FINAL PROGRESS REPORT

Project title: Development of Nanostructured Materials with Improved Radiation Tolerance for Advanced Nuclear Systems

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Recipient: Texas Engineering Experiment Station

Address: Texas Engineering Experiment Station
TEES Research Services
006 WERC, Mail Stop 3406 TAMU
College Station, TX 77843-3406
Tel: 979-845-1264
Fax: 979-845-9643
URL: trsweb.tamu.edu

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Contact(s):

Principal Investigator: Xinghang Zhang, 979-845-2143 (O), zhangx@tamu.edu

Co-PI: K. Ted Hartwig, 979-845-1585 (O), thartwig@tamu.edu

1. Project Objective:

This project will explore the fundamental mechanisms through which interfaces in nanolayered structures and grain boundaries of bulk nanomaterials are able to attract and rapidly eliminate point defects and unwanted foreign species. Candidate materials that will be studied include both nanostructured multilayer composites synthesized by magnetron sputtering (a bottom-up approach) and structural bulk nanomaterials produced by severe plastic deformation, equal channel angular extrusion (a top-down approach).

This project will have profound and broad impact on the understanding of the fundamental science of improving radiation resistance by inducing interfaces and grain boundaries in nanomaterials and by designing and engineering structural nanomaterials for advanced nuclear reactors. Data from this study will be used for estimating defect capture rates and lifetimes of multilayered structures and bulk nanomaterials in conditions that would seriously degrade conventional microstructures. Researchers expect this project to benefit a broad spectrum of DOE programs associated with fission technology research and development.

2. Background:

The goal of the project is to explore the fundamental mechanisms whereby interfaces in nanolayered structures and grain boundaries of bulk nanomaterials attract and rapidly eliminate point defects and unwanted foreign species. In the proposal, the candidate materials to be studied include nanostructured multilayer composites synthesized by magnetron sputtering, a bottom-up approach, and structural bulk nanomaterials produced by severe plastic deformation - equal channel angular pressing (ECAP), a top down approach. The materials to be processed by ECAP will be HT-9 alloy, T91, EP-823, 304 and 316L stainless steels. HT-9 has shown certain irradiation tolerance during neutron radiation tests, whereas 316L stainless steel is one of the most popular structural materials that could potentially be used as the wall materials for nuclear reactors. The nanolayer coatings to be studied include Fe/W, Al/Nb, Cu/Nb and Cu/V multilayers. Fe/W has a high melting point and body centered cubic (bcc) structure that could enable good radiation tolerance at higher temperature. Al/Nb could possess good corrosion resistance as well as radiation tolerance at moderate temperature, a few hundred degrees centigrade. Cu/Nb and Cu/V are both immiscible systems. The two components in each

multilayer system have positive heat of mixing and therefore possess high temperature stabilities. The status report will describe our efforts following the two approaches.

3. Project progress

3. 1. ECAP processed alloys

3.1.1. ECAP processing of ferritic T91 alloys

Processing of ferritic/martensitic steels using ECAP has never been done before. The relatively high strength of these materials makes ECAP processes very challenging. The unique high temperature processing capability at TAMU provide us great opportunities in tailoring the microstructure of these materials. Using equal channel angular pressing (ECAP) we have processed a series of alloys (bulk 304, 316L stainless steel, HT-9 alloys, 9Cr-1Mo steel, and EP823) received from Dr. Stuart Maloy at Los Alamos National Laboratory (LANL)). Processing conditions are summarized in Table 1. Some of these materials are very special (such as HT-9, 9Cr-1Mo, EP823) and are only available through limited resources, such as LANL. Some of these as processed specimens (316L SS and HT-9 alloy) were sent to Drs. Stuart Maloy and Ning Li for radiation studies. They performed annealing studies on these as-processed materials to obtain thermal stability of these materials. Preliminary studies have shown that as-processed 316L and HT-9 have hardness much higher than unprocessed specimens. Some of these specimens were sent to synchrotron irradiation facility in Switzerland to perform high dose, year-long irradiation tests in 2005. One of the focuses is to evaluate the influence of fine microstructures (small grain sizes) on radiation tolerance of these materials. Dr. Maloy will communicate with Switzerland to get the test results.

Table 1. Summary of processing conditions using equal channel angular pressing (ECAP).

<i>Specimen</i>	<i>Pass/Route</i>	<i>Processing temperature (°C)</i>
304 Stainless steel	1B	300
304 Stainless steel	2B	300
EP823	not processed	
316L stainless steel	1A	700
9Cr-1Mo	1B	700
9Cr-1Mo	2B	600

The microstructures of as processed T91 alloys have been characterized using a transmission electron microscope (TEM). The grain size of T91 has been reduced from a few micron in the as-received alloy to around 300 nm after ECAP processing. An example of such fine microstructure is shown in Fig. 1. Besides fine grain sizes, dislocations walls were also observed in these grains.

Fig. 1 (a)

Fig. 1(b)

Fig.1. TEM micrograph of T91 alloys processed at 700°C for 2 passes. The average grain size has been refined dramatically down to $\sim 250\text{nm}$ with a large increase in dislocation density. (a) Bright field TEM (b) corresponding dark field TEM micrographs.

The hardnesses of T91 alloys measured using Fischerscope 2000 XYp are plotted as a function of $d^{-1/2}$, (d is the average grain sizes as shown in Fig. 2. Hardness increases from about 2.5 GPa (as-received) to about 4 GPa after ECAP processes. A linear fit of the experimental data indicates that the hardening in ECAP processed T91 is dominated by grain boundary mediated dislocation activities, or typically known as Hall-Petch model that describes strengthening due to dislocation pile-ups within grains.

Fig.2. Indentation hardness (H_{IT}) plotted vs. $d^{-0.5}$, where d is the average grain size of T91 alloys. A linear increase of H_{IT} with $d^{-0.5}$ indicates that the strengthening is primarily attributed to Hall-Petch dislocation pile-up mechanism.

3.1.2. ECAP processing of martensitic T91 alloys

We have recently processed another batch of bulk T91 alloys with martensitic structures. Extrusions temperatures were varied from 500 to 700°C in an attempt to study the influence of extrusion temperature on the refinement of microstructures. Most of these materials were extruded by 1 pass, with several extruded to 3 passes. The total strain, accumulated during extrusion experiments, will be increased by increasing the number of extrusion pass. It is known that greater extrusion strain typically lead to the refinement of microstructure. We provide two examples on the extruded specimens in this report.

Bulk T91 LA1 (hardness = 250 HV for as-received materials) alloys were annealed for one hour at 1050°C and ECAP processed in nickel cans for 1 pass at 700°C and 2B at 600°C. The T91 sample dimension was significantly larger than the initial set of extruded T91 alloys in Fall 2005, allowing for more complete examination. Samples for TEM, microhardness/annealing, ion implantation and tensile testing were extracted via wire electro-discharge-machining (EDM). Microhardness was analyzed on a Fischerscope 2000 XYP at a load of 200 grams with depth resolution of 1nm. Tensile tests were conducted on an MTS machine at 0.04 in/min. XRD was performed on a Bruker-AXS D8. Microstructures were analyzed using a JEOL 2010 TEM operated at 200 kV. Annealing for some specimens was performed for one hour in a low 10^{-6} torr vacuum tube furnace and vacuum cooled, unless otherwise noted.

XRD examination revealed no phase changes in the material and peak broadening is not sufficient for grain refinement estimation. Bulk T91 LA1 (hardness = 250 HV for as-received materials) was annealed for one hour at 1050°C and ECAP processed in nickel cans for 1 pass at 700°C (700 °C / 1 pass), and 2B at 600°C (600 °C / 2 pass). The microstructure of LA1 1050°C annealed specimen is given in Fig. 3a. After annealing and rapid cooling, the specimen transformed almost completely into martensites, indicated by 200 nm or so platelets, with highly texture as shown by inserted diffraction pattern. ECAP processing of this specimen at 700°C has an effect of both extrusion and tempering. As a result the average grain size seems to be larger, ~1µm, and martensite seems to transform to ferrite during processing, as shown in Fig. 3b. Specimens (LA1 1050 °C annealed) processed via ECAP at 600 °C has much smaller average grain size, ~300nm, as shown in Fig. 3b. In this case martensite has been transformed to ferrite during tempering, followed by significant grain refinement due to extrusion, as shown in Fig. 3c.

Figure 3. TEM micrographs of T91 alloys. (a) LA1 1050 °C annealed specimens (b) LA1 1050 °C annealed specimens followed by ECAP processing at 700°C/1pass. (c) LA1 1050 °C annealed specimens followed by ECAP processing at 600°C/2passes.

Microhardness - LA1 R2

Figure 4. Vickers hardness of as-received, 1050°C annealed, and ECAP processed T91 alloys. LA1 and LA2 stands for specimens received in September 2005 and summer 2006, respectively. Red data points are obtained from this study of ECAP processed 1050°C pre-annealed LA1 alloys.

Hardening due to grain refinement has been systematically studied in LA1 specimens. Hardness increase after annealing of LA1 specimens at 1050 °C, as shown in Fig. 4, is due to the formation of martensite after cooling of austenized T91 alloys. Very fine martensite precipitates may have been performed and will be examined in details via high resolution TEM experiments. The high hardness of as-received LA2 T91 alloys is presumably due to the same reason.

Tensile testing was performed on T91 coupons in order to obtain a more detailed mechanical behavior data set. The results are presented in Figure 5. Note the unusual necking behavior in the annealed sample. In general the variation of yield strength and ultimate tensile strength with processing (annealing) condition is very consistent with the variation of specimen hardness. Specimens with higher hardness have higher yield and ultimate tensile strength. It is worthwhile to point out that ECAP processed LA1 specimens at 600°C has a combination of high strength and considerable ductility.

Fig. 5. Comparison of tensile properties of T91 alloys processed at various conditions subjected to uniaxial tensile test.

Fracture surfaces of tensile specimens were examined by SEM. The as-received material, shown in Figure 6, has river patterns indicating ductility is conserved in specimens. Sharp edges

and clear outlines of many elongated features also indicate that inter granular fracture may have occurred and could be related to the limited ductility of as-received specimens.

Figure 6. SEM micrograph of tensile fracture surface of as-received T91 alloy. River pattern indicates that specimen have certain ductility. Clear edges that outline the granular features indicate intergranular type of fractures and could be the major reason for limited ductility.

Fracture surface of ECAE process specimens, Fig. 7a, shows a more complicated morphology. Many pits, 5-10 micron in diameter, are observed probably because of pulling out of materials during tests. Magnified SEM micrograph, Fig. 7b, shows spheres, 2-5 micron in diameter visible in most of the pits. Surrounding regions typically are filled with ductile dimples with dimension of 1 micron or less. EDS did not reveal obvious compositional difference between these spheres and the surrounding material. We will attempt to use WDS to quantify the phase of these spheres.

Figure 7. SEM micrograph of tensile fracture surface of ECAE processed T91 alloy. (a) Low magnification SEM micrograph shows large number of pits, 5-10 micron in diameter. (b) Spheres, 2-5 micron in diameters are typically observed in these pits. Ductile dimples at much smaller length scale (1 micron or less) are observed in surrounding regions.

In order to study the thermal stability of this material, annealing was carried out under 10^{-6} torr vacuum for one hour followed by vacuum cooling. Microhardnesses of annealed samples are summarized in Figure 8. The general trend is clear, i.e. hardness decreases after annealing at around 700°C due to tempering of martensite precipitates.

Thermal Stability

Figure 8. One hour vacuum annealing study of LA1 as-received (AR), 1050°C anneal/ECAP 1A 700C, 1050°C/ECAP 2B 600C, re-annealed 1050°C, and annealed LA2 AR specimens.

Some of these ECAP processed specimens have been test corrosion resistance studies by Dr. Ning Li in Delta loop at LANL. Delta loop simulates environment similar to Pb-Bi cooled reactor. Two types of specimens for corrosion tests are prepared as follows. In the first case, specimens with fine microstructure and high hardness (after ECAP process) are first selected. Second, these specimens were cut into rectangular coupons with dimensions appropriate for corrosion test. These specimens were then polished on both sides with 50 nm colloidal silica. Finally either metallic multilayer films (2 micron in thickness) or approximately 100-200 nm TiN coatings were deposited on both sides of the coupons with a mask so that only the center portion of the coupons is coated with TiN. In the second case, no TiN coatings were applied on ECAP processed specimens. Such studies have two purposes: (i) influence of ECAP processing on corrosion resistance of T91 alloys; and (ii) the influence of TiN coatings on ECAP processed T91 specimens. Preliminary studies have shown that ECAP processed T91 have improved radiation and corrosion resistance, and TiN coating as well as several metallic multilayer coatings have improved corrosion resistance of such an alloy. Some of these processed materials

will be implanted with He ions at Los Alamos National Laboratory in collaboration with Dr. J. G. Swadener and Ion Beam Materials Laboratory at LANL.

3.1.3. Radiation damage in ECAP processed martensitic T91 alloys

We have performed a series of He ion irradiation studies on ECAP processed T91 alloys by using ion irradiation facilities in Dr. Lin Shao's laboratory at Texas A&M University. Radiation dose was 7×10^{16} ions/cm² at 140 keV, producing a peak dose of 5 dpa at 650 nm according to SRIM calculations.

After ECAP processing of ferritic T91 alloys, the average grain size has been refined by an order of magnitude, from a few micron in as-received alloys down to ~ 300 nm in 2B 300 and 2B 700 specimens. To investigate the influence of radiation hardening, we performed nanoindentation measurement before and after radiation experiments. Hardness measurements were performed at 350 nm depth as shown in Figure 9.

Figure 9. Hardness of T91 alloys before and after He⁺ ion implantation. Ferritic starting material is in dark blue, martensitic is light blue. Corresponding implanted material is red and orange. The meaning of symbols is illustrated in Table 1.

The values indicate a clear trend in the ferritic material, with a smaller increase in hardness for the fine-grained 2B700 and 2B300 material compared to the as-received T91 alloys. Radiation also induced hardening in martensitic steels. Specifically, radiation induced hardening is suppressed in ECAP processed T91 alloys with fine microstructures, as shown in Fig. 10. We are performing more detailed microstructure analysis to examine radiated specimens.

These preliminary studies seem to indicate that additional boundaries added to the ferritic material after ECAP processing may act successfully as defect sink. We will perform detailed transmission electron microscopy (TEM) studies on radiated T91 alloys to examine the evolution of microstructure post radiation. These studies will help us to understand the influence of grain boundaries density on radiation damage.

Also more ion irradiation experiments are in progress to check reproducibility of data. Additionally we have prepared numerous ECAPed T91 specimens precutted into dog-bone shapes (by EDM) for long term radiation experiments (Matrix II in France), in collaboration with Dr. Stuart Maloy and Ning Li at Los Alamos National Laboratory.

Fig.10. Hardness increase after He ion implantation of T91 alloys for the following LA1 specimens, including as-received, heat treated at 1050 °C for one hour and vacuum cooled, ECAP/700 °C /1 pass, and ECAP/600 °C /2 pass.

T91 specimens have been subjected to SCW reactor environment for corrosion studies in collaborations with Dr. Todd Allen at University of Wisconsin, Madison. As can be seen in

Figure 11, ECAP processed T91 samples have the best corrosion resistance among all specimens (including those as-received and T91 prepared by shot peening). Additional samples, including LA1 and LA2 material, are now undergoing long-term corrosion testing at SCW reactor at U. Wisconsin. Microstructure and homogeneity of specimens may play an important role to enhance corrosion resistance of T91 alloys. We are performing detailed microscopy, and chemical analysis to understand the fundamental mechanisms of enhanced corrosion resistance by ECAP processing in collaboration with Dr. Todd Allen.

Fig.11. Comparisons of weight gain after corrosion test in SCW reactors at University of Wisconsin, Madison (in collaboration with Dr. Todd Allen). Green upper triangle – as received T91 specimen from TAMU; red circles – shot peened T91 alloys; blue down-triangle- as received T91 from U Wisconsin, Madison; black square – ECAP processed T91 (from TAMU). The comparisons shows that T91 alloys processed by ECAP processing seem to have improved corrosion resistance compared to as-received states. Compare to degradation of corrosion resistance after shot peening, ECAP processing seem to be a promising route to improve corrosion resistance of T91 alloys.

3. 2. Nanolayered metallic thin films and coatings.

In this section we will discuss ion irradiation studies of several metallic multilayer systems, including Cu/Nb, Cu/V, Al/Nb and Fe/W. In general all multilayers were DC sputter deposited at room temperature on Si (100) substrates that have a native SiO₂ layer. The sputter chamber was evacuated to a base pressure of $\leq 5 \times 10^{-8}$ torr prior to deposition. The constituent layers within

the multilayers had equal thicknesses, which were varied from 1 to 500 nm, and the number of bilayers deposited was such that the total multilayer film thickness was $\approx 2 \mu\text{m}$. The deposition rate is typically $\sim 0.5 \text{ nm/sec}$ for specimens with all layer thicknesses.

3.2.1. Evolution of microstructure of immiscible Cu/Nb multilayers.

Cu/Nb multilayers with equal Cu and Nb layer thicknesses varying from 2.5 nm to 100 nm each layer were synthesized by dc magnetron sputtering technique. After deposition, 500 nm thick Cu films and Cu/Nb 4nm multilayers with a total film thickness of 240 nm were implanted at room temperature by 33 keV He^+ ions with a dose of $6 \times 10^{16}/\text{cm}^2$, whereas annealed 1 mm thick Cu sheet, Cu/Nb2.5nm and Cu/Nb 100nm multilayers with a total film thickness of around 500-600nm were implanted by 150 keV He^+ ions with a dose of $1 \times 10^{17}/\text{cm}^2$. Evolution of microstructures before and after ion irradiation was examined by cross-section transmission electron microscopy (XTEM). TEM and high resolution TEM (HRTEM) were performed on a JEOL 3000F microscopes operated at 300kV.

SRIM calculation of He ion irradiation has been performed on Cu/Nb multilayers with a nominal layer thickness of 80 nm each layer. Three ion irradiation conditions have been used to compare the distribution of He in films using simulation. In the first case, irradiation was simulated at 33keV He^+ ions with a dose of $1.5 \times 10^{17}/\text{cm}^2$, representing ion irradiation experiments done recently in Cu/Nb multilayers. In the second case, irradiation was simulated for He^+ ions at 33keV with a dose of $6 \times 10^{16}/\text{cm}^2$. In the last case, simulation was carried out for He^+ ions at 150keV with a dose of $1 \times 10^{17}/\text{cm}^2$. The simulation parameters for the last two cases are the same as experimental conditions in this study. Figure 12 shows the variation of He concentration vs. implantation depth. The He ion peak concentration for the first case is about three times higher than that of the last two cases. The simulation predicts that implantation in the last two cases will produce similar He peak concentration, whereas the He ion peak occurs much deeper under film surface, $\sim 425\text{nm}$, at 150keV, compared to $\sim 150 \text{ nm}$ under film surface radiated at 33keV. Implantation of the first two experiments will generate He peak concentration at similar depth under film surface due to the usage of same implantation energy (33keV).

Fig. 12. SRIM calculations that simulate the variation of He concentration vs irradiation depth at various irradiation conditions.

Ion irradiated specimens were examined by XTEM. Bulk Cu sheet metal and Cu films irradiated using He ions (150keV at a dose of $1 \times 10^{17}/\text{cm}^2$) were shown in Fig. 13a and 13b. Radiations induce vacancy clusters, interstitial loops and He bubbles, typically observed in bulk metals. He bubbles with diameter on the order of 2-3 nm were observed in 500nm thick Cu films irradiated with 33keV He ions at a dose of $6 \times 10^{16}/\text{cm}^2$.

Fig. 13. XTEM micrograph of bulk Cu sheet ion irradiated with He ions of 150 keV at a dose of $1 \times 10^{17}/\text{cm}^2$ (a), and 33keV with a dose of $6 \times 10^{16}/\text{cm}^2$ (b). Vacancy clusters, interstitial loops and He bubbles were observed in (a) and mostly He bubbles with approximately 2-3 nm in diameter were seen in (b).

We also examined the microstructure of Cu100/Nb100nm multilayers (600 nm total film thickness) ion irradiated using He ions at 150keV with a dose of $1 \times 10^{17}/\text{cm}^2$, as shown in Fig. 14a. A magnified image of the box in Fig. 14a is shown in Fig. 14b. The selected region is expected to have peak He concentration as indicated by SRIM calculation (Fig. 12). Helium bubbles were observed in both Cu and Nb layers and their concentration seems to be higher along layer interface as indicated by dense packing of He bubbles along interfaces. Defocusing technique was used in TEM experiments to reveal irradiated induced He bubbles. Figure 14c shows a defocused HRTEM micrograph of ion irradiated Cu100/Nb100nm films. He bubbles with approximately 1nm in diameter were seen along layer interfaces and in Cu and Nb layers.

Fig. 14. (a) Low magnification XTEM micrograph of Cu100/Nb100 nm multilayer films ion irradiated with He ions at 150keV with a dose of $1 \times 10^{17}/\text{cm}^2$. (b) Magnified image (small box in Fig. 14a) shows a large number of He bubbles in Cu and Nb layers with a larger bubble concentration along layer interfaces. (c) Defocused HRTEM micrograph of Cu/Nb interfaces indicated He bubbles in each constituent has approximately 1-2 nm in diameter and aligned along interface.

He ion irradiation experiments at the same condition (150keV with a dose of $1 \times 10^{17}/\text{cm}^2$) were performed in Cu2.5/Nb2.5 nm multilayer films. Surprisingly such irradiation conditions did not seem to generate He bubbles in this case as shown in Fig. 15. A series of defocus conditions were used without detection of He bubbles in these multilayer films. Furthermore the layer structure remains unchanged after irradiations. Similar phenomena have been observed in Cu4/Nb4 nm multilayer films irradiated with 33 keV He ions with a dose of $6 \times 10^{16}/\text{cm}^2$.

In previous experiments, He bubbles have been observed in Cu4/Nb 4nm multilayer films irradiated with $1.5 \times 10^{17}/\text{cm}^2$ He ions at 33 keV, and a measured peak He concentration of 13-21at%. Peak Helium concentrations in current experiment approach 7at% in Nb and 5at% in Cu, much lower than that in previous experiments. Furthermore as a result of collision cascade, He ions will produce approximated 6-9 dpa in Cu and/or Nb at peak He concentration. The number of vacancies produced by collision cascade is a lot lower than that produced in the previous experiments (with a total of around 50 dpa at peak He concentration).

Fig. 15. Cu2.5/Nb2.5 nm multilayer films subjected to He ion irradiation at 150keV with a dose of $1 \times 10^{17}/\text{cm}^2$. No He bubbles were detectable. Microstructure remains unchanged, i.e. layer interfaces is still continuous and Cu and Nb are unmixed, after ion irradiation.

The irradiation conditions in current experiment will still produce a large number of He bubbles in both single layer Cu (Fig. 13) and Nb (not shown here) films. However, He bubbles were not seen in multilayer films with small layer thickness on the order of a few nm. Our MD simulation has shown that collision cascade produced vacancies and interstitials will be attracted to Cu/Nb interface. Due to a large excess free volume of interface (grain boundaries) and higher

diffusivity for defects along interfaces, vacancy and interstitials have a probability to recombine with each other after being attracted to interfaces. Such recombination if occurs could reduce the probability for the formation of vacancy cluster that could host He ion in multilayer films with a few nm layer thickness.

Furthermore He has a higher diffusivity along grain boundaries, interfaces and dislocations. Such characteristics will reduce He concentration in the center of Cu and Nb in multilayer films even further. The amount of He is therefore diluted when the area density of interfaces is very high as in the case of Cu/Nb multilayers with a few nm layer thickness. Such low He concentration may be below the threshold for the nucleation of He bubbles in Cu/Nb multilayer films with a few nm layer thickness. On the other hand, vacancies and interstitials formed away from interfaces will have a much lower probability of recombination. Therefore the vacancies have a large opportunity to aggregate and form bubbles that will trap He ions. The influence of layer thickness on suppressing the formation of He bubbles will be much less in thicker multilayer films. As a result He bubbles were seen in Cu/Nb 100nm multilayer films. The small He bubbles with around 1 nm in diameter is likely to be attracted to layer interface due to the interaction of stress field between interface and that originated along He bubbles. It is worthwhile to point out that even at the finest layer thickness of 2.5 nm, no obvious layer intermixing was observed in Cu/Nb multilayers contrary to the predicted 10 nm mixing zone using SRIM calculation for the current experiment. The present studies reveal that Cu/Nb multilayer films with a few nm layer thickness have remarkable He and defect storage capabilities compared to their bulk counterparts. The size of Helium bubbles in these fine multilayers if any is below the bubble detection limit of current TEM microscope (~ 0.5 nm). Further studies will focus on identification of critical layer thickness that may suppress the nucleation of He bubbles.

Some of the previous data has been accepted for publishing in Nuclear Instrument Method, B. We will investigate ion irradiation induced defects in immiscible systems in more details. Collaborations with LANL on molecular dynamics simulations will help us to understand the fundamental mechanisms of interface-irradiation defects interaction at molecular levels.

3.2.2. Microstructure and hardness of as-deposited Cu/V multilayer films

Distinct Cu (111) and V (110) peaks are observed in XRD patterns of Cu 50 nm/V 50 nm multilayers as shown in Figure 16. The two peaks start to overlap at smaller layer thickness and eventually, at a layer thickness of 2.5 nm, only one broad peak is observed centered at a two-theta value between Cu (111) and V (110).

Figure 16. XRD of Cu/V multilayers. Two distinct peaks, corresponding to Cu (111) and V (110), are observed in Cu 50 nm/V 50 nm multilayers. The two peaks tend to overlap at smaller layer thickness, Cu 10 nm/V 10 nm multilayers, and eventually only a single peak is observed in Cu 2.5 nm/V 2.5 nm multilayers.

Figure 17a is the cross-sectional TEM micrograph of as-deposited Cu 2.5 nm/V 2.5 nm multilayer films. The layer interface between Cu and V is clearly distinguishable. The inserted selected area diffraction pattern (SAD) indicates a strong fiber texture with Kurdjumov-Sachs (K-S) orientation relationship, i.e. $\{111\}_{\text{Cu}} // \{110\}_{\text{V}}$ and $\langle 110 \rangle_{\text{Cu}} // \langle 111 \rangle_{\text{V}}$. The columnar grain sizes of Cu and V are much greater than layer thickness. The cross-sectional TEM micrograph and the corresponding SAD pattern of Cu 100nm/ V 100nm multilayers are shown in Figure 17b. Both constituents have polycrystalline microstructures with a weak texture.

Figure 17. (a) Cross-sectional TEM micrograph of as-deposited Cu/V 2.5nm multilayer films with K-S orientation relationship between fcc Cu and bcc V grains. Inset is selected area diffraction pattern. (b) Cross-sectional TEM micrograph and diffraction pattern (inset) of as-deposited Cu/V 100nm multilayer films. K-S orientation relation ship is not observed clearly.

The hardnesses of Cu/V are compared to that of Al/Nb and several other multilayers as a function of $h^{-1/2}$, as shown in Figure 18. The hardness data of Cu/Cr and Cu/Nb metallic multilayers are also shown in the same plot for comparison. When layer thickness is greater than ~ 50 nm, the hardnesses of all multilayers increase approximately linearly with $h^{-1/2}$. The Hall-Petch slope is the highest for Cu/Cr multilayer, followed by Cu/Nb, Cu/V and Al/Nb multilayers. Such linear relation is quickly deviated at smaller layer thicknesses. Peak hardnesses are approached at approximately the smallest layer thickness for all systems, except in Cu/Cr system, where the peak hardness is approached at 10 nm individual layer thickness and stays constant thereafter. Among these four systems, the peak hardnesses of Cu/Cr and Cu/Nb, almost identical at ~ 6.8 GPa, are the highest, and Al/Nb has the lowest peak hardness at ~ 4.8 GPa.

Figure 18. Comparison of hardness vs. $h^{-0.5}$ plots for various fcc/bcc metallic multilayer systems, including Cu/Cr, Cu/Nb, Cu/V and Cu/Nb, where h is the thickness of each layer.

The mutual solubility between Cu and V is very small, approximately 2.5 wt% Cu in V matrix at 800 °C. Such immiscible nature, derived from thermodynamics, is consistent with the observation of chemically discrete interfaces in all Cu/V multilayer films. Cu/V multilayer with smaller individual layer thickness (10 nm or less) has stronger fiber texture with K-S orientation relationship, whereas a weaker texture is observed in Cu/V multilayers at layer thicknesses of 50 nm or greater. The evolution of texture intensity and K-S orientation relationship are similar in Al/Nb multilayer films. Although phase diagram shows the formation of several intermetallic phases between Al/Nb, we did not observe significant intermixing, and no new phases are

identified by either XRD or TEM in current studies. The retention of interface between miscible Al and Nb is partly attributed to the fact that all deposition was performed all at room temperature at which there is not sufficient thermal energy to promote inter diffusion. Furthermore heating was prohibited during TEM specimen preparations. We have studied the microstructures of Cu/Cr and Cu/Nb previously. Both systems have fcc/bcc type of layer interfaces, and the texture and K-S orientation relationship are similar to the current cases. Phase diagrams of Cu/Cr and Cu/Nb indicates that both systems are basically immiscible.

Comparison of Hall-Petch slope of fcc/bcc multilayer systems

The phenomena that hardness is proportional to $h^{-1/2}$ at layer thickness of 50 nm or greater in all cases can be explained by the Hall-Petch model, based on dislocation pile-ups at layer interfaces. Dislocation pile-ups become more and more difficult at smaller layer thicknesses. The deviation from the Hall-Petch linear relationship occurs when the number of dislocations (n) in the pile-up is less than 2 for a circular pile-up ($n \leq 3$ for a double-ended pile-up and $n \leq 6$ for a single -ended pile-up).

Hall-Petch slope, k , is a measure of interface barrier strength for slip transmission and can determine the rate of strength increase with decreasing h . Hall-Petch slope was calculated using

$$k = 0.18G\sqrt{b} \quad (1),$$

where G and b are the shear modulus and the magnitude of Burgers vector of the stiffer component of the multilayers, respectively. The magnitude of Burgers vector is $a\sqrt{2}/2$ in fcc phase and $a\sqrt{3}/2$ in bcc phase, where a is lattice parameter. The calculated k values for each multilayer system are given in Table 2. Briefly the experimental Hall-Petch slopes are in good agreement with that of calculated values. For instance, in Cu/Nb and Cu/V systems, Cu is the stiffer phase. Therefore the calculation predicts that the Hall-Petch slope of the two systems shall be the same. This is precisely what the experimental results have shown in Table 2. In Cu/Cr, the calculated k based on the stiffer component, Cr is slightly lower than experimental result. In Al/Nb multilayers, the calculated slope based on the stiffer Nb phase is similar to experimental value. These studies indicate that in thicker multilayer composites, at length scale of tens of nanometers or greater, the interface barrier strength of multilayers could be dominated by the strength of the stiffer component.

Table 2 Calculated and experimental H-P slope of nanoscale metallic multilayers

Metallic multilayers	Cu/Cr	Cu/Nb	Cu/V	Al/Nb
Average shear modulus* (GPa)	70	42	46	31
Calculated k, (MPa $\sqrt{m}$)	0.29	0.14	0.14	0.11
Experimental k (MPa $\sqrt{m}$),	0.33	0.16	0.15	0.12

* Shear modulus (GPa): Cu (46), Cr (93), Nb (38), V (46), and Al (25)

Comparison of peak hardnesses of various fcc/bcc multilayer systems

The peak hardnesses of four fcc/bcc multilayer systems are listed in Table 3, together with the heat of mixing and mismatch strain between fcc {111} and bcc {110} interplanar spacing. The peak hardness is the highest for Cu/W, then Cu/Cr and Cu/Nb, followed by Cu/V and Al/Nb in descending sequence. We will attempt to understand the difference in their peak hardness based on factors that may determine the interface barrier strength, including average shear modulus and modulus mismatch and dislocation core spreading along interfaces.

At layer thickness of a few nanometers, the metallic multilayer films typically reach peak hardness, and thereafter, the hardness varies very little with layer thickness. At length scales of a few nanometers, dislocation pile-ups are less likely; instead the strength of multilayer films is dominated by the strength of interface barrier to the transmission of single dislocation.

Table 3. A comparison of peak hardness of several multilayers

System	Average biaxial modulus (GPa)	Indentation modulus (GPa)	Mismatch strain* (%)	Heat of mixing (kJ/mol) [26]	Peak hardness (GPa)
Cu/W	415	228	13.1	22	8.9
Cu/Cr	296.5	170	2.3	12	6.8
Cu/Nb	211.5	115	10.5	3	6.8
Cu/V	228	111	2.5	5	5.2
Al/Nb	138	95	0.02	-18	4.8

* Mismatch strain between the fcc {111} and bcc {110} interplanar spacing

In earlier literature, it was postulated that the Koehler stress plays a dominant role in determining the peak strength, especially in systems with large elastic modulus mismatch. We examine this by plotting the peak hardness as a function of the average biaxial modulus of the multilayers. A plot of the peak hardness versus indentation modulus revealed essentially identical trends as in Fig. 19. While there is a general trend of the peak hardness scaling with the modulus, there are significant departures from this trend as well. For example, Cu/Nb is significantly harder than Cu/V in spite of similar moduli, and Cu/Cr and Cu/Nb have similar peak strengths in spite of a large difference in moduli. Thus, the peak strengths of these fcc/bcc multilayers cannot be interpreted solely based on the Koehler stress.

Figure 19. The peak hardness as a function of the average biaxial modulus of the various fcc/bcc metallic multilayers. Average biaxial modulus for fcc/bcc multilayer is the average value of the biaxial modulus between the fcc (111) and bcc (110) plane.

Molecular dynamics simulations of slip transmission across the incoherent Cu/Nb interfaces revealed that these interfaces have low shear strengths. As a result, the stress field of a glide dislocation can locally shear the interface and lead to dislocation core spreading along the interface plane. This trapping of the glide dislocation in the interface plane due to core spreading makes the slip transmission difficult. The extent of core spreading is inversely proportional to the interfacial shear strength and may be the key to determining the interface barrier to slip transmission in incoherent fcc/bcc interfaces. The interfacial shear strength (and hence the core spreading and the peak strength of the composite) of fcc/bcc interfaces with Kurdjumov-Sachs orientation relationship may depend on a combination of factors such as heat of mixing, lattice

parameter mismatch and the atomic structure of the interface. This will be investigated via atomistic modeling in our future work.

3.2.3. Evolution of microstructures subjected to radiation in Cu/V multilayers

As-deposited Cu/V multilayers with different individual layer thicknesses, h , of 1 – 100 nm were radiated by He ions of 50 keV and various doses: 6×10^{15} ions/cm² (0.5 dpa peak dose), 6×10^{16} ions/cm² (5 dpa peak dose) and 1.2×10^{17} ions/cm² (10 dpa peak dose). In the following section, we will evolution of microstructure and hardness of Cu/V multilayers after radiation.

XRD patterns of as-deposited and radiated Cu/V 50nm and Cu/V 2.5 nm multilayers are shown in Figure 20. Cu (111) and V (110) peaks are distinguishable in Cu/V 50 nm, and the overlap of the two peaks is observed in Cu/V 2.5 nm multilayers. The XRD studies show reduced peak intensity after ion irradiation indicating disordered crystalline structures due to radiation. Also the magnitude of reduction in peak intensity is greater in specimens radiated at higher peak dose. In Cu/V 50 nm multilayers with a low peak dose (0.5 dpa), V (110) peak shifts slightly to lower angle by $\sim 0.13^\circ$. However such peak shifts to a lower angle by $\sim 0.46^\circ$ when the dose increases to 5 dpa. The Cu (111) peak in Cu/V nanolayer subjected high dose shifts to the left by $\sim 0.09^\circ$, slightly higher than a left shift of 0.02° in low dose radiated Cu/V. The deconvolution of overlapped peaks in Cu/V 2.5 nm nanolayers, according to Gaussian and Lorentzian function, shows that the magnitude of peak shifts is much smaller in specimens subjected to both low and high dose radiation than that in radiated Cu/V 50 nm specimen.

(20a) Cu/V nanolayers subjected to He ion irradiation with a peak dose 0.5 dpa

(20b) Cu/V nanolayers subjected to He ion irradiation with a peak dose of 5 dpa

Figure 20. XRD pattern of as-deposited and ion irradiated Cu/V nanolayers with individual layer thickness of 50 nm and 2.5 nm. Peak shift and decrease of peak intensity after radiation are observed, indicating lattice distortions after ion irradiation.

These XRD studies show that radiation induced lattice expansion is pronounced in V (110), whereas negligible for Cu (111). The primary damage event during radiation is displacement of

one or more atoms and consequently the vacancy, self-interstitial type lattice defects and foreign elements are created. In FCC Cu with low stacking fault energy (SFE), approximately 90% of radiation-induced defects are stacking fault tetrahedra (SFT), which are essentially vacancy clusters. Recent MD simulations indicate that vacancies, up to a few atomic percent, only induce slight reduction in lattice parameter in FCC Cu. In BCC V, SFT were not detected. Instead defects generated by ion irradiation are most probably of interstitial type. Interstitials will increase the lattice parameter, in agreement with our XRD studies. The magnitude of peak shift in the samples with 0.5 dpa ion irradiation is much smaller than that in ion irradiated nanolayers with 5 dpa due to lower concentration of interstitial generated by lower dose.

TEM experiments were performed to examine the evolution of microstructure after radiation in details. Cross-sectional TEM (XTEM) images of as-deposited Cu/V 50 nm and Cu/V 2.5 nm nanolayers in Figure 21 (a) and (b) show layer interfaces between Cu and V are clearly distinguishable without intermixing. The inserted selected-area diffraction (SAD) pattern in Cu/V 50 nm indicates both constituents have polycrystalline nature with a weak texture, whereas Cu/V 2.5 nm specimen possesses a strong fiber texture with Kurdjumov–Sachs (K–S) orientation relationship, i.e. Cu $\{1\ 1\ 1\}$ // V $\{1\ 1\ 0\}$ and Cu $\langle 1\ 1\ 0 \rangle$ // V $\langle 1\ 1\ 1 \rangle$. Figure 21 (c) and (d) show the underfocused XTEM images of these specimens after 5 dpa He ion irradiations. The layer morphology is not degraded in spite of a high He concentration and peak dose. Inserted SAD patterns indicate radiated films have similar texture as before. Superimposed on the images are two depth profiles of He concentration from surface (solid curve) obtained by SRIM simulations on Cu/V 50nm and Cu/V 5nm nanolayers using experimental radiation parameters. The simulated maximum He concentration is 4-5 at % at a depth of ~ 200 nm with a peak dpa of 5-6. Peak damage regions in both cases, $\sim 150\text{ nm}^2$ indicated by two boxes in 21(c) and (d), are magnified and shown in Figure 21 (e) and (f). Careful examination of these figures shows that white dots, typical signatures of He bubbles, appear in both Cu and V. Distributions of He bubble density along the implantation path, obtained from detailed microscopy studies, in Cu/V 50 nm and Cu/V 2.5 nm nanolayers are already shown in the previous quarter report. The maximum bubble density appears approximately 275 nm and 225 nm underneath surfaces in Cu/V 50 nm and Cu/V 2.5 nm, respectively. Cu/V 50 nm nanolayer has 3-4 times higher peak He bubble density than that in Cu/V 2.5 nm.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 21. XTEM images of Cu/V nanolayers. (a) (b) shows as-deposited Cu/V 50nm and Cu/V 2.5nm nanolayers. Ion irradiated Cu/V 50nm (c) and Cu/V 2.5 nm multilayer with superimposed SRIM simulation plot. Layer interface remain distinguishable after radiation. Two boxes taken from peak damage regions, $\sim 150 \text{ nm}^2$, in (c) and (d) are magnified and compared in (e) and (f).

Scanning TEM (STEM) and EDX analysis were performed to examine the integrity of radiated layer interface. Results of Cu/V 2.5 nm specimens are shown in Figure 22 and 23. A 1 nm probe size was used for STEM and EDX analysis. In Fig. 22, it shows qualitatively that radiated Cu/V 2.5 nm layer interface retain chemically abrupt in the peak damage region. Semi-quantitative analysis via EDX shows the composition profile of radiated Cu/V along a straight line drawn normal the layer interface. Three different regions were examined, including slightly underneath surface with medium damage, peak damage region, and a region deep enough to avoid any radiation damage. As shown in Fig. 23, the composition profiles for these three regions are essentially the same, indicating that radiation induced interdiffusion across interface, if any, is under the resolution limit of such technique.

Figure 22. STEM images of ion-irradiated Cu/V 2.5 nm nanolayers with 5 dpa peak dose in various regions (a) little damage region, (b) peak damage region.

Figure 23. Chemical analysis of Cu and V from several EDX spectra of line scans along direction normal to layer interface in Cu/V 2.5 nm specimens. There is no chemical degradation of layer interface after radiation.

Figure 24. Variation of d-spacing in radiated Cu/V 2.5 nm and Cu/V 50 nm specimens as a function of depth along implantation path.

Depth dependent lattice expansions, calculated from systematic SAD studies along implantation path, are shown in Fig. 24 for Cu/V 2.5 nm and Cu/V 50 nm nanolayers. The dependence of lattice expansions on depth seems to correlate well with the distribution of He bubble density, and the overall magnitude of lattice expansion is 3-4 times lower in Cu/V 2.5 nm specimens than that in Cu/V 50 nm nanolayers. Given the difficulty of distinguishing Cu (111) from V (110) in SADs, the average value of the two is used in Fig. 24.

Evolution of bubble size and density in radiated Cu/V nanolayers

To determine the helium bubble size, a series of XTEM images of ion irradiated Cu/V 2.5 nm and 50 nm were taken at different under-focus conditions. Figure 25 shows the image size of bubble as a function of under-focus conditions. The results show that bubble size increases at larger under-focus distance. The average bubble size at in-focus condition, determined by the intercept of linear fit with y axis, is 0.6 nm. The average bubble size of ion irradiated Cu/V 50 nm was determined to be 0.7 nm as shown in Figure 26. The similar bubble size in radiated different Cu/V nanolayers indicates that bubble size depends less on the individual layer thickness.

Figure 25. Estimation of bubble size in ion irradiated Cu/V 2.5 nm through a series of underfocused XTEM micrographs. The average bubble size is estimated to be ~ 0.6 nm from the intercept of linear fit with y axis.

Figure 26. Average bubble size in ion irradiated Cu/V 50 nm is estimated to be ~ 0.7 nm through a series of XTEM micrographs taken at different under focus conditions.

Our TEM studies then focused on examining the influence of layer thickness on bubble density in ion irradiated Cu/V nanolayers. Figure 27 shows He bubble density as a function of depth below film surface in radiated Cu/V nanolayers. He bubble density was calculated in TEM micrographs taken with a underfocus distance of -400 nm. In all cases, He bubble density increases rapidly to maxima at around 225 nm below surface, consistent with the prediction by SRIM calculations (shown in an earlier quarter report). Peak He bubble density decreases with decreasing layer thickness by a factor of 2, comparing bubble density in radiated Cu/V 50 nm and Cu/V 2.5 nm specimens. The ion irradiated Cu/V 50nm nanolayer has the similar peak bubble density to that in the single layer polycrystalline Cu films at the same ion irradiation condition. Such studies indicate that higher interfacial area density through a reduction in layer thickness may effectively suppress the nucleation and growth of He bubbles, and thus alleviate radiation damage in certain metals.

To provide a rough estimation of radiation induced void swelling, the total volume of He bubbles was calculated after the bubble size and bubble density were determined. Figure 28 shows the total bubble volume per nm^3 in different samples. The ion irradiated Cu/V 2.5 nm has approximately an order of magnitude lower overall bubble volume than that in ion irradiated Cu/V 50 nm, indicating a likely dramatic reduction of void swelling.

Figure 27. Comparison of Helium bubble density distribution along the depth below the surface in ion irradiated Cu/V nanolayers. Peak He bubble density is reduced by a factor of 2 in Cu/V 2.5 nm, in comparison to that in Cu/V 50 nm specimen.

Figure 28. Comparisons of total volume of He bubbles as a function of layer thickness in ion irradiated Cu/V nanolayers. The total bubble volume has been reduced by about an order of magnitude in Cu/V 2.5 nm comparing to that of Cu/V 50 nm specimens. Total bubble volume percentage in ion irradiated samples.

3.2.4. Evolution of mechanical properties of Cu/V pre- and post-radiation

Indentation hardnesses of as-deposited and ion-irradiated multilayers Cu/V with various individual layer thicknesses were measured at indentation depths of up to 200 nm. Nine indents were performed at each depth to get an average hardness value. A more significant hardness enhancement was observed, in radiated specimens with greater individual layer thickness, h , whereas hardness barely increases when h is ≤ 2.5 nm as shown in previous quarter report. To test the reproducibility, two more sets of radiation and hardness measurements were performed. The results of radiation hardening are shown in Figure 29. The three sets of experiments show a convincing trend that radiation hardening is more significant at greater h , and no obvious hardening when h is ≤ 2.5 nm.

Ion irradiation induces vacancies and interstitials in the metals that migrate and agglomerate into clusters. The vacancy clusters trap helium to become helium bubbles, while mobile interstitials form interstitial (dislocation) loops. Helium bubbles and dislocation loops are likely to play an important role in radiation hardening.

Figure 29. Radiation hardening vs. $h^{-0.5}$ plot for Cu/V nanolayers, where h is the thickness of each layer. Significant hardness enhancement has been observed in Cu/V at greater h , whereas hardnesses barely change in radiated Cu/V when h is ≤ 2.5 nm. The three sets of results are consistent with one another.

Two types of dislocation barrier models have been used to describe radiation hardening in metals. The dispersed barrier model is more appropriate for strong obstacles such as dislocation loops. The estimation of the radiation hardening dislocation loops by using this model has been discussed in the previous quarter report. Friedel, Kroupa and Hirsch (FKH) developed another model to estimate radiation hardening from weak obstacles, such as He bubbles. The following equation has been used based on FKH model:

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

where ΔH is radiation hardening, M is the Taylor factor taken as 3.06 for equiaxed fcc and bcc metals, μ is shear modulus, b is Burgers vector of the primary glide dislocations, and d and N are bubble size and bubble density. The helium bubble size and average bubble density in ion irradiated Cu/V nanolayers were used to calculate the estimation of hardness enhancement by using FKH model. The results were shown in Figure 30. Open symbols represent experimental results, and the red solid circles show the calculations based on FKH model. The results show that hardness enhancement due to helium bubbles is negligible comparing to the overall radiation hardening. Such study indicates that radiation is probably mainly due to dislocation loops.

Figure 30. Comparison of calculated radiation hardening due to He bubbles based on FKH model (solid red dots) with the experimental results (open symbols). He bubble induced hardening seems to be negligible.

3.2.5. Dose dependent radiation damage in Cu/V nanolayers

The simulation of He ion irradiation on the Cu/V multilayer was performed by the stopping and range of ions in matter (SRIM) computer program based on Monte Carlo method. The nominal individual layer thickness of Cu/V multilayer in the simulation was 50 nm. Three ion irradiation fluences, 6×10^{19} , 6×10^{20} and $1.2 \times 10^{21} / \text{m}^2$, corresponding to real experiments were simulated with a He ion energy of 50 keV, respectively. The corresponding peak damages, induced by He collision and calculated from the output of simulation, were 0.6 dpa, 6 dpa and 12 dpa, respectively. Figure 31 shows the variation of He concentration as a function of ion penetration depth predicted by SRIM for the three cases. In all cases with the increase of implantation depth, He concentration increases to the peak value at a depth of around 200 nm and then decreases to zero at depth of 380 nm. Higher total fluences result in greater He concentration and higher radiation damage. The He concentration at the total fluence of $1.2 \times 10^{21} / \text{m}^2$ is twenty times greater than that in specimens irradiated at the total fluence of $6 \times 10^{19} / \text{m}^2$. The maximum implantation depth is the same in all three cases due to the use of identical He ion energy.

Figure 31. Depth profile of helium concentration from SRIM simulation in Cu/V 50 nm multilayers subjected to He ion irradiation at 50 keV with a total fluence of $6 \times 10^{19} / \text{m}^2$, $6 \times 10^{20} / \text{m}^2$ and $1.2 \times 10^{21} / \text{m}^2$, respectively.

The examination of the chemical integrity of layer interface after irradiation was performed by STEM based on the contrast of different materials. Figure 32 shows a STEM micrograph of ion irradiated Cu/V 50 nm specimen. The darker layers are V, sandwiched by the brighter Cu layers. This STEM micrograph examined three different regions of the sample predicted by SRIM simulation. These three regions include a film surface region with low to medium damage, a peak damage region at a depth of around 200 nm, and a no damage region that is deeper than the ion projected range. STEM image clearly shows chemically abrupt layer interfaces in all the three regions. This indicates the remaining of integrity of interface structure after high dose He ion irradiation. Furthermore, semi-quantitative chemical composition analysis via EDX (not shown here) indicates that the composition profiles for the three regions are

essentially the same, implying that radiation induced interdiffusion across layer interface, if any, is under the spatial resolution limit of such a technique.

Figure 32. STEM image of Cu/V 50 nm with He ion irradiation at a total fluence of $1.2 \times 10^{21} / \text{m}^2$.

XTEM micrographs in the previous studies show the sputtered Cu/V 50 nm and 2.5 nm multilayer samples, having columnar grain structure, exhibit distinguishable interfaces without significant intermixing. The interfaces in both samples have Kurdjumov-Sachs (K-S) orientation relationship, i.e. Cu $\{111\} // \text{V } \{110\}$ and Cu $\langle 110 \rangle // \text{V } \langle 111 \rangle$, with weak fiber texture in Cu/V 50 nm and strong fiber texture in Cu/V 2.5 nm sample. The depth profile of He bubble distribution in ion irradiated Cu/V multilayer films indicates the He bubble density increases to peak value at a depth of 200 nm and then decreases to zero at a depth of 380 nm. The radiation damage in terms of He bubbles across the entire radiation depth in the irradiated Cu/V multilayers with various radiation levels were examined by XTEM. The comparison of the de-

focused TEM micrographs of Cu/V 50 nm multilayer after He irradiation to a total fluence of $6 \times 10^{19} / \text{m}^2$, $6 \times 10^{20} / \text{m}^2$, and $1.2 \times 10^{21} / \text{m}^2$ indicates the numbers of He bubbles in Cu/V 50 nm sample irradiated at the highest fluence are much higher than that in Cu/V 50 nm multilayer with the lowest fluence. This indicates that higher fluence leads to more significant radiation damage, consistent with the SRIM predictions. The comparison of corresponding SADs shows no significant change in the texture after ion irradiation. The defocused TEM images of the irradiated Cu/V 2.5 nm to a total fluence of $6 \times 10^{19} / \text{m}^2$, $6 \times 10^{20} / \text{m}^2$, and $1.2 \times 10^{21} / \text{m}^2$ shows similar trend, i.e. higher dose leads to great concentration of He bubbles. However, no significant He bubbles are observed in ion-irradiated Cu/V 2.5 nm at a fluence of $6 \times 10^{19} / \text{m}^2$. The comparison of numbers of He bubbles in the irradiated Cu/V 50 nm and Cu/V 2.5 nm at the same radiation fluence indicates the Cu/V 50 nm multilayer films have much more He bubbles than the Cu/V 2.5 nm samples, which has been observed in previous studies. At the lowest irradiation fluence in the study, irradiated Cu/V 2.5 nm multilayer has no detectable He bubbles, however, irradiated Cu/V 50 nm does. All the figures show clear interfaces between Cu and V without apparent intermixing in the irradiated Cu/V multilayers.

Next, the focus will be to compare the *peak damage regions* of Cu/V multilayers subjected to different radiation fluences. Figure 33a-c show under-focused XTEM micrographs of the peak damage regions in the irradiated Cu/V 50 nm multilayers subjected to the different dosages. He bubbles appeared in all peak damage regions. The number of He bubbles in Cu/V 50 nm upon the lowest fluence (Figure 33a) is much less than those irradiated at higher fluences. The interfaces in all peak damage regions are clear without significant intermixing.

Figure 33. XTEM micrographs of peak damage images of ion irradiated Cu/V 50 nm multilayer films subjected to different radiation levels. (a) 0.6 dpa, (b) 6 dpa, (c) 12 dpa.

Figure 34a-c show the under-focused XTEM micrographs of the peak damage region of Cu/V 2.5 nm multilayers by He ion irradiation to a total fluence of $6 \times 10^{19} / \text{m}^2$, $6 \times 10^{20} / \text{m}^2$, and $1.2 \times 10^{21} / \text{m}^2$, respectively. In the peak damage region in all ion irradiated 2.5 nm, the interfaces between Cu and V remain abrupt without significant mixing. With the increase of ion irradiation dose, the number of He bubbles increases in the peak damage region. However, no bubbles are detected in Cu/V 2.5 nm subjected to a radiation fluence of $6 \times 10^{19} / \text{m}^2$. The

number of He bubble increases with the increase of the total fluence from $6 \times 10^{20} / \text{m}^2$ to and $1.2 \times 10^{21} / \text{m}^2$.

Figure 34. XTEM micrographs of peak damage images of ion irradiated Cu/V 2.5 nm multilayer films subjected to different radiation levels. (a) 0.6 dpa, (b) 6 dpa, (c) 12 dpa.

Overall, layer interfaces retain in all irradiated multilayers in spite of a high He concentration and a highest fluence of $1.2 \times 10^{21} / \text{m}^2$. The SAD patterns (not shown here) for all the samples indicates the orientation relationship between the Cu and V at interfaces remains unchanged, and

no extra diffraction spots were identified. The comparison between ion irradiated Cu/V 50 nm and Cu/V 2.5 nm subjected to the same dose indicates that Cu/V 50 nm multilayers contain more radiation damage in terms of He bubbles, compared to ion irradiated Cu/V 2.5 nm multilayer specimens.

To compare the radiation damage quantitatively at various fluences, a plot of peak He bubble density, counted from TEM micrographs taken at an under-focus distance of 400 nm, as a function of fluence for ion irradiated Cu/V 50 and 2.5 nm multilayers samples is shown in Figure 35. Overall, the bubble density in the peak damage regions of irradiated Cu/V 50 nm multilayer is a factor of 3 higher than that in irradiated Cu/V 2.5 nm multilayer at the same radiation dose. The peak He bubble density significantly increases with increasing fluence to $6 \times 10^{20} / \text{m}^2$ and then slightly increases with increasing fluence to $1.2 \times 10^{21} / \text{m}^2$ in ion irradiated Cu/V 50 nm multilayers. The He bubble density increases continuously with increasing fluence in Cu/V 2.5 nm multilayer. Although the peak helium bubble density shows the trend to reach saturation in Cu/V 2.5 nm at a fluence of $1.2 \times 10^{21} / \text{m}^2$, it is speculated that the Cu/V 2.5 nm multilayer may reach the same level of peak helium peak bubble density as Cu/V 50 nm multilayer after it is subjected to even higher total helium ion fluence.

Figure 35. Comparison of Helium bubble density in the peak damage region in irradiated Cu/V multilayers. Peak He bubble density is reduced by a factor of 3 in Cu/V 2.5 nm, in comparison to that in Cu/V 50 nm specimen.

The lattice expansion deduced from the shift of X-ray diffraction peak position of Cu/V multilayers with Si (100) substrates before and after irradiations with various fluences was characterized by X-ray diffraction (XRD). Si (400) peak from Si substrate is used as a reference for calibration purpose. Figure 36a shows the XRD patterns of Cu/V 50 nm multilayer samples. Two distinct peaks of V (110) and Cu (111) are observed in all Cu/V 50 nm multilayer samples. With the increase of total fluences, labeled by peak damage of 0.6 dpa, 6 dpa and 12 dpa, respectively, both the V (110) and Cu (111) peaks shifted to lower angle. Also the magnitude of peak shift in V (110) is more significant, compared to that of Cu (111) peak. Similarly, the comparison of peak shift in XRD patterns of as-deposited and irradiated Cu/V 2.5 nm is shown

in Figure 36b. An overlapped V (110) and Cu (111) peak is observed in all Cu/V 2.5 nm multilayer samples. After He ion irradiation at different fluence levels, the peak shift of overlapped peak to low angle increases insignificantly with respect to the as-deposited Cu/V 2.5 nm, and the magnitude of peak shift is much smaller than that observed in irradiated Cu/V 50 nm multilayers.

The lattice expansion deduced from the peak shift of XRD patterns as a function of fluence in Cu/V 50 nm and Cu/V 2.5 nm is shown in Figure 36c. At the lowest fluence $0.6 \times 10^{20} / \text{m}^2$, the lattice expansion in V layer is 0.15 % in Cu/V 50 nm multilayers, however, its lattice expansion increases to 1.38 %, when the fluence increases to $1.2 \times 10^{21} / \text{m}^2$. The expansion of lattice parameter in Cu layer subjected to the highest fluence of $1.2 \times 10^{21} / \text{m}^2$ is 0.36 %, which is also higher than that (0.08 %) in the sample subjected to lower fluence. Much smaller position shift of the overlapped peak in Cu/V 2.5 nm multilayers shows that magnitude of lattice expansion in Cu/V 2.5 nm specimens is much smaller than that in Cu/V 50 nm specimen subjected to the same irradiation fluence.

Figure 36 (a) and (b), XRD pattern of as-deposited and irradiated Cu/V multilayers with individual layer thickness of 50 nm and 2.5 nm.

Figure 36 (c), Lattice expansion ratio from XRD pattern as a function of fluence for ion irradiated Cu/V multilayers with individual layer thickness of 50 nm and 2.5 nm.

To examine dose dependent radiation hardening, the hardness of irradiated Cu/V multilayers were measured by nanoindentation technique. Dose rate was essentially the same during radiation experiments and loading rate was kept constant during nanoindentation. Figure 37a shows the evolution of hardness change (radiation hardening) at different fluence levels as a function of h . The trend of radiation hardening in specimens irradiated at different fluences is similar, i.e., radiation hardening is more significant at greater h and decreases with decreasing h . A greater fluence (from $6 \times 10^{19} / \text{m}^2$ to $6 \times 10^{20} / \text{m}^2$) leads to more significant radiation hardening when $h > 1$ nm. Hardening is negligible for fine ($h \leq 2.5$ nm) multilayers at all fluence levels in the study. No radiation hardening is observed in Cu/V 1 nm multilayers even at a fluence of $6 \times 10^{21} / \text{m}^2$. The hardness enhancement seems to reach a saturation value at a fluence of $6 \times 10^{20} / \text{m}^2$. The hardness enhancement in Cu/V multilayer with greater h is more significant at higher dose. The hardness increases in Cu/V multilayer films with different individual layer thickness as a function of radiation fluence are compared in figure 37b. Overall the hardness increases with the increase of fluence in all these three Cu/V multilayer films. However, the magnitude of hardness increase in Cu/V 2.5 nm is much less than that in Cu/V 10 nm and Cu/V 50 nm multilayers subjected to the same radiation fluence.

Figure 37 (a), Comparison of radiation hardening vs. h at different radiation Levels.

Figure 37 (b), Comparison of radiation hardening vs. different radiation fluence levels.

Ion mixing along the interfaces between dissimilar materials induced by bombardment of energetic particles has frequently been observed in many miscible systems such as Cu/Au [2], Hf/Ti [3], Fe/W [4] and Al/Nb [5], however, as for the immiscible Cu/V interface, the chemical analysis study of STEM in present study has shown clear interfaces without significant intermixing. The simulation for Cu recoil atoms into V layer and V recoil atoms into Cu layer due to He ion irradiation has been performed by SRIM computer code using the experimental ion energy of 50 keV. The distribution of recoil atoms into layers can be well fitted by Gauss functions

$$f(x) = ae^{-\frac{(x-b)^2}{2c^2}} \quad (3)$$

Where a , b , and c are constant. The parameter c is related to the full width at half maximum (FWHM) of the peak. The value of FWHM of diffusion regions in He ion irradiated Cu/V from SRIM simulation is within the range from 9 Å to 14 Å. The ion mixing region along the interface at a depth of 150 nm has the maximum FWHM value of 14 Å, which is above the limitation of STEM resolution and can be detected by chemical analysis. However, when the fluence increases to $1.2 \times 10^{21} / \text{m}^2$, no significant ion intermixing region with a length of 1.5 nm along the interface between layers was observed by the chemical analysis in the STEM images. the XTEM micrographs of irradiated Cu/V 50 nm and Cu/V 2.5 nm (figure 33c and 34c) still show clear interface without intermixing. There is a very limited mutual solid solubility between Cu and V. According to the phase diagram, only approximately 2.5 wt % Cu can be dissolve in V at 800 °C, which results in a positive heat of mixing of ~ 5 kJ/mol [6]. The positive heat of mixing leads to a driving force for de-mixing process between Cu and V. The competition result between mixing and de-mixing is that the de-mixing process canceled the influence of ion

mixing on the Cu/V interface. Therefore, no significant ion intermixing between Cu/V interfaces was observed. Similar phenomena showing a lack of irradiation induced intermixing have been observed in several multilayer systems such as Cu/W [2], Cu/Nb [7] and Hf/Ni [3], which are all immiscible systems and have positive heat of mixing.

Radiation induced He bubbles and lattice expansion

Radiation damage, such as He bubbles, has been observed in the irradiated Cu/V multilayers. The interactions between the projectiles and the atoms in the solid result in the collision cascade, composed of the vacancy clusters core and interstitial shell. After collision, the recombination of interstitial and vacancy occurs immediately by which most of point defects recover to the original site. However, a small fraction of interstitial and vacancy will remain in the matrix and develop to either the dislocation loops or voids. He atoms introduced by ion irradiation can combine with vacancy clusters and consequently form He bubbles. The density of He bubbles is a direct measure of the magnitude of radiation damage. Radiation damage during ion solid interactions can be described by the modified Kinchin-Pease displacement damage function. When the energy of the implanted particles is greater than the minimum displacement energy of atoms, the modified Kinchin-Pease displace damage function is given by

$$\langle N_d(E) \rangle = \frac{\xi \nu(E)}{2E_d} \quad (4)$$

Where $\langle N_d(E) \rangle$ is the vacancy-interstitial pairs (Frenkel pairs) generated by a primary knock-on effect, E_d is minimum displacement energy, and ξ is parameter suggested to be 0.8 by both analytical theory and computer simulations. $\nu(E)$ is nuclear stopping power and is given by $\nu(E) = dE / dx$ [8].

This equation is used to calculate the Frenkel pairs and estimate the radiation damage. Before that, the nuclear and electronic stopping power is required. It is well known that the contribution to ion stopping in solids originates from two different mechanisms – nuclear and electronic stopping [8]. Nuclear stopping, the loss of energy by ion-target nucleus collisions, plays a dominant role in displacing the atoms from their lattice sites. In the case of electronic stopping, ions lose energy by collision with target electrons. The nuclear and electronic stopping power can be obtained through SRIM simulation, but their stopping power as a function of projected range can not be obtained directly from SRIM. Firstly, a table regarding stopping powers as a function of energy can be calculated by SRIM. After that the energy was converted into the corresponding depth for 50 keV He ions. The comparison of the electronic and nuclear stopping powers of He ions in the Cu/V multilayer based on SRIM simulation is shown in figure 8. Electronic stopping is reduced with increasing depths, while nuclear stopping increases with increasing of depth and reaches the peak at a depth of the range between 150 nm and 200 nm, which is consistent with the depth where peak damage region was observed experimentally in Figure 33 and 34.

Figure 38. The comparison of the electronic and nuclear stopping powers of He ions in the Cu/V multilayer based on SRIM simulation

Based on the nuclear stopping power functions, the Frenkels pairs generated by a primary knock-on effect as a function of depth can be calculated. At a given total fluence ϕ , the displacements per atom (dpa) as a function of depth is given by [8]

$$dpa(x) \cong \frac{N_d(x)}{N} = \frac{0.8\phi}{2NE_d} \cdot \left. \frac{dE}{dx} \right|_n \quad (5)$$

Where $N_d(x)$ is the Frenkel pairs generated by knock-on effect at a given fluence of ϕ , N is the atomic density of the solid, and $\left. \frac{dE}{dx} \right|_n$ is nuclear stopping power as a function of depth. Another approach to calculate $dpa(x)$ is given by SRIM simulation, which used the same analytic method as above. The SRIM simulation can output the value of D , which has the unit of displaced atoms per ion per unit thickness. In the calculation, therefore, the $dpa(x)$ is given by [8]

$$dpa(x) = D \cdot \phi / N \quad (6)$$

Based on this analytic method, the plot of $dpa(x)$ for He ion irradiated Cu/V 50 nm upon a total fluence of $1.2 \times 10^{21} / \text{m}^2$ is shown in Figure 39. The peak radiation damage is around 12 dpa at a depth of 150 nm in Cu layer. Similarly, the plot of $dpa(x)$ in He ion irradiated Cu/V 50 nm at $6 \times 10^{19} / \text{m}^2$ and $6 \times 10^{20} / \text{m}^2$ has the same distribution of radiation damage, but corresponding magnitude of dpa is smaller than that irradiated to a fluence of $1.2 \times 10^{21} / \text{m}^2$ by a factor of 20 and 2, respectively. This is the reason why higher irradiation fluence level results in heavier radiation damage, observed in both irradiated Cu/V 50 nm (Figure 33) and Cu/V 2.5 nm (Figure 34) where the He bubbles are more frequently observed in Cu/V multilayers upon higher fluence of He ion irradiation.

Figure 39. the plot of $dpa(x)$ for He ion irradiated Cu/V 50 nm upon a total fluence of $1.2 \times 10^{21} / \text{m}^2$.

The SRIM simulation results predict the similar irradiation damage generated in Cu/V multilayers with various h at the same irradiation fluence based on the calculation method above, however, it is noted that the comparison of de-focused XTEM micrographs of the irradiated Cu/V multilayer samples indicates the irradiated Cu/V 2.5 nm samples have less radiation damage with respect to the Cu/V 50 multilayer sample subjected to the same fluence levels.

Figure 40a and 40b show the depth dependent He concentration profiles of Cu/V 50 nm and Cu/V 5 nm multilayers predicted by SRIM simulation, respectively. The simulation assumes no interface effect to the radiation damage. The vertical dashed lines, obtained from the de-focused TEM images of figure 33 and figure 34, indicate the depth range over which bubbles are observed. The intersection of the vertical dashed lines with the SRIM simulated He concentration profiles indicates that the minimum He concentration at which the bubbles are observed. In Cu/V 50 nm upon highest fluence in the study, the minimum He concentration where the bubbles are detectable is approximately 0.27 at.% at ~ 5 nm underneath the film surface. This value is very similar with that in Cu/V 50 nm multilayer upon lowest fluence, although the depth where the bubbles can be observed is around 140 nm. On the other hand, the threshold of He concentration in Cu/V 2.5 nm upon the highest fluence is around 1.8 %. Note the He concentration introduced into Cu/V 2.5 nm at the lowest fluence of $6 \times 10^{19} / \text{m}^2$ in the study is smaller than the threshold of He concentration, so no He bubbles are observed. This indicates the Cu/V 2.5 nm has higher threshold of He concentration to form the He bubbles and thus has more radiation tolerance than Cu/V multilayers with greater h .

Figure 40. (a) and (b) show the depth dependent He concentration profiles of Cu/V 50 nm and Cu/V 5 nm multilayers predicted by SRIM simulation, respectively.

On the other hand, the aforementioned discussions are based on the assumption that the interfacial regions do not trap or reduce the radiation damage. However, it is well accepted that grain or phase boundaries may act as sinks for radiation induced point defects and their clusters, where recombination of interstitial and vacancy could occur and such recovery process assists the interfaces in maintaining their ability to continuously absorb point defects [9-13]. The Cu/V 2.5 nm has 20 times of volume fraction of interfacial region as the Cu/V 50 nm nanlayers at a given total thickness. This means the Cu/V 2.5 nm may have less radiation damage than that predicted by SRIM simulation due to the strong effect of interfaces. This hypothesis has been confirmed by the experimental observation of both de-focused XTEM of peak damage regions in figure 33 and figure 34, and the peak bubble density in figure 35. In the peak damage regions, the irradiated Cu/V 2.5 nm has less radiation damage in terms of He bubbles compared to Cu/V 50 nm upon the same fluence of irradiation. Consequently, the peak bubble density in irradiated Cu/V 2.5 nm is much lower than that in irradiated Cu/V 50 nm at the same fluence level as well. In the previous study, we already discussed the phenomena of reduction of He bubble density in irradiated Cu/V 2.5 nm with respect to the irradiated Cu/V 50 nm. The equilibrium distribution function of He bubbles with the number of vacancies, n , and gas atoms, x [14],

$$\rho^0(n, x) = M_x \exp \left\{ n \ln S_v - \xi n^{2/3} + x \ln \left(\frac{MHn\Omega}{xkT} \right) \right\} \quad (7)$$

is determined by $S_v = \frac{C_v}{C_{v_0}}$ in Cu/V 2.5 nm and 50 nm multilayers.

The interfacial regions are expected to act as effective sinks for radiation induced defects due to the tendency of point defect migration to the interface. Cu/V 2.5 nm has smaller C_v due to the annihilation of vacancies with interstitials and larger value of C_{v_0} due to the interface effect. The reduction of He bubble density in multilayers is thus a combined effect of enhanced

defect storage capacity (increasing C_{V_0}) and increased probability of defect annihilation at interfaces (decreasing C_V).

The magnitude of the peak shift in both peak Cu (100) and peak V (110) in irradiated Cu/V 50 nm increases with the increase of radiation fluence. In Cu/V 2.5 nm sample, the magnitude of peak shift increases very small even subjected to the highest fluence of $1.2 \times 10^{21} / \text{m}^2$ in the study. These observations result in the conclusion that the peak shift in Cu/V 50 nm is more significant than that in Cu/V 2.5 nm. Peak shift is related to the change of d-spacing or lattice parameter induced by defects. Higher magnitude of peak shift implies more radiation damage. In Cu/V 2.5 nm, less peak shift indicates a large number of interface can effectively absorb the radiation induced point defects.

Lattice expansion deduced from XRD studies shown in figure 7c provides another means to evaluate the radiation damage level. A couple of factors can contribute to lattice distortions, such as dissolution of solute atoms, vacancies, He bubbles, interstitials, and interstitial loops. The previous study indicated insignificant contributions to lattice distortion from interstitials and interstitial loops. Up to 2 at. % of Cu can be dissolved in V according to phase diagram, so the maximum lattice expansion induced by dissolution of Cu in V is 0.46 % with assumption of a maximum of 2 at % Cu into V. Other major contribution to lattice expansion is the He bubbles according to previous studies. Pressurized He bubbles could lead to lattice expansion based on the point source dilatation mechanism [15]. The less lattice expansion in Cu/V 2.5 nm compared to Cu/V 50 nm confirms again the Cu/V multilayer with smaller h has less defects and thus has more radiation tolerance than that with greater h .

Radiation hardening mechanisms

Radiation hardening and its strengthening mechanism together with the effect of interface in irradiated Cu/V multilayer films have been discussed previously. The increase of the hardness after irradiation is attributed to the interactions of dislocations with two types of radiation-induced defects, which are strong obstacles, such as interstitials, interstitial loops, SFTs and precipitates, and relatively weak obstacles, such as He bubbles [16-18]. Based on this description, the dispersed barrier model for strong obstacles and FKH model for weak obstacles were applied to explain and estimate the radiation hardening in irradiated Cu/V multilayer films, respectively. The magnitude of radiation hardening is reduced continuously with decreasing h , and became negligible at $h \leq 2.5$ nm. In the irradiated Cu/V multilayer with a few nanometer length scale, the negligible radiation hardening was consistent with the estimation of He bubbles induced hardening based on the FKH model. This indicates the He bubbles play a dominant role in the radiation hardening of the irradiated Cu/V multilayers at small length scale. As the radiation fluence varies to the Cu/V multilayers with small h , radiation hardening changes slightly based on the distribution of He bubbles. But the magnitude of radiation hardening remains low. For example, the estimation of He bubble induced radiation hardening in irradiated Cu/V 2.5 nm multilayer with a fluence of $1.2 \times 10^{21} / \text{m}^2$ is 0.12 GPa, according to FKH model, which is very close to the experimental observation of radiation hardening of 0.2 GPa. The difference between them could be attributed to the other defects induced hardening at higher radiation fluence.

On the other hand, when the irradiated Cu/V multilayers have greater h , radiation hardening is induced not only by the He bubbles but also by other defects, such as interstitial loops. The interstitial loop induced hardening can be estimated by the dispersed barrier model

based on the fact that they are treated as the strong obstacles to the trespassing of the dislocations. Due to the difficulty to quantify interstitial loop density from the XTEM experiments, it is very hard to estimate the interstitial loop induced hardening by obtaining the interstitial loop density. But dispersed barrier model can be used to estimate average interstitial loop density assuming a known interstitial loop induced hardening. In this study, it is given by subtracting the He bubble-induced-hardening from the observed experimental hardening. The estimation of average interstitial loop density with an assumption of size of 2 nm is estimated as $0.7 \times 10^{23} / \text{m}^3$ for Cu/V 50 nm multilayer upon $1.2 \times 10^{21} / \text{m}^2$ of He ion irradiation fluence, which is on the same order of the interstitial loop density of $6.7 \times 10^{23} / \text{m}^3$ and $2.3 \times 10^{23} / \text{m}^3$ in neutron-irradiated polycrystalline pure Cu and V metals subjected to a total dose of 0.92 dpa and 0.69 dpa, respectively [19].

In addition to the similar trend of the radiation hardening observed in irradiated Cu/V multilayers upon He ion irradiation with various fluences, another significant observation is the saturation of radiation hardening when the radiation fluence reaches a certain value. The dispersed barrier hardening model indicates the magnitude of radiation hardening increases as $N^{1/2}$, where N is the defect density. In the absence of mechanisms for the destruction of obstacles, N is proportional to the total fluence of ion irradiation, so the radiation hardening should be proportional to $(\phi)^{1/2}$ and can be expressed by [20]

$$\Delta\sigma_s \propto (\phi)^{1/2} \quad (8)$$

Where $\Delta\sigma_s$ is the increase of yield strength and ϕ is the radiation fluence. At low doses, the radiation hardening is estimated accurately and can be fit with a $(\phi)^{1/2}$ dependence quite well by the equation above. This equation indicates radiation hardening will continue to increase with

increasing radiation fluence without a limit. Hence it will clearly overestimate the hardening once the radiation induced defect density reaches saturation. At higher fluence, the radiation usually reaches saturation because of cascade overlap [21, 22]. In trying to account for saturation of radiation hardening, Makin and Minter proposed that the displacement cascade can not create new zone in the neighborhood of an existing zone or cluster because the reduced volume available for new zones formation cause it harder to form as the concentration increases [23]. They suggested a two parameter equation to predict radiation hardening;

$$\Delta\sigma_s = A[1 - \exp(-B\phi)]^{1/2} \quad (9)$$

Where A and B are regression coefficients. This expression shows a progress transition from the low-dose region with $(\phi)^{1/2}$ dependence to the saturation regime with an asymptotic value A at very high dose [24].

For simplicity, another approach called the power-law expression can also be used to evaluate the saturation of radiation hardening.

$$\Delta\sigma_s = m\phi^n \quad (10)$$

Where m and n are regression coefficients, ϕ is the radiation fluence, and can be replaced by dpa [25, 26].

When the radiation dose is greater than the saturation dose, the exponent n for Cu and V is 0.01 and 0.13, where the saturation dose is 0.05 dpa for Cu and 0.003 dpa for V, respectively [24]. The corresponding coefficient m , representing the magnitude of radiation hardening, is 290 MPa for Cu and 280 MPa for V, respectively [24]. In the case the saturation dose is much smaller than the present study, so the coefficient of m and n can be used to estimate the saturation of radiation hardening in the irradiated Cu/V multilayers. When h is 50 nm in the

Cu/V multilayer irradiated up to a total fluence of $1.2 \times 10^{21} / \text{m}^2$, the average dose deduced from Figure 39 is 6 in Cu layer and 4 in V layer. The estimation of radiation hardening is the average value of the hardening contributed from both Cu and V layers. By incorporating the dose, m and n , the calculation of radiation hardening based on power-law expression is 0.85 GPa in Cu/V 50 nm multilayer irradiated by fluence of $1.2 \times 10^{21} / \text{m}^2$. Similarly, the calculated value for radiation hardening in irradiated Cu/V 50 nm with a fluence of $6 \times 10^{20} / \text{m}^2$ is 0.81 GPa. Both values are slightly greater than the experimental data of 0.60 GPa and 0.50 GPa of radiation hardening in irradiated Cu/V 50 nm multilayer. The slight difference between the calculation and experiment value could be due to the reduction of radiation damage (dpa) induced by the effect of interface. Better regression coefficients of m and n for this case can be obtained by fitting the experimental data based on the power-law expression.

Compared to Cu/V 50 nm multilayer, Cu/V 5 nm multilayer has much larger volume fraction of atoms at interfacial regions. Previous study shows the interfacial region can significantly reduce the radiation damage, so the regression parameters used in estimating hardening by power-law expression in irradiated Cu/V 50 nm multilayer will deviate to evaluate the hardening in irradiated Cu/V 5 nm multilayers due to a higher density of interfaces. For an example, by using the m and n of regression coefficients together with the radiation damage from SRIM for irradiated Cu/V 5 nm, the radiation hardening is estimated to be 0.86 GPa and 0.82 GPa, which is much greater than the experimental value of 0.40 GPa and 0.36 GP in irradiated Cu/V 5 nm with fluence of $1.2 \times 10^{21} / \text{m}^2$ and $6 \times 10^{20} / \text{m}^2$, respectively. The discrepancy could be due to the reduced radiation damage induced by greater density of interfacial region in irradiated Cu/V 5 nm, whereas the SRIM failed to consider the strong interfacial effect. On the other hand, regression coefficients of m and n can be fitted according

to the experimental values in irradiated Cu/V 50 and Cu/V 5 nm multilayers with various fluences based on the power-law equation when radiation damage is known. For an example, the fitting power-law expression based on experimental data multilayer with various fluences of $6 \times 10^{20} / \text{m}^2$, $1.2 \times 10^{21} / \text{m}^2$, and $1.8 \times 10^{21} / \text{m}^2$ for irradiated Cu/V 50 nm is

$$\Delta\sigma_s = 133.9 (\phi/10^{20})^{0.175} \quad (11)$$

where $m = 133.9 \text{ MPa}$ and $n = 0.175$, and for irradiated Cu/V 5 nm is

$$\Delta\sigma_s = 106.6 (\phi/10^{20})^{0.123} \quad (12)$$

where $m = 106.6 \text{ MPa}$ and $n = 0.123$. The values for the exponent $n = 0.175$ and $n = 0.123$ are within the range of 0.07-0.18 and 0.01-0.24 in the high-dose regime in BCC and FCC metals, respectively [24]. This fitting expression could evaluate the radiation hardening in irradiated Cu/V 50 nm and irradiated Cu/V 5 nm with various fluences, which are greater than the saturation dose.

3.2.6. Thermal stability of Cu/V nanolayers

To investigate the thermal stability of Cu/V nanolayers, a series of annealing experiments were performed on Cu/V films deposited on oxidized Si substrates under 10^{-6} torr vacuum at 400 °C and 600 °C for 1 h. XRD experiments were performed by using Bruker-AXS D8 VARIO high-resolution X-ray diffractometer.

X-ray diffraction patterns of Cu/V 1 nm, 2.5 nm and 50 nm nanolayers annealed at 400 °C and 600 °C are shown in the Figure 41 (a), (b) and (c), respectively. The overlap of V (110) and Cu (111) has been observed in as-deposited Cu/V nanolayers with smaller layer thickness ($h = 1$ nm and 2.5 nm) in the previous studies. In Cu/V 1 nm and Cu/V 2.5 nm specimens, after annealing at 400 °C for an hour, the overlapped peak tends to separate into two peaks and the peak intensity is higher than that in as-deposited samples. The peak separation is complete when the annealing temperature increases to 600 °C. As shown in Figure 41(c), annealing at 400 °C leads to stronger Cu (111) and V (110) peaks. However, annealing at 600 °C leads to the

disappearance of V (110) peak with an even stronger Cu (111) peak. The evolution of microstructure is to be explored by XTEM in detail.

Figure 41. XRD pattern of as-deposited and annealed Cu/V nanolayers with individual layer thickness of (a) 1 nm, (b) 2.5 nm, and (c) 50 nm.

The hardness and indentation modulus of films was measured by means of an indentation load and depth sensing apparatus, a commercial Fischerscope HM2000XYp, using a Vicker's indenter. Indentation depth was kept at about 200 nm for all experiments. The effect of annealing

temperature on the hardness of the Cu/V nanolayers is shown in Figure 42. When h is ≥ 25 nm, only slight hardening is observed after annealing up to 600 °C. When h is ≤ 10 nm, annealing at 400 °C leads to obvious hardening, and the magnitude of hardening increases with decreasing layer thickness. However, hardness decreases in all specimens after annealing at 600 °C. It is unclear why annealing leads to the observed hardness variation. XTEM studies are underway to investigate the role of microstructure on hardness change.

Figure 42. Comparison of hardness of as-deposited and annealed Cu/V nanolayers vs. $h^{-0.5}$, where h is the individual layer thickness.

3.2.7. Evolution of microstructure and mechanical properties of miscible Al/Nb multilayers after He irradiations

Al/Nb nanolayers were deposited by magnetron sputtering technique. The cross-sectional TEM (XTEM) micrograph of as-deposited Al 5 nm/Nb 5 nm (referred to as Al/Nb 5nm) multilayers is shown in Fig. 43a. No significant intermixing is observed. Furthermore the multilayer has strong fiber texture, Al {111} and Nb {110}, with a K-S orientation relationship. HRTEM micrograph of the Al/Nb interface shown in Fig. 43b indicates little intermixing along

interfaces. Fast Fourier transforms from the micrograph confirm a K-S orientation relationship, and more importantly show that atomic arrangement is such that Al{111} and Nb{110} atomic planes are continuous across interface.

Fig. 43. (a) Cross-sectional TEM micrograph of as-deposited Al/Nb 5nm multilayer films with Kurdjumov-Sachs orientation relationship between bcc Nb and fcc Al grains. The film has strong {111} Al and {110} Nb fiber texture as shown by the inserted SAD pattern. (b). Cross-sectional view of high resolution TEM (HRTEM) micrograph of as-deposited Al/Nb 5nm multilayer films. The micrograph indicated near perfect Al and Nb crystal structures along interface without sign of intermixing.

SRIM simulation

SRIM simulations of He ion irradiation have been performed on Al/Nb multilayer films with a nominal layer thickness of 50 nm each layer. The radiation was simulated at 100 keV He⁺ ions with a dose of 6×10^{16} ion/cm². Fig. 44a shows the variation of He concentration vs. implantation depth and Fig. 18b shows the DPA as a function of depth. Comparing to Fe/W system irradiated with similar energy and dose, the He ions penetrated much deeper in Al/Nb system with peak damage of approximately 450 nm underneath the film surface than that, ~ 250 nm peak damage in Fe/W multilayers.

Fig. 44. (a) He concentration vs. implantation depth in Al/Nb 50 nm multilayer films. (b) Dpa vs. depth in Al/Nb 50 nm multilayer films. The energy is 100keV and with the same dose of 6×10^{16} ion/cm².

In Fig. 45, XRD profiles of Al/Nb 2.5nm before and after radiation are shown. Before radiation, the peak position of Al (111) and Nb (110) are indistinguishable, as shown in Fig. 45a, because the values of d spacing of the two peaks are essentially the same. The multilayer film also shows strong Al (111) and Nb (110) fiber texture. The first order superlattice satellite peaks are shown and marked as +1 and -1. After radiation, the peak intensity decrease, indicating certain magnitude of disordering of crystalline structure due to radiation damage. The intensity of satellite peaks also decreases, indicating a potential degradation of layer interfaces. The maximum single peak also evolves into a major peak with a shoulder peak to the right. Such peak dissociation behavior is investigated in detail in Fig. 45b. A peak deconvolution is performed and the shoulder peak is indexed to be AlNb₃ (210) diffraction peak. Hence XRD studies indicate the formation of an intermetallic phase after He ion irradiation. Radiation at the same dose and energy did not lead to any intermetallic phases in Cu/V nanolayers (as shown in previous quarter reports). Such a comparison indicates the role of immiscibility (Cu and V are immiscible) on the formation of new phases after radiation.

Fig. 45. (a) XRD profile of Al/Nb 2.5nm before and after He ion irradiation. Before Radiation, the Al (111) and Nb (110) peaks overlap due to their identical d spacing values. The two satellite peaks are labeled as +/-1, originated from nanolayer superlattice structures. After radiation, the peak intensity decreases indicating certain magnitude of disordering of crystalline structure. The occurrence of small shoulder peak is magnified in (b). A peak deconvolution shows the shoulder peak indicates the formation of AlNb₃ intermetallic phase.

After He ion irradiation, XTEM and STEM were used to examine the evolution of layer interface. Fig. 46a shows the bright field XTEM image of Al/Nb 10nm specimen in peak radiation damage region. Layer interface remain geometrically abrupt. However, in STEM mode, the composition maps of Al and Nb, shown in Fig. 46b and 46c show typical “saw tooth” structure along interface. Roughness of layer interface clearly indicates that noticeable interdiffusion occurs along layer interface.

Fig. 46. (a) Bright field XTEM image of Al/Nb 10 nm after radiation. EDX mapping in STEM mode of (b) Al, and (c) Nb.

XTEM image of radiated Al/Nb 100 nm multilayer is shown in Fig. 47. Fig. 47a is the low magnification image of radiated region. Indexing of the inserted SAD pattern shows that certain Al/Nb intermetallic compounds have formed. Fig. 47b and c show the magnified image taken at the peak damage region and a region with slight radiation. A large number of He bubbles are observed in Al in Fig. 47b, whereas bubble density clearly lower in adjacent Nb. In Fig. 47c, He bubble density are very low in Al.

Fig. 47. (a) XTEM image of Al/Nb 100 nm after radiation. Inserted SAD shows the formation of intermetallic compound. Magnified image of Al and Nb at peak radiation damage region (b) and a region with less radiation damage (c), 560 nm below the surface.

Fig. 48. XTEM micrographs of radiated Al/Nb 1 nm multilayers. (a) Peak radiation damage region shows few He bubbles with distinguishable yet distorted layer interfaces. (b) Geometrically abrupt layer interface in a region with little radiation damage.

Fig. 48 shows a series of XTEM snapshots of radiated Al/Nb 1 nm along implantation path. In region of peak radiation damage, 48 (a), layer interface retains but distorted, and He bubbles are occasionally observed. In deeper regions, 48 (b), few He bubbles are observed in clearly distinguishable nanolayers.

Fig. 49. Investigation of radiation damage in a surface region of Al/Nb 2.5 nm nanolayers. (a) XTEM image indicates a rough interface after radiation. (b) HRTEM studies show a saw-tooth type of rough interface after radiation. The interface roughness is estimated to be ~ 1.2 nm. (c). STEM studies of layer interfaces in the same region. Layer interface seems be chemical abrupt without clear indications of interruption of layer interfaces. (d) EDX mapping with a 1 nm probe size on a line drawn normal to the layer interfaces as shown in 49c. Interdiffusion clearly occurs along layer interfaces.

Systematic HRTEM studies were performed to investigate the evolution of interfaces after radiation of Al/Nb 2.5 nm multilayers. Figures 49-51 show the evolution of microstructure in radiated Al/Nb 2.5 nm specimen at locations of close to the surface (Fig. 49), peak damage (Fig. 50), and a very deep region with little damage (Fig. 51).

As shown in Fig. 49a representing the surface region, the Al/Nb layer interfaces is rough, but remain distinguishable. The saw-tooth type of roughness is magnified in Fig. 49b. The roughness is approximately 1.2nm. The observation of saw-tooth interface indicates that interdiffusion may have occurred along layer interface. Scanning transmission electron microscopy (STEM) and EDX analysis were performed to examine the integrity of irradiated layer interface and the results are shown in Fig. 49c and d. A 1 nm probe size was used for STEM and EDX analysis. Fig. 49c shows qualitatively that the layer interfaces retain without clearly indication of the saw-tooth structures. Semi-quantitative composition analysis via EDX shows the composition profile along a straight line drawn normal to the layer interface (shown in 49c). As shown in Fig. 49d, there is clearly some inter-diffusion along layer interfaces, consistent with the HRTEM observations in Fig. 49b, and XRD studies in Fig. 45b. These studies also indicate that the formation of intermetallic phases seem to occur along layer interfaces, and HRTEM studies suggest that the intermetallic phase (AlNb_3) is not amorphous.

Fig. 50. Evolution of microstructure and chemistry in peak damage region of Al/Nb 2.5 nm multilayers. (a) XTEM image show the retention of layer interfaces at a peak dpa value of 5. (b) HRTEM images confirm the crystalline nature of each phase along interface. (c) STEM analysis of layer interface. The interface roughness seems to be higher in peak damage region than that in Fig. 50c. (d) The position profiles from the line scan shown in Fig. 5d. Intermixing clearly occurs along layer interface.

Similar studies were performed in peak radiation damage region, ~ 400 nm underneath film surfaces, of the same specimen and results are shown in Fig. 50. Layer interface seems to be well distinguishable without indication of saw-tooth type of interface roughness as shown in Fig. 50a and 50b. Chemical analysis via STEM, shown in Fig. 50c, seems to indicate that interfaces are not as sharp as those in Fig. 49c (surface region). Again chemical analysis from line profile confirms interdiffusion along layer interfaces. The magnitude of interdiffusion (from 50c) in the peak damage region seems to be more severe than that in the surface region.

At a region of around 1500 nm below the surface, there is very little radiation damage. As shown in Fig. 51a and 51b, layer interface is clearly distinguishable without detectable roughening. HRTEM micrograph also indicates crystalline nature of Al and Nb without the formation of amorphous phase along layer interfaces. STEM analysis coupled with EDX line

scan confirmed that the layer interfaces are chemically abrupt without signs of intermixing as shown in Fig. 51c and 51d.

Fig. 51. At a depth of 1500 nm underneath film surface, the Al/Nb 2.5 nm nanolayer has structure essentially the same as those of as-deposited film. (a) XTEM micrograph shows clearly distinguishable Al/Nb layer interfaces (b) HRTEM image of the same area shows the retention of crystalline structure. The thickness of each layer is uniform without signs of rough interface. (c) STEM analysis of the same area shows the chemically abrupt layer interfaces. (d) EDX line scan with a resolution of 1 nm from the blue line shown in Fig. 51c, shows very little intermixing along layer interfaces.

We now attempt to estimate the radiation hardening observed in radiation Al/Nb multilayers. As shown in Fig. 52, radiation induces hardening in essentially all specimens with h varying from 100 to 1 nm. Furthermore the magnitude of radiation hardening seems to increase with decreasing h .

Fig. 52. Evolution of hardness after radiation in irradiated Al/Nb multilayers. The hardness of as-deposited and two batches of irradiated multilayers are shown as a function of $h^{-1/2}$, where h stands for individual layer thickness. In both as-deposited and ion-irradiated multilayers, hardness increases with decreasing h . Radiation induces hardening in all multilayers, and the magnitude of radiation hardening increases with decreasing h .

Fig. 53. The formation of an intermetallic layer, AlNb_3 , along Al/Nb layer interfaces lead to a trilayer type of structure.

As shown from XRD, and STEM analysis, radiation induces the formation of an intermetallic phase, AlNb_3 , along layer interfaces. Essentially a trilayer structure may be formed as shown schematically in Fig. 53. The thickness of the intermetallic phase is ~ 1 nm, and we assume its thickness remain constant for all irradiated multilayers with different h . The hardness of the intermetallic AlNb_3 phase is very high, approximately 9.8 GPa, based on literature studies of the bulk alloys. We now estimate radiation hardening due to the formation of this intermetallic phase by using a rule-of-mixture type of composite model. The hardness of single layer Nb and Al films are also determined independently. The results of

hardening, ΔH , is plotted vs. $h^{-1/2}$ as shown in Fig. 54. Calculation based on rule-of-mixture

principle is shown by a dash line. The calculation seems to describe size dependent radiation hardening very well.

Fig. 54. Radiation hardening vs. $h^{-1/2}$ for ion irradiated Al/Nb multilayers. The calculation based on rule-of-mixture values seems to fit experimental results very well. A tri-layer structure is used as a prototype based on the formation of AlNb₃ intermetallic layer.

3.2.8. Evolution of microstructure and mechanical properties of Fe/W before and after ion irradiation.

Fe/W was chosen as both constituents have high melting point and could be beneficial for high temperature use in nuclear reactor. Furthermore, both materials have relatively open crystal structure, body-centered cubic structure (bcc), and could enhance the capability of damage storage induced by radiation.

SRIM calculation of He ion irradiation was performed on Fe/W multilayer films with a nominal layer thickness of 50 nm each layer. Three ion irradiation conditions (different energy, 50, 100, 150 keV, but same dose 6×10^{16} ions/cm²) have been used to compare the distribution of He in films using simulation. Figure 55 show the variation of He concentration and displacement per atoms (dpa) vs. implantation depth. For the case of $E = 100$ keV, the simulation

predicts that He peak occurs between 200 nm and 350 nm under film surface, and damage region occurs between 100 nm and 250 nm underneath film surface.

Fig. 55. SRIM simulation of He ion irradiation of Fe/W 50 nm multilayers with ion energy of 50, 100 and 150 keV, and the same dose of 6×10^{16} ion/cm² (a) He concentration vs. implantation depth. (b) dpa vs. depth.

Microstructure evolution of irradiated Fe/W multilayer films

Distinct Fe (110) and W (110) peaks are observed in XRD patterns of Fe /W 50 nm and Fe /W 5 nm multilayers as shown in Figure 56. After ion implantation, peak intensity drops accompanied with peak broadening and peak shift.

Fig.56. X-ray diffraction patterns of Fe/W 50 nm and Fe/W 5nm multilayers showing peak intensity drop, peak broadening and peak shift after He ion irradiations.

We have performed transmission electron microscopy on some of sputter-deposited Fe/W multilayers. Fe/W 5nm multilayer films have uniform layer structure and clearly distinguishable interface between Fe and W as shown in the TEM micrograph of Figure 57. Selected area diffraction pattern (SAD) from the micrograph has indicated (110) Fe and (110)W fiber texture as shown in the inset of Fig. 57. Such observation is consistent with the result of x-ray experiments. Figure 58a show the cross-sectional microstructure of as-deposited Fe50nm/W50nm multilayer films. Both constituents have polycrystalline microstructures. The polycrystalline nature of the films is confirmed by inserted selected area diffraction pattern. The multilayer films have weak $\{110\}$ texture perpendicular to the layer interfaces. The interface between Fe and W is straight and clear without signs of intermixing. Figure 58b is a magnified micrograph taken from the same specimen. It indicates that both Fe and W have nanocrystalline grain size and their grain sizes are smaller than the layer thickness.

Fig. 57. Cross-sectional TEM micrograph of as-deposited Fe/W 5nm multilayer films. Interface between Fe and W are clearly distinguishable. The multilayer films have $\{110\}$ fiber texture in both Fe and W as shown in the inserted selected area diffraction pattern (SAD).

Fig. 58. Cross-sectional TEM micrograph of Fe50nm/W50nm multilayer thin films. Interfaces are clear and straight without signs of interface intermixing.

Cross-sectional TEM (XTEM) image of Fe/W 50nm and 5 nm multilayer films after He irradiations show He bubbles, 1-2 nm, in both Fe and W, and along interface in peak radiation damage zone. Evolution texture is consistent with XRD observations.

Fig. 59. Cross-sectional TEM micrograph of ion irradiated Fe/W 5nm multilayer films. Radiation induce bubbles with an average diameter of approximately 1-2 nm. Ion irradiation did not change the film texture (110)Fe and (110)W. There is no indication for the formation of new phase after ion irradiation.

SRIM calculations have shown that under current ion implantation condition, the radiation damage will possess a Gaussian distribution with peak damage occurring at around 400 nm

underneath film surfaces. We have examined the microstructure of ion irradiated Fe/W 5nm and 50nm multilayer films. Figure 59 shows the cross-sectional view of the microstructure of ion irradiated Fe/W 5nm in heavily ion-irradiated region (400nm underneath film surface). Ion irradiation has introduced He bubbles in these very fine multilayer films. The average diameter of He bubbles is approximately 1-2 nm. The layer structure of Fe/W multilayer films seem to be rather stable. Such phenomenon is a little surprising as significant intermixing is expected due to the miscibility between Fe and W according to phase diagram. A variety of new phases are also indicated on the phase diagram at intermediate temperature. However, both TEM and XRD studies of ion implanted Fe/W 5nm multilayer films do not show the generation of new phases. Such new phases are expected to form due to significant intermixing that could be generated during ion irradiation. The suppression of the new phase and the integrity of interface stability after ion irradiation could be understood as follows: (i) both Fe and W possess bcc structure, with a lower packing density than fcc metals. Cu and Ni multilayer films with fcc structures in both layer are subjected to ion irradiation at the similar conditions. The layer interfaces are completely destroyed after ion irradiation. It is conceivable that the inherent low packing density of bcc metal alleviate ion irradiation induced intermixing along layer interfaces. (ii) W has a very high melting point ($T_m = 3370^\circ\text{C}$), the displacement per atoms generated in W is less than that in Fe ($T_m = 1535^\circ\text{C}$) according to the SRIM calculation. At the current ion irradiation condition (150keV), the radiation may not be sufficient to induce intermixing or new phases. We will investigate such phenomenon in more details. For instance, scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) will be employed to detect the trace of new phases along Fe/W interface after ion irradiation.

Fig. 60. Microstructure of Fe/W 50nm films after He ion irradiation. (a) 800 nm underneath film surface. Such region is little affected by ion irradiation. (b) 400 nm underneath film surface. Such region is around peak irradiation dose. He bubbles with 1-2 nm in diameter can be seen in both Fe and W layers.

The microstructure of ion implanted Fe/W50nm multilayer films (total film thickness is around 1 μm) is shown in Fig. 60. Figure 60a shows Fe/W multilayer films at around 800 nm underneath the film surface. Microstructure of Fe/W multilayer films remains similar to as-deposited films as such region has undergone a minimal ion irradiation. Figure 60b shows a dramatic different microstructure. The under focused TEM micrograph clearly shows that He bubbles with around 1-2 nm in diameter have formed in both Fe and W layers with a larger He bubble concentration at along Fe/W interfaces. The formation of He bubbles is a result high dose He ion irradiation. Helium bubbles align along grain boundaries and layer interfaces as indicated by arrows in Fig. 60b. Interface and grain boundaries seem to play certain role in accumulating He bubbles. The SAD of the micrograph of heavily ion irradiate region does not reveal extra diffraction spots except that of pure Fe and W. It again indicates that the formation of new intermetallic phase is under the detection limit of current technique.

Figure 61a is the XTEM overview image of Fe/W 1nm multilayer films after He ion irradiation. We took micrographs from seven different depths starting from film surface to 1200 nm underneath film surface. The goal is to examine the distribution of radiation induced defect as a function of depth under film surface. Figure 61b was taken at about 75nm beneath the film surface. It shows that after He ion irradiation, layer structure disappeared, and no obvious sign of He bubbles. Figure 61c and 61d, taken at about 260 and 340 nm below the film surface, reveal a large number of He bubbles without layer structure. This is heavily radiated region as predicted by SRIM calculations. Figure 61e taken at 420 nm below the surface shows a reduction of He bubble concentration, and signs of layer structure at the bottom region of the image, indicating reduced He ion irradiation damage. Radiation damage continues to decay and layer structure becomes more and more clear in the following regions, as shown in Figure 61f and 61g. Finally at about 1200nm underneath the surface, the microstructures look identical to unirradiated specimens, as shown in Figure 61h, i.e., layer structures are clearly visible without signs of intermixing.

Figure 61 (a) XTEM images of Fe/W 1nm multilayer film after He ion irradiation. (b) – (h) XTEM micrograph taken at different depth underneath film surface as marked in 61a. Radiation damage in the form of He bubbles, and layer intermixing were detected.

The hardnesses of as-deposited Fe/W multilayer films are compared to that of ion irradiated Fe/W multilayer films as a function of $h^{-1/2}$, as shown in Figure 62a. After He ion irradiation, the hardness of multilayers increases for $h \geq 5$ nm specimens. When the individual layer thickness is ≤ 2.5 nm, the hardness only increases slightly.

Fig. 62. (a) Comparison of hardness as a function of $h^{-1/2}$ plots for as-deposited and ion irradiated Fe/W multilayer films. (b) Hardness enhancement vs. individual layer thickness showing that hardness increases by about 2 GPa for $h \geq 5$ nm specimens. When h is ≤ 2.5 nm, the hardness only increases slightly or barely changes.

Hardness enhancement after irradiation as a function of h is replotted in Figure 62b. It is clear that hardness change decreases when $h \leq 2.5$ nm, and barely change when $h = 1$ nm. Layer interface in peak damage zone of Fe/W 1 nm multilayer film has disappeared due to intermixing. It is known that the peak hardness of metallic nanolayers is dominated by interfacial barrier strength. The loss of layer interface may degrade the hardness of multilayers. Such an effect may counterbalance the hardness increase due to the entrapment of radiation induced point defects.

3. 3. Project management

Personnel

Dr. Zhang has supported two Ph.D. graduate students working on the project, Mr. Engang Fu and Mr. Nan Li. Mr. Fu started in fall 2005 and has successfully finished his Ph.D. defense and thesis in August 2009. He was awarded a postdoctoral associate position at Los Alamos National Laboratory. Mr. Fu has also been awarded MRS best poster award in 2008, and American Vacuum Society (AVS) Fellowship in 2009. He will receive the AVS fellowship at the AVS annual meeting in November 2009.

Mr. Nan Li started in Jan. 2006, and has successfully defended his Ph.D. prelim exam. Nan's paper on Fe/W ion irradiation damage also has been awarded the first prize by TMS (The Metals, Minerals and Materials Society) and is to attend the award ceremony in spring 09. The first prize award is a nationally and internationally recognized award given to only one student per year.

Dr. Hartwig has a M.S. graduate student, Mr. David Foley, started in Fall 2005 and graduated with M.S. in summer 07. David continues to work for his Ph.D. on the project. Dr. Zhang's graduate students focus on radiation tolerant nanolayer thin films and coatings, whereas Dr. Hartwig's graduate student works on ECAP-processed bulk ultra fine grained and nanocrystalline materials.

Zhang has recruited a US minority MS student, Mr. Jeremy Gonzalez, who is working on radiation damage in bulk 304L and 316L stainless steel. The list and role of personnel is given in Table 2. Four undergraduate students have been recruited to work on specimen preparations for transmission electron microscopy, scanning electron microscopy in the PIs' laboratory. Undergraduate students are supervised by the PIs and work with graduate students on hardness measurement for bulk materials and coatings using nanoindenter.

Table 3. Roles of personnel in the project.

Team members	Role	Supplemental information
Dr. Xinghang Zhang	PI	Nanolayer coatings, ECAP Microscopy, nanoindentation
Dr. K. Ted Hartwig	Co-PI	ECAP processing of bulk materials
Mr. Engang Fu	Ph.D. student	work with Dr. Zhang on Cu/V and Cu/Nb nanolayers
Mr. Nan Li	Ph.D. student	work with Zhang on Fe/W and

		Al/Nb nanolayers
Mr. Jeremy Gonzalez	MS student	work with Zhang on radiation damage in 304L and 316L SS
Mr. David Foley	M.S. student	Work with Dr. Hartwig on ECAE processed bulk materials
Mr. Josh Nichols	undergraduate student	Work with Dr. Hartwig on ECAE processed bulk materials
Mr. Zach Cook	undergraduate student	Work with Dr. Zhang on TEM sample prep
Mr. Bryan Crawford	undergraduate student	Work with Dr. Zhang on TEM sample prep
Mr. Yu Yue	undergraduate student	Undergraduate research grant \$5,000 awarded by TAMU Work on radiation damage in T91 alloys

There are very strong connections between the two approaches (nanolayers and bulk materials) led by X. Zhang and K. T. Hartwig. A team meeting is held every week to discuss the progress of the project. All graduate students working on the projects are trained together on TEM specimen preparations, hardness measurement and differential scanning calorimetry experiments in Zhang's laboratory.

Outreach activities

X. Zhang and his graduate students, Engang Fu, Nan Li and David Foley have attended 08 TMS annual meeting in New Orleans. They have presented latest research results at this meeting in three oral presentations. Wide collaborations with national laboratories (LANL, Oak Ridge National Laboratory, Idaho National Laboratory, and several universities) and participating universities have been planned. The project is intimately integrated within the AFCI program led by Dr. Stuart Maloy. Mr. Nan Li is working on his multilayer project at Sandia National Laboratory with Dr. Jianyu Huang in summer 08. This collaboration is based on Dr. Zhang's user proposal selected by Center for Integrated Nanotechnologies at Sandia National Laboratory.

X. Zhang spent two summer weeks at Los Alamos National Laboratory to work on the project with Los Alamos collaborators. Extensive collaborations will be strengthened between Texas A&M University and Drs. Stuart Maloy, Ning Li for irradiation and corrosion studies. We have been collaborating with Dr. Hoagland at LANL on modeling of radiation induced damage in Cu/Nb multilayer thin films. Drs. Amit Misra and Mike Nastasi provided access to their thin

film synthesis equipment to Zhang and his graduate students. Such collaborations ensure that we will intimately work with LANL AFCI team led by Dr. Maloy and remain focused throughout the project. The collaborations also enable a maximum usage of research sources and significantly reduce the cost for this DOE funded project.

Collaboration has been established with Dr. Todd Allen at U. Wisconsin for stress corrosion cracking studies of ECAE processed T91 and HT9 alloys. Collaboration with Prof. Lin Shao at Nuclear Engineering Department, Texas A&M University has been established. Prof. Shao has recently acquired two tandem accelerators with 1.0 and 1.7MeV capability. Additionally ion implantation at various energy and temperature is available at his laboratory at TAMU.

X. Zhang has attended the GNEP/AFCI workshop held in July 07 in Oak Ridge. He presented latest research results at this meeting. Wide collaborations with national laboratories (LANL, Oak Ridge National Laboratory, Idaho National Laboratory, and several universities) and participating universities have been planned. The project is intimately integrated within the AFCI program led by Dr. Stuart Maloy. X. Zhang has also attended the TMS 2007 meeting held in February, 2007 in Florida. He presented some research results at this meeting.

X. Zhang spent one summer month at Los Alamos National Laboratory to work on the project with Los Alamos collaborators. Extensive collaborations will be strengthened between Texas A&M University and Drs. Stuart Maloy, Ning Li for irradiation and corrosion studies. We have been collaborating with Dr. Hoagland at LANL on modeling of radiation induced damage in Cu/Nb multilayer thin films. Drs. Amit Misra and Mike Nastasi provided access to their thin film synthesis equipment to Zhang and his graduate students. Such collaborations ensure that we will intimately work with LANL AFCI team led by Dr. Maloy and remain focused throughout the project. The collaborations also enable a maximum usage of research sources and significantly reduce the cost for this DOE funded project.

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4. Patents: N/A

5. Publications/Presentations:

Presentations:

1. X. Zhang and K. T. Hartwig, “Development of Nanostructured Materials with Improved Radiation Tolerance for Advanced Nuclear Systems”, DOE-AFCI and Gen IV Materials Working Group meeting, Albuquerque, March 30, 2005.
2. K. T. Hartwig and X. Zhang, “Development of Nanostructured Materials with Improved Radiation Tolerance for Advanced Nuclear Systems”, Invited talk, University of Wisconsin, Madison, June 2005.
3. X. Zhang, invited talk, “Interface Induced Strengthening in Nanolayered Materials”, graduate seminar in the Department of Nuclear Engineering, hosted by Prof. Yassin Hassan, 2005.
4. X. Zhang and K. T. Hartwig, “Development of Nanostructured Materials with Improved Radiation Tolerance for Advanced Nuclear Systems”, DOE-AFCI and Gen IV Materials Working Group meeting, Santa Fe, NM, March 1, 2006.
5. X. Zhang, invited talk, “Radiation Effects in Nanostructured Metallic Materials”, 19th International Conference on the Application of Accelerators in Research and Industry, Dallas, TX, August, 2006.
6. X. Zhang, “Thermal stability of metallic thin films with nanoscale growth twins”, 2007 TMS Annual meeting, Orlando, FL, 2007.
7. X. Zhang and K. T. Hartwig, “Development of Nanostructured Materials with Improved Radiation Tolerance for Advanced Nuclear Systems”, DOE-AFCI and Gen IV Materials Working Group meeting, Oak Ridge National Laboratory, TN, July 2007.

8. X. Zhang, “Radiation induced damage in nanostructured metallic multilayers”, Los Alamos National Laboratory, July 2007, invited talk.

9. X. Zhang, “Radiation induced damage in nanostructured metallic multilayers”, Sandia National Laboratory, Albuquerque, NM, July 2007, invited talk.

10. D. Foley, K. T. Hartwig, S. Maloy, and X. Zhang, “Grain refinement and radiation damage in ECAP processed T91 alloys”, Society of Engineering Sciences (SES) Conference, Oct. 2007, College Station, TX.

11. X. Zhang, E.G. Fu, and Nan Li, “Mechanical properties of Cu-based nanolayers”, invited talk, SES conference, Oct. 2007, College Station, TX.

12. E.G. Fu, Nan Li, A. Misra and X. Zhang, “Mechanical properties of ion irradiated Cu/V nanolayers”, SES conference, Oct. 2007, College Station, TX.

13. Nan Li, E.G. Fu, A. Misra and X. Zhang, “Mechanical properties of ion irradiated Fe/W nanolayers”, SES conference, Oct. 2007, College Station, TX.

14. E.G. Fu, Nan Li, A. Misra and X. Zhang, “Interface enhanced radiation tolerance in radiated Cu/V nanolayers”, 2008 TMS annual meeting, New Orleans, LA.

15. Nan Li, E.G. Fu, A. Misra, S. A. Maloy, and X. Zhang, “He ion irradiation in Fe/W nanolayers”, 2008 TMS annual meeting, New Orleans, LA.

16. D. Foley, K. T. Hartwig, S. Maloy, and X. Zhang, “Microstructure refinement of T91 for enhanced radiation tolerance”, 2008 TMS annual meeting, New Orleans, LA.

17. X. Zhang, “Microstructure and mechanical properties of radiated T91 and metallic nanolayers”, Los Alamos National Laboratory, 2008 summer.

18. X. Zhang, “Radiation tolerant metallic nanolayers”, MS&T 2008, invited talk, Pittsburgh, PA.
19. E.G. Fu, and X. Zhang, “Radiation damage in Cu/V nanolayers”, TMS annual meeting, 2009, San Francisco, CA.
20. Nan Li and X. Zhang, “Radiation damage in Al/Nb and Fe/W nanolayers”, TMS annual meeting, 2009, San Francisco, CA.

Publications:

1. X. Zhang, A. Misra, H. Wang, J.G. Swadener, A. L. Lima, M. F. Hundley and R.G. Hoagland, “Thermal Stability of Sputter-deposited 330 Austenitic Stainless Steel Thin Films with Nanoscale Growth Twins”, **Applied Physics Letters**, **87** (2005) 233116. Note: The journal is a premier journal with physicists, chemists, materials scientists and industrial researcher as general audience. The impact factor of this journal is higher than 4.0.
2. X. Zhang, A. Misra, H. Wang, X.H. Chen, L. Lu, K. Lu and R. G. Hoagland, “High-strength Sputter-deposited Cu Foils with Preferred Orientation of Nanoscale Growth Twins”, **Applied Physics Letters**, **88** (2006) 173116.
3. X. Zhang, O. Anderoglu, A. Misra, and R. G. Hoagland, “*Influence of Deposition Rate on the Formation of Nanoscale Growth Twins in Sputtered 330 Stainless Steel Thin Films*”, **Applied Physics Letters**, **90**, 153101 (2007).
4. X. Zhang, R. K. Schulze, H. Wang, and A. Misra, “Thermal Stability of Sputtered Cu/304 Stainless Steel Multilayer Films”, **Journal of Applied Physics**, **101**, 124311 (2007)..
5. X. Zhang, N. Li, O. Anderoglu, H. Wang, J. G. Swadener, T. Höchbauer, A. Misra and R. G. Hoagland, “Nanostructured Cu/Nb Multilayers Subjected to Helium Ion Irradiation”, **Nuclear Instrument Method in Physics Research B**, v 261, n 1-2, August, 2007, p 1129-1132.
6. H. Wang, R. Araujo J.G. Swadener, Yongqiang Wang, X. Zhang, E. G. Fu and T. Cagin *Ion Irradiation Effects in Nanocrystalline TiN Coatings*, submitted to **Nuclear Instruments and Methods in Physics Research B**, v 261, n 1-2, August, 2007, p 1162-1166.
7. “Microstructure and Mechanical Properties of Sputter-deposited Cu-V and Al-Nb multilayer Films” by E.G. Fu, Nan Li, H. Wang, A. Misra, and X. Zhang, **Materials Science and Engineering, A**, 493 (2008) 283–287.

8. A. Misra, M.J. Demkowicz, X. Zhang and R.G. Hoagland, “The Radiation Damage Tolerance of Ultra-High Strength Nanolayered Composites”, **JOM**, Sep. 2007, p62. (Invited review article).
9. N. A. Mara, A. V. Sergueeva, T. Tamayo, X. Zhang, A. Misra and A. Mukherjee, “*High Temperature Mechanical Properties of Cu/Nb Nanoscale Multilayers at Diminishing Length Scales*”, **Thin Solid Films**, v 515, n 6, Feb 12, 2007, p 3241-3245.
10. Nan Li, M.S. Martin, O. Anderoglu, A. Misra, L. Shao, H. Wang, and X. Zhang, “He ion irradiation damage in Al/Nb multilayers”, *Journal of Applied Physics*, v 105, n 12, p 123522 (8 pp.), 15 June 2009.
11. Nan Li, E.G. Fu, H. Wang, J.J. Carter, L. Shao, S.A. Maloy, A. Misra, and X. Zhang, “He ion irradiation damage in Fe/W nanolayer films”, *Journal of Nuclear Materials*, **389** (2009) 233–238.
12. E.G. Fu, J. Carter, G. Swadener, A. Misra, L. Shao, H. Wang, and **X. Zhang**, “Size dependent enhancement of helium ion irradiation tolerance in sputtered Cu/V nanolaminates”, *Journal of Nuclear Materials*, **385** (2009) 629–632.
13. T.D. Foley, K.T. Hartwig, S.A. Maloy, P. Hosemann, and X. Zhang, “Grain refinement of T91 alloy by equal channel angular pressing”, *Journal of Nuclear Materials*, **389** (2009) 221–224.
14. Carter, J.; Dvorak, B.M.; Fu, E.G.; Bassiri, G.; Theodore, N.D.; Lucca, D.A.; Martin, M.; X. Zhang, Lin Shao; Guoqiang Xie; Hollander, M. Source: *Nuclear Instruments & Methods in Physics Research, Section B (Beam Interactions with Materials and Atoms)*, v 267, n 8-9, p 1518-21, 1 May 2009.
15. E.G. Fu, Jesse Carter, Michael Martin, Guoqiang Xie, X. Zhang, Y.Q. Wang, Rick Littleton and Lin Shao, “Electron irradiation-induced structural transformation in metallic glasses”, *Scripta Materialia* 61 (2009) 40–43.

Manuscript submitted or in preparation

16. E.G. Fu, J. Carter, G. Swadener, A. Misra, L. Shao, H. Wang, and X. Zhang, “Size dependent enhancement of He ion irradiation tolerance in sputtered Cu/V nanolaminates”, under review.
17. “Microstructure and Mechanical Properties of Sputter-deposited Fe/W multilayer films” by N. Li, EG. Fu, H. Wang, K. T. Hartwig, J. G. Swadener, A. Misra, and X. Zhang, submitted.

18. "Thermal stability of ECAP processed T91 alloys", D. Foley, K. T. Hartwig, S. Maloy, P. Hosemann, N. Li and X. Zhang, in preparation.
19. E.G. Fu, L. Shao and X. Zhang, "Thermal stability of sputtered Cu/V nanolayers", in preparation.
20. E. G. Fu and X. Zhang, "Dose dependent radiation damage in Cu/V nanolayers", in preparation.

6. Milestone Status Table

Key milestones and delivery date (month)	Planned completion date	Actual completion date	Comments
1. Obtain materials	06/30/05	06/30/05	
2. Process materials			
2a. Produce bulk alloys with ECAE	10/31/05 10/31/06 05/31/07	08/30/05 (HT-9, 316L SS, 304 SS, EP823, 9Cr-1Mo) 10/06/06 (HT-9, 316L SS, 304 SS, EP823, 9Cr-1Mo, ODS steels) T91 and HT-9 11/06	(HT-9 and 316L SS were sent to Dr. Maloy at LANL for studies)
2b. Synthesize multilayers by magnetron sputtering	(Fe/W) 10/31/05 10/31/06 05/31/07	07/30/05 (Fe/W and Al/Nb) multilayers (330 SS coatings deposited) 06/10/07, Cu/V, Fe/W	

3. Irradiation with ion implantation experiment	11/30/05	10/30/05 (Fe/W)	
	12/30/06	07/26/06 (Al/Nb)	
	07/31/07	03/26/07 (Cu/V)	
4. Materials characterization			
4a. DSC - Identify stable temperature range for nanomaterials	09/30/05		Working on
	04/01/06	T91 alloys obtained	T91 alloys
	09/30/06	Working on T91	
	04/01/07	Cu/V in progress	
	09/30/07		
4b. Resistivity - identify stable temperature range for nanomaterials	09/30/05		TAMU
	04/01/06	12/05, Fe/W	collaborators
	09/30/06	06/06, Fe/W	are working on
	04/01/07		Al/Nb
	09/30/07	06/06, Cu/V 07/07, Cu/V	
4c. Hardness, modulus - Determination of ion damage tolerance	11/30/05	09/05, T91, 316L	
	04/01/06	03/06, Fe/W, Al/Nb	
	09/30/06	Fe/W, Al/Nb tested	
	04/01/07	02/07, Cu/V	
	07/31/07	Irradiated Cu/V	
4d. Tensile tests (ductility) Determination of ion damage tolerance	01/31/06	Plan to test T91 and HT9 alloys	
	04/01/07	02/07, T91 tested	
	09/30/07	08/07, T91,	
4e. XRD - Determination of grain size and strain etc.		Done on T91, HT-9, and nanolayers	Replaced with TEM
4f. SEM - Determination of swelling	01/31/06	01/12/06 No	

resistance from surface morphology	01/31/07 08/31/07	swelling in Fe/W Fracture surface of T91 alloys (03/07)	
4g. TEM and STEM - Determination of defect accumulation and migration	11/30/05 06/30/06 10/31/06 03/31/07 07/31/07 12/31/07	10/30/05, (Fe/W) 03/01/06 (T91, Al/Nb) 06/06 (Fe/W, Al/Nb) HRTEM of Cu/V, Al/Nb TEM of Fe/W, Cu/V, 11/07	Will do more TEM
4h. Corrosion resistance - Determination of corrosion resistance of nanomaterials	05/31/06 11/30/06 07/31/07 02/28/08	07/06, T91 and Al/Nb and Fe/W in Delta Loop	
5. Communication			
5a. 2 conference papers per year anticipated	04/31/06 04/31/07 04/31/08	A total of 17 conference presentations to date.	
5b. Journal publications 3-4 papers per year anticipated	04/31/06 04/31/07 04/31/08	A total of 10 journal articles to date (10/07)	Six papers in preparation
5c. Quarter Report to DOE	Due date 07/30/05 10/30/05 01/31/06 04/31/06 07/31/06	07/28/05 10/28/05 01/05/06 04/08/06 07/29/06	

	10/31/06	10/28/06	
	01/31/07	01/28/07	
	04/30/07	04/26/07	
	07/31/07	07/29/07	
	10/30/07	10/29/07	
	01/30/08	01/21/08	
	04/30/08	04/26/08	
5d. Annual and Other Reports to DOE	Due date		
	10/31/05 (annual)	10/28/05	
	11/09/05 (AFCI semi-annual)	11/08/05	
	01/15/06 (NERI annual report)	12/21/05	
	NERI annual report	10/29/06	
	10/31/06	10/29/06	
	10/31/07	10/29/07	
	10/31/08	10/28/08	
	08/31/09	08/15/09	

7. Budget Data (as of date: August 15, 2009):

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year1	4/15/05	4/14/06	\$209,485	\$70,000	\$279,485	\$139,617	\$43,399	\$183,016
Year2	4/15/06	4/14/07	\$179,948	\$0	\$179,948	\$138,188	\$0	\$138,188
Year3	4/15/07	4/14/08	\$185,756	\$0	\$185,756	\$170,006	\$26,598	\$196,604
	4/15/08	5/31/09				\$125,354	\$3	\$125,357
Totals			\$575,189	\$70,000	\$645,189	\$573,165	\$70,000	\$643,165