AF, Hoagland RG, Nastasi M, Uberuaga BP. Science (2010) 327:1631.
- [24] Chen D, Wang J, Chen T, Shao L. Sci. Rep. (2013) 3:1450.
- [25] Yu KY, Bufford D, Sun C, Liu Y, Wang H, Kirk M, Li M, Zhang X. Nat. Commun. (2013) 4:1377.
- [26] Yu KY, Bufford D, Khatkhatay F, Wang H, Kirk MA, Zhang X. Scripta Mater. (2013) 69:385.
- [27] Bringa EM, Monk JD, Caro A, Misra A, Zepeda-Ruiz L, Duchaineau M, Abraham F, Nastasi M, Picraux ST, Wang YQ, Farkas D. Nano Letters (2011) 12:3351.
- [28] Fu EG, Caro M, Zepeda-Ruiz LA, Wang YQ, Baldwin K, Bringa E, Nastasi M, Caro A. Appl. Phys. Lett. (2012) 101:191607.
- [29] Sun C, Bufford D, Chen Y, Kirk M, Wang Y, Li M, Wang H, Maloy S, Zhang X. Sci. Rep. (2014) 4:3737.
- [30] Fu EG, Carter J, Swadener G, Misra A, Shao L, Wang H, Zhang X. J. Nucl. Mater. (2009) 385:629.
- [31] Fu EG, Misra A, Wang H, Shao L, Zhang X. J. Nucl. Mater. (2010) 407:178.
- [32] Fu EG, Wang H, Carter J, Shao L, Wang YQ, Zhang X. Philos. Mag. (2013) 93:883.
- [33] Li N, Carter JJ, Misra A, Shao L, Wang H, Zhang X. Philos. Mag. Lett. (2010) 91:18.
- [34] Gao Y, Yang T, Xue J, Yan S, Zhou S, Wang Y, Kwok DTK, Chu PK, Zhang Y. J. Nucl. Mater. (2011) 413:11.
- [35] Li N, Martin MS, Anderoglu O, Misra A, Shao L, Wang H, Zhang X. J. Appl. Phys. (2009) 105:123522.
- [36] Wei QM, Li N, Mara N, Nastasi M, Misra A. Acta Mater. (2011) 59:6331.
- [37] Wei QM, Wang YQ, Nastasi M, Misra A. Philos. Mag. (2010) 91:553.
- [38] Heinisch HL, Gao F, Kurtz RJ. J. Nucl. Mater. (2004) 329–333:924.
- [39] Yu KY, Liu Y, Fu EG, Wang YQ, Myers MT, Wang H, Shao L, Zhang X. J. Nucl. Mater. (2013) 440:310.
- [40] Yu KY, Sun C, Chen Y, Liu Y, Wang H, Kirk MA, Li M, Zhang X. Philos. Mag. (2013) 93:3547.
- [41] Li N, Fu EG, Wang H, Carter JJ, Shao L, Maloy SA, Misra A, Zhang X. J. Nucl. Mater. (2009) 389:233.
- [42] Setyawan W, Gerboth M, Yao B, Henager CH, Devaraj A, Vemuri VRSR, Thevuthasan S, Shutthanandan V. J. Nucl. Mater. (2014) 445:261.
- [43] Li N, Nastasi M, Misra A. Int. J. Plast. (2012) 32:1.
- [44] Liu Y, Chen Y, Yu KY, Wang H, Chen J, Zhang X. Int. J. Plast. (2013) 49:152.
- [45] Liu Y, Bufford D, Wang H, Sun C, Zhang X. Acta Mater. (2011) 59:1924.
- [46] Oliver WC, Pharr GM. J. Mater. Res. (1992) 7:1564.
- [47] Egerton RF. Springer, 2011.
- [48] Nastasi M. Cambridge University Press, 1996.
- [49] Ziegler JF, Biersack JP. Calculation using the Stopping and Range of Ions in Matter (SRIM) Code. <<http://www.srim.org/>>. (2008).
- [50] Stoller RE, Toloczko MB, Was GS, Certain AG, Dwaraknath S, Garner FA. Nucl. Instrum. Methods Phys. Res., Sect. B (2013) 310:75.
- [51] Wonnell SK, Delage JM, Bibol M, Limoge Y. J. Appl. Phys. (1992) 72:5195.
- [52] Bufford D, Bi Z, Jia QX, Wang H, Zhang X. Appl. Phys. Lett. (2012) 101:223112.
- [53] Bufford D, Liu Y, Zhu Y, Bi Z, Jia QX, Wang H, Zhang X. Mater. Res. Lett. (2013) 1:51.
- [54] Baibich MN, Broto JM, Fert A, Van Dau FN, Petroff F, Eitenne P, Creuzet G, Friederich A, Chazelas J. Phys. Rev. Lett. (1988) 61:2472.
- [55] Brandt W, Khan JM, Potter DL, Worley RD, Smith HP. Phys. Rev. Lett. (1965) 14:42.

- [56] Datz S, Noggle TS, Moak CD. Nuclear Instruments and Methods (1965) 38:221.
- [57] Tabor D. Oxford university press, 2000.
- [58] Mata M, Anglada M, Alcalá J. J. Mater. Res. (2002) 17:964.
- [59] Hirth JP, Lothe J. New York: Wiley, 1982.
- [60] Duesbery MS. Modelling Simul. Mater. Sci. Eng. (1998) 6:35.
- [61] Ullmaier H, Camus E. J. Nucl. Mater. (1997) 251:262.
- [62] Kroupa F, Hirsch PB. Discuss. Faraday Soc. (1964) 38:49.
- [63] Anderson PM, Foecke T, Hazzledine PM. MRS Bulletin (1999) 24:27.

Figure captions

Fig.1. The depth profile of He ion radiation damage in unit of displacements per atom (dpa) and helium concentration obtained from SRIM simulation (using the Kinchin-Pease option) of $\text{Cu}_{50}\text{Co}_{50}$ compound subjected to He ion irradiation at 100 keV with a total fluence of 6×10^{20} ions/m². The peak damage approaches ~ 2.5 dpa at 300 nm from surface, and the projected ion penetration depth is ~ 500 nm.

Fig.2. X-ray diffraction (XRD) patterns of as-deposited (AD) and He ion irradiated Cu/Co multilayers with various individual layer thickness h . (a) $h = 10 - 100$ nm and (b) $h = 1 - 5$ nm. For as-deposited films, when $h \geq 5$ nm, only Cu (200) and face-centered cubic (FCC) Co (200) peaks were detected. Further decrease of h led to a fully coherent peak located between Cu (200) and Co (200). Satellite peaks appeared when $h \leq 10$ nm. After radiation, the intensity of all diffraction peaks decreased. When $h \leq 5$ nm, the coherent peak became broader after radiation. No hexagonal closely packed (HCP) Co peaks were detected both before and after radiation.

Fig. 3. TEM images of as-deposited (100) Cu/Co multilayers. (a) High density of inclined stacking faults (SFs) were observed in Co in Cu/Co 100 nm multilayer. (b) In Cu/Co 10 nm multilayers, SFs were observed occasionally in Co layers. (c-d) No SFs appeared in Cu/Co 2.5 nm and Cu/Co 1 nm multilayer films. No bubbles or little dislocation loops were detected in any as-deposited Cu/Co multilayers.

Fig. 4. Cross-section TEM (XTEM) images of He ion irradiated Cu/Co 100 nm multilayer. (a) Overview of the irradiated multilayer at low magnification. The superimposed solid curve shows the depth profile of He concentration calculated by SRIM. The embedded selected area diffraction (SAD) pattern of irradiated region confirmed the film retained single-crystal like FCC Cu and Co phase. The boxes b-e at different penetration depths are shown at higher magnification in the succeeding figures. (b) Bubbles were observed with random distribution. (c) and (d) show high-density bubbles observed in Cu and Co layers, respectively. (e) In location e, fewer He bubbles were observed in Co layer.

Fig. 5. XTEM images of irradiated Cu/Co 5 nm multilayer. (a) In the peak damage region, He bubbles were distributed both within the layers and along layer interfaces. (b) In a region deeper than maximum radiation damage, clear alignment of He bubbles along layer interfaces was observed. The embedded SAD pattern shows the film retained epitaxial structure with fully coherent Cu/FCC Co stacking. (c1-c2) A typical irradiated region captured at underfocus (c1) and overfocus (c2) conditions confirmed the alignment of He bubbles at interfaces. Bubbles appeared as white (dark) dots in underfocus (overfocus) condition.

Fig. 6. XTEM images of He ion irradiated Cu/Co 1 nm multilayer. (a) A panoramic view of the irradiated specimen incorporating the depth dependent profile of He concentration calculated by SRIM simulation. The embedded SAD pattern of the irradiated region confirmed the retention of

epitaxial Cu/Co crystal structure. The boxes b-d at different penetration depths are shown at higher magnifications. (b) Close to the surface of irradiated specimens, He bubbles were randomly distributed with barely discernable layer interfaces. (c) High-density bubbles were observed in box c in peak damage region in absence of layer structures. (d) Layered structure can be distinguished with few He bubbles at the end of the irradiated region.

Fig. 7. Comparison of the evolution of He bubble density along penetration depth in several Cu/Co multilayers. The peak damage region in irradiated Cu/Co 100 and 50 nm coincides with the calculated peak of He concentration profile (the dash line), while penetration depth is somewhat deeper in irradiated Cu/Co 5 and 1 nm multilayers. The overall penetration depths in all specimens are beyond calculated damage region. The peak He bubble density in Cu/Co 5 and 1 nm is ~ 60% of that in Cu/Co 100 and 50 nm counterparts.

Fig. 8. (a) A typical load-displacement curve with the maximum indentation depth of ~ 150 nm for He ion irradiated Cu/Co 5 nm multilayer is displayed, which is adopted to calculate indentation hardness at a specific depth of the film. (b) The average indentation hardness is determined when hardness value reaches a plateau, nearly independent of indentation depth. (c) Comparison of hardnesses of as-deposited and irradiated Cu/Co multilayers as a function of $h^{-1/2}$. The hardness of as-deposited Cu/Ni (100) [45] is also provided for comparison. After radiation, radiation hardening is prominent in Cu/Co multilayers, and the Hall-Petch slope (when $h = 50 - 200$ nm) increases significantly to a value close to that of as-deposited Cu/Ni (100). The peak hardness of Cu/Co increases from ~3.8 to 5 GPa after radiation, comparable to the peak hardness of as-deposited Cu/Ni (100). (d) Inverse size dependent radiation hardening in Cu/Co. The magnitude of radiation hardening is greater at smaller h . In contrast, radiation hardening in

irradiated Ag/Ni [39], Ag/V [36], Cu/V [31] with immiscible incoherent interfaces have opposite size dependence, that is the smaller the h , the less the radiation hardening.

Fig. 9. Hypothetical schematics illustrate strengthening mechanisms in as-deposited and irradiated Cu/Co (100) multilayers at small h ($h = 5$ nm). (a1-a2) In as-deposited films, partials can trespass layer interfaces due to low stacking fault energy of Cu and Co. (b1-b2) However, after radiation, bubbles at layer interface disrupt the transmission of partials. Consequently these partials may have to constrict to full dislocation before proceeding to the adjacent layers. Thus a stronger layer interface arising from He bubbles leads to prominently enhanced radiation hardening.

Fig. 10. Hypothetical schematics illustrate different strengthening mechanisms in as-deposited and irradiated Cu/Co (100) multilayers at large h ($h = 50-200$ nm). (a) In as-deposited state, partial dislocations can transmit across the Cu/Co interface relatively easily, in other words, interface is a weak barrier for dislocation transmission. The mechanical strength of as-deposited multilayers with large h is determined primarily by high-density stacking faults in Co with an average spacing of a few nm. The inset TEM figure shows a typical Co layer with high-density stacking faults. (b) After radiation, high-density He bubbles are distributed both along the layer interface and within the layers. Consequently partials may be constricted into full dislocations within layers. The He bubble modified layer interface thus becomes stronger barrier against the pile-up of full dislocations.

Fig2a-XRD

Fig2b-XRD

Fig4-CuCo-100 nm

Fig5-CuCo-5 nm

Fig6-CuCo-1 nm

Fig7-bubble density

Fig8a--load-displacement curve

Fig8b--determining hardness

Fig8c-hardness data

Fig8d-radiation hardening

Fig9-schematic-small h

as-deposited: partial transmission

apply stress

irradiated: partial constriction

Fig10-schematic-large h