Precipitation kinetics of dilute Cu-W alloys during low-temperature ion irradiation

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Abstract

The kinetics of W precipitation in dilute Cu-W alloys during room temperature irradiation is investigated using *in situ* electrical resistivity measurements and transmission electron microscopy. For a series of alloys with W concentrations varying from ~1 at.% to 6 at.%, resistivity measurements show that high dose irradiation leads to steady-state solubility values which are concentration dependent, while electron microscopy shows that the precipitate structures are stabilized at high doses at a size of about 2 nm. These steady states are independent of the initial alloy microstructure: whether it is a solid solution or it contains large W precipitates within the Cu matrix. The effective tracer impurity diffusion coefficient of W in Cu in energetic displacement cascades is determined by *in situ* electrical resistivity measurements on multilayer structures of alternating Cu/W layers, yielding a value of 2.1 nm²/dpa. These multilayer structures are observed to undergo significant interfacial roughening during irradiation, showing signs of transforming from a 2-dimensional to 3-dimensional structure under prolonged irradiation. A model based on a dynamical competition between recoil mixing and thermal spike diffusion is proposed to explain these various results; it is implemented in kinetic Monte Carlo simulations.

1. Introduction

Nanostructured materials have become of interest in the nuclear industry for structural applications owing to their inherently high strength and resistance to irradiation damage [1-4]. The difficulty of using nanostructured materials for engineering applications, and nuclear applications in particular, arises from their tendency to coarsen during exposure to high temperatures and prolonged irradiation. While research on stabilizing the microstructure of nanomaterials at high temperatures has greatly improved in recent years [5-9], far less progress has been achieved in stabilizing these materials under non-equilibrium, irradiation conditions. It is well known, for example, that nanocrystalline metals undergo extensive grain growth during irradiation, even at very low temperatures [10, 11]. Phase stability in nanostructured materials, moreover, also shows sensitivity to irradiation owing to the small length scales of the underlying microstructure and the high energies involved in the ballistic relocation of atoms. For example, typical structural metals such as Fe or Ni have irradiation-induced diffusion rates at low temperatures on the order of $1 \text{ nm}^2\text{-dpa}^{-1}$ [12], where r^2 is the mean square displacement per atom, and dpa is the irradiation dose measured in units of displacements per atom (dpa). As a consequence interdiffusion distances due to ion beam mixing are on the order of some nanometers after a dose of 1 dpa. Since nuclear materials can be subjected to irradiation fluences well over 100 dpa during their service lifetime, the stability of nanostructured materials becomes questionable. At elevated temperatures, radiation-enhanced diffusion can also play a role in the mixing, often increasing the rates of interdiffusion by orders of magnitude [13, 14].

Attempts to overcome this inherent incompatibility of nanostructured materials with nuclear environments have largely focused on utilizing strongly phase-separating systems, including highly immiscible alloys such as Cu-W [9, 15, 16] and Cu-Nb [17, 18], or compound forming precipitates such as nano-ODS (oxide dispersive strengthened) steels [1, 19]. Indeed, an extensive body of work on the stability of nano-ODS martensitic-ferritic steels during irradiation has evolved, owing to the importance of these alloys for nuclear applications. Nano-ODS steels, however, are quite complex, and not well

suited for ferreting out basic mechanisms controlling the stability of nanoprecipitates under irradiation more generally. The present work thus examines the phase evolution during irradiation at room temperature in a similar, but far less complex system, dilute Cu-W alloys. Our study on Cu-W alloys is additionally motivated by past work that showed that nanostructured Cu-10 at.%W alloys were particularly tolerant of irradiation, with grain boundaries and nanoprecipitates remaining stable during irradiation from temperatures ranging from room temperature up to $\sim 0.85 T_m$ where T_m is the melting temperature of Cu [9].

The interest in strongly phase-separating systems for nuclear applications stems largely from past work that showed these alloys, which have high heats of solution > 1 eV/atom (in infinite dilution), tend to be resistant to intermixing during irradiation [15, 20-22]. This finding is rationalized, at least qualitatively, on the basis that mixing within energetic displacement cascade occurs predominantly within the thermal spike phase of a cascade by thermally activated diffusion in a liquid-like zone. Since these systems are quite immiscible, even within the liquid phase, they tend to phase separate, i.e., de-mix, under irradiation [23]. Extensive MD simulations on Cu-Nb alloys have recently elaborated on this problem in some detail [24]. At high temperatures, radiation-enhanced diffusion can further enhance the de-mixing of the alloy. Despite this rather large body of work on ion beam mixing and radiation-enhanced diffusion in immiscible alloys, it remains beyond current capabilities to predict how these systems will evolve under prolonged irradiation. Many fundamental questions, in fact, remain. For example: Will nanoprecipitates dissolve or grow? Will multilayers remain two-dimensional structures, or will they convert to three dimensional morphologies? What determines the mutual solubilities of the two-phase alloys during low-temperature irradiation or the length scales of the two-phase morphologies, assuming they do form? Do these systems ever reach a steady state, or do they slowly coarsen? We attempt to provide answers in this study. First we present a series of experiments using *in situ* electrical resistivity measurements during ion irradiation to follow the kinetics of the phase evolution in systems that are initially solid solutions or multilayers. This is followed by a detailed characterization of the microstructures using transmission

electron microscopy. We then discuss these findings in terms of a simple kinetic model, which we implement using Monte Carlo simulation.

2. Experimental Methods

Four-point electrical resistivity measurements were employed to probe the concentration of W in solution in Cu, while the TEM characterization was used to determine the size distribution of the W precipitates and the stability of the multilayer structures. Figure 1 shows a schematic image of the resistivity measurement setup. The specimens were fabricated through a set of masks on MgO (100) single crystal substrates, using DC magnetron to either co-sputter Cu and W to form the solid solutions, or to sputter pure Cu and pure W alternatively to form the multilayers. The background pressure in the growth chamber was $\approx 2 \times 10^{-8}$ Torr. Up to five samples with different W concentrations could be deposited on a single piece of substrate, labeled as ①-⑤ in Figure 1. The thicknesses of the samples were ≈ 300 nm, while the gauge length and width were ≈ 2 mm and ≈ 0.4 mm, respectively. Rutherford Backscattering (RBS) was used to determine the compositions and the film thicknesses of the solid solution samples, and the alternating layer thicknesses in multilayer samples. The MgO substrates were glued to a piece of leaded chip carrier, as shown in Figure 1. Gold wires were ball-bonded to connect the leads. With this configuration and the instrument settings, the changes in resistivities of the five samples could be measured simultaneously to an accuracy of one part in 10^5 , at a frequency of ~ 0.5 Hz. Irradiations were performed using the 3.0 MeV Van de Graaff accelerator in the Frederick-Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign. The vacuum conditions were better than $\approx 5 \times 10^{-8}$ Torr. The 1.8 MeV Kr ion beam was rastered to provide a uniform flux (~ 100 nA) over an area $\approx (4.5 \text{ mm})^2$, as illustrated by the grey square covering sample ①-④ in Figure 1. The fifth sample was left unirradiated and served as a reference to correct the resistivity for possible beam heating induced temperature drift, although this was typically small, < 10 °C. This small amount of beam heating should not influence the precipitation kinetics as Vo *et al* [9] reported only a very weak dependence of the size of W precipitates on irradiation temperature between room temperature and ≈ 700 °C.

The samples used for TEM characterization were also fabricated using magnetron sputtering onto MgO substrates, but without the application of masks. These samples were subjected to the same irradiation treatments as experienced by the resistivity samples. The TEM sample was prepared in plane view if the sample was initially a solid solution, and in cross section if the sample was a multilayer. Both used traditional polishing-and-milling methods. High angle annular dark-field imaging (HAADF) (Z-contrast imaging) was performed in a JEOL 2010F EF-FEG scanning transmission electron microscope (STEM) and bright field (BF) imaging in a JEOL 2010 LaB₆ microscope.

3. Experimental Results

3.1 Electrical resistivity:

We report first the room temperature (RT) electrical resistivity measurements on as-grown Cu-W solid solutions as a function of W composition. These results are presented in Figure 2 in square symbols, where it is observed that the resistivity increases approximately linearly with W concentration for solute concentrations up to 4.6 at.%. X_W in this figure represents the molar fraction of W in the unit of atomic percent. The measured resistivity for $X_W = 0$ ($\rho = 1.87 \mu\Omega \cdot \text{cm}$) is very close to that of pure, bulk Cu at RT ($\rho = 1.82 \mu\Omega \cdot \text{cm}$), illustrating that the resistivity of the sputtered pure Cu sample is negligible compared to the alloy samples, and that electron scattering due to imperfections in the lattice (e.g. grain boundaries) and the film surfaces can be neglected in the Cu-W alloys. A fit to the resistivity data assuming Matthiessen's rule yields

$$\rho = 1.87 + 11.8 X_W \mu\Omega \cdot \text{cm}. \quad (1)$$

The value at 4.4 at.% W is in good agreement with that reported by Vüllers and Spolenak [25].

The changes in the resistivities of different alloy films are shown in Figure 3 as a function of irradiation dose during exposure to the Kr ion beam at RT; the average dose rate in the films was

$\approx 1.6 \times 10^{-2}$ dpa- s⁻¹. The resistivities of the alloy films initially decrease with dose, but then saturate at different levels. These steady state values of the resistivities are shown in Figure 2 as (red) circular symbols. The change in the resistivity of the pure Cu film in Figure 2 is quite small, although a rapid increase in resistivity of $\approx 0.18 \mu\Omega \cdot \text{cm}$ at the beginning of irradiation is observed, and it is followed by a slow, steady increase of $\sim 2 \times 10^{-3} \mu\Omega \cdot \text{cm}/\text{dpa}$ with increasing dose. The initial increase in resistivity is consistent with a steady state concentration of point defects of $\sim 1 \times 10^{-3}$ [26], which is reasonable for copper at room temperature [27]. The slow increase at higher doses can be explained by sputter erosion of the sample assuming a sputter yield of ~ 5 , which again is quite reasonable. For all of the alloy samples, we will assume in the following that only W atoms in solution contribute to the impurity scattering, i.e., that incoherent W precipitates have little influence. This approximation is justified by noting that the electron mean free path in these W-saturated Cu alloys is $\lambda \sim 3$ nm (see e.g., [28]), which is smaller than the W precipitate spacing after irradiation (see below). The changes in X_W due to irradiation using this assumption are presented in Table 1. While the solubility of W in Cu has decreased significantly during irradiation, it remains orders of magnitude greater than the equilibrium solubility at room temperature [29]. The rates of change of the resistivity with dose, i.e., $d\rho/d\phi$ are shown as inset in this figure. The maxima in these derivatives scale approximately with the square of the as-grown value of X_W , perhaps suggestive of second-order kinetics. The loss of W from solution was also observed using X-ray diffraction from the shifting of the alloy (111) Bragg peak position relative to that of pure Cu peak, but solubilities deduced from these data are less accurate than the resistivity results and therefore not presented here.

X_W -as grown (at.%)	1.1	1.6	3.1	4.7
X_W -irradiation (at.%)	0.76	0.84	1.32	1.92

Table 1 List of W concentrations in as-grown solid solutions and the steady-state W concentrations in RT irradiation.

We tested whether the steady state values of the W solubilities observed in Figure 2 represent true steady states characteristic of irradiated, dilute Cu-W alloys, or whether they depend on the initial microstructure. One of the samples, Cu-1.6 at.% W, was thus first irradiated at RT, similar to the samples in Figure 2, but then annealed at 600 °C for 1 hour. Previous work on Cu-10 at.% W indicated that W becomes mobile and begins to precipitate out of solution in Cu by ~ 450 °C [9]. As shown in Figure 4, the resistivity decreases significantly after this annealing at 600 °C, by ~ 60% from 12.7 $\mu\Omega\cdot\text{cm}$ to 5 $\mu\Omega\cdot\text{cm}$. The sample was then re-irradiated at room temperature under the same beam conditions as before, and as shown in Figure 4, the resistivity increases, returning to within ~1% of its value following the initial RT irradiation. These results thus demonstrate that the irradiation-induced solubility depends primarily on the alloy concentration and not the initial microstructure. This reversibility is an important finding in understanding the kinetic response of irradiated Cu-W, which will be discussed in more detail below. Also shown in Figure 4 are the derivatives, $d\rho/d\phi$, showing the time scale for the annealed alloy to relax during irradiation. Starting from the solid solution the time constant is ~ 0.2 dpa, which is similar to those found in Figure 3 for all of the alloys. For the system having undergone pre-annealing at 600 °C and precipitation, the time constant is somewhat larger but of similar magnitude.

Electrical resistivity measurements were also employed to examine the kinetics of the dissolution process using a series of multilayer samples comprised of pure Cu and pure W layers. The W layers were 10 nm thick, while the Cu layers varied from 10 nm to 100 nm. The idea of this set of experiments is that the resistance of the sample will increase as W diffuses into the Cu layers, providing irradiation-induced diffusion rates for W in Cu. Figure 5 plots the electrical resistivity of the irradiated sample versus dose, showing that ρ increases more slowly with dose as the thickness of the Cu layers increases. This observation illustrates that the change in Cu resistivity is not an interface effect but rather reflective of the transport of W into the Cu layers, although roughening of the interface may also play some role. In the specimen with the thinnest Cu layers, 10 nm, the resistivity has nearly saturated at high irradiation doses indicating that W has nearly homogenized across the Cu layers. The continued increase in resistivity at

high doses is attributed to significant interface roughening and a change in the layer morphology, as discussed below. For the samples with 50 nm or 100 nm Cu layers, the resistivities increase nearly linearly with dose and much more slowly, up to a dose of ≈ 60 dpa, illustrating that the W has not yet diffused throughout the Cu layer at that point.

3.2 Transmission electron microscopy:

The effect of irradiation on the precipitate structure in the various Cu-W alloys was examined using TEM. Reported in Figure 6 is a series of HAADF images of the initially solid-solution alloys after room temperature irradiation, along with the size distributions of the W precipitates. The sizes were found by measuring the cross sectional area of the precipitates and assuming the precipitates are spherical. The fundamental result emerging from these micrographs is that the density of the nano precipitates increases dramatically with alloy concentration, but the size distributions are only little changed, with the volume-averaged diameter of ~ 2 nm. We use volume-averaged sizes to better represent the precipitate sizes containing most of the W atoms. The images also reveal that in the more concentrated alloys, the W nanoparticles begin to impinge on one another. The size distributions in Figure 6 count abutting particles as individual nanoparticles and not as a single entity, although in some cases there is uncertainty whether the precipitate is a single coagulated nanoparticle or two particles in close proximity. We checked whether irradiation at much lower temperatures also results in size stabilized W precipitates, or whether a solid solution is formed. A Cu-3 at.% W alloy was thus irradiated at liquid N₂ temperature. W precipitates were again observed, although their average size was somewhat smaller, ~ 1.5 nm. This smaller size is consistent with a somewhat reduced diffusivity of W during irradiation at the lower temperature, but this will be discussed in more detail below.

Experiments were also performed to check whether the size distributions of the W precipitates are reversible, as found for the W solubility, i.e., independent of the initial alloy structure. For these

experiments, the 3 at.% W alloy was first annealed at 700 °C for 1 h, to create large precipitates, and then irradiated at RT to ≈ 55 dpa. Micrographs showing the final precipitate sizes after annealing and after subsequent RT irradiation are presented in Figure 7 (a) and (b), respectively; the corresponding volume-averaged size distributions are plotted in Figure 7 (c). Figure 7 clearly shows that (i) the sizes of the W nanoparticles after annealing are significantly larger than after the initial RT irradiation of the as-prepared samples, on average 4.4 nm after annealing at 700 °C versus 1.9 nm after initial room temperature irradiation, and (ii) re-irradiation of these annealed samples indeed reduces the size of the W precipitates, returning the size distribution to one close to the distribution for the as-prepared sample irradiated at RT. The small differences in these two distributions possibly arise from the annealed alloy not yet reaching steady state during irradiation – note the electrical resistivity showed that the time constant for steady state is larger for the initially precipitated samples. Nevertheless, these results showing nanoparticle shrinkage, in combination with the electrical resistivity measurements showing reversible solubilities, provide convincing evidence that the microstructure presented in Figure 6 represents a steady state of the irradiated Cu-W alloy.

The structure and morphology of the Cu-W multilayer samples were also examined by TEM. Shown in Figure 8 are bright field images of sample with 10nm-W/100nm-Cu: (a) as prepared; (b) irradiated at RT to a dose of ~ 60 dpa; (c) irradiated at RT and subsequently annealed at 600 °C for 1 hr. The sample irradiated at RT reveals that small W precipitates form close to the Cu/W interface, within ~ 5 nm. Subsequent annealing of this sample at 600 °C, Figure 8 (c), leads to significantly more precipitation, with precipitates appearing farther from the interface. This extended precipitation zone in the annealed sample provides a qualitative measure of the W concentration profile following RT-irradiation (assuming W precipitates form proportionately to their local W concentration). After a dose of 60 dpa, the W layers roughen, but they appear to remain continuous, as seen in Figure 8(b). Figure 9, on the other hand, shows that the interface morphology of the W layers in the 10nm-Cu/10nm-W multilayer film are strongly affected by the high dose irradiation. This is, perhaps, not too surprising since from Figure 8 we see that

the roughness of the W layer in 100nm-Cu/10nm-W film is $\sim 5\text{nm}$. Adjacent W layers in the 10nm-Cu/10nm-W sample, therefore, are interacting. These results thus indicate that the structure of this sample may be transforming to a three dimensional morphology, but higher doses would be necessary to confirm this conjecture.

4. Discussion

We first examine the tracer-impurity diffusion coefficient of W atoms in Cu during RT irradiation from the resistivity experiments. Previous work on such so-called ion beam mixing in metals alloys typically employed Rutherford backscattering [21]; however, this method is not suitable for Cu-W, owing to the very low concentrations of W soluble in irradiated Cu. Electrical resistivity and X-ray diffraction measurements, on the other hand, had been employed to probe ion beam mixing in Cu-W under irradiation, but these studies examined predominantly chemical interdiffusion under irradiation, not tracer diffusivity [30]. The analysis on multilayer Cu-W samples in the present work assumes (i) the Cu/W interfaces remain sharp during irradiation, at least relative to the thickness of the Cu layers; (ii) the W concentration in the Cu phase at the Cu/W interface is fixed at the saturation concentration of W in irradiated Cu; (iii) the resistivity of the W layers are not much affected; (iv) the resistivity can be defined locally as a function of position since, as noted above, the electron mean free path is small in the Cu-W alloy. The diffusion equation for a layered structured is then solved numerically for this geometry and compared with the experimental curves to obtain the diffusion coefficient. The four experimental resistivity curves shown by the solid lines in Figure 10 represent the resistivity of just the Cu layers (unlike Figure 5, which is the average resistivity of the Cu-W specimen – a resistivity of $50\ \mu\Omega\text{-cm}$ was assumed for the W layers [31]). Except for the 10nm-Cu/10nm-W alloy, the experimental data fit quite well with the calculated values (represented by circular points) using an irradiation-induced diffusivity of $D_W^{irr} = 2.1\ \text{nm}^2\text{-dpa}^{-1}$ and a solute resistivity of $12\ \mu\Omega\text{-cm/at.\% W}$ (see eq. (1)). The 10nm-Cu/10nm-W was not used in the fitting since the approximations employed in the model break down at high dose, as it is shown in Figure 9 that the layer structure is becoming unstable at high doses. Although we do not use

the 10nm-Cu/10nm-W alloy for fitting, the initial portion of the resistivity curve does fit the model quite well. It is interesting to compare our value for the tracer diffusion coefficient of W in irradiated Cu with that of *self* diffusion in irradiated Cu, which was measured using secondary ion mass spectrometry (SIMS) after irradiation at 6 K. The value for D_{Cu}^{irr} is $\sim 3.5 \text{ nm}^2\text{-dpa}^{-1}$ [21] and thus only somewhat greater than the value of D_W^{irr} found here. We note, however, that while D_{Cu}^{irr} was measured at 6 K and D_W^{irr} measured at RT, past measurements on tracer diffusion of Au markers in Cu under similar irradiation conditions showed that D_{Au}^{irr} varies by only $\sim 50\%$ between these two temperatures [32].

We can use the value of D_W just obtained to explore the precipitation kinetics in the solid solution samples. If we assume that W diffuses primarily in the liquid-like thermal spike and that the precipitation occurs by an agglomeration-coagulation process, then the concentration of W precipitates per unit volume (N) can be obtained using the Smoluchowski model [33], i.e.,

$$\frac{1}{N(t)} - \frac{1}{N(0)} = \frac{4kT}{3\mu} \cdot t \quad (2)$$

The effective viscosity, μ , in this thermal spike model can be estimated using our value of D_W^{irr} using Stoke's Law, $\mu = \frac{kT}{6\pi D_W^{irr} r}$. Figure 3 and Figure 4 show that the change in the resistivity saturates after a dose $\tau_R \sim 0.2\text{-}0.5 \text{ dpa}$, which indicates that for $X_W \sim 2 \text{ at.}\%$. Using at this dose (or time) in Eq.(2) yields $N \sim 0.2\text{-}0.4 \text{ nm}^{-3}$, and each W precipitate contains $\sim 5\text{-}10$ atoms. The spacing between precipitates is correspondingly $\sim 1.4 \text{ -} 1.8 \text{ nm}$, and thus comparable to the electron free path in W-saturated Cu. Further aggregation, therefore, would have only a minor effect on the resistivity. While these values are all very approximate, they nevertheless do add support for the presumed precipitation mechanism. We will expand on this issue in more detail below, using KMC modeling.

We next turn to the observation that the radiation-induced W precipitates in the initially solid solution samples appear to adopt a characteristic size, ~ 2 nm, after prolonged, (i.e., steady-state) irradiation. In previous work on Cu-10 at.% W alloys, Vo *et al.* suggested that the sizes of the precipitates were fixed by the spatial dimensions of displacement cascades, ~ 5 nm [9]; precipitates larger than the molten cascade zone could not move. The present results show that the average size of the W precipitates are significantly smaller than 5 nm, closer to 2 nm. For the most part, only the density of W precipitates increases with increasing W concentration, not their size. The model by Vo *et al.*, which is essentially described by eq. 2 but with an upper limit on size, also fails to explain why large precipitates shrink during irradiation; that model only explains why they cannot grow. We suggest that such a size selection, one that is independent of the initial precipitate size, represents a self-organizing process, somewhat akin to the patterning that has been reported for high-temperature irradiation of moderately immiscible alloys, such as Cu-Ag, Cu-Fe [17], and Cu-Co [34]. Self-selection of precipitate size in those systems has been explained on the basis of a dynamical competition between ordering and disordering reactions [35-38]. Disorder is effected by so-called ballistic events in energetic displacement events, which displace atoms randomly; thermodynamic driving forces are considered negligible in these high-energy events. For the moderately immiscible alloys noted above, these ballistic events occur predominantly in the thermal spike phase of the cascade, but some also occur by recoil events involving energetic two-body collisions. In this high-temperature model, ordering (i.e., precipitation) is achieved through thermally-activated diffusion processes, such as radiation-enhanced diffusion. Theory and modeling have shown that patterning occurs when these two processes are of comparable strength, but operate over different length scales. i.e., ballistic relocation processes transport atoms further than one atomic distance, whereas thermally activated diffusion moves atoms exactly one atomic distance (see Ref. [38] for details).

In the present situation, Cu and W are immiscible in the liquid, and thermal-spike interdiffusion is small near interfaces, as demonstrated in previous experiments (see the introduction section and the references therein). W is nevertheless mobile in the thermal spikes, and it migrates freely while in dilute

liquid Cu solutions. We have thus coupled the high temperature model for self-organization with the model by Vo *et al* by assuming that ballistic transport of W occurs entirely by energetic recoil events (and not thermal spikes), and that the thermally activated diffusion occurs by liquid diffusion in the thermal spike (eq.(2)) (and not by radiation-enhanced diffusion). The diffusion coefficient in the thermal spike is known from the experiments described above, and the recoil mixing is readily calculated by Monte Carlo methods, such as SRIM [39]. The model is implemented using a simplified kinetic Monte Carlo procedure, as follows. First, a simple cubic lattice is created with x percent B atoms and the rest A atoms (referred to hereafter as W and Cu atoms, respectively). All W atoms, regardless of their location, can undergo recoil events, with the recoils occurring in random directions. For simplicity we do not use the full recoil displacement distribution, but rather assume all recoils are transported a distance $R = 2$ lattice constants, approximately the value obtained for W recoils in Cu found by SRIM. The number of recoils is determined by assuming a recoil probability, per atom, of 0.1 per dpa (also estimated using SRIM). At the same time, all isolated W atoms and small W precipitates diffuse according to Stokes-Einstein Law [40] (i.e., inversely proportional to their radius) using the above measured value D_W for determining the mobility of a single W atom. W clusters larger than the size of a thermal spike, ~ 5 nm, are assumed immobile since they are not completely immersed in liquid Cu. If during a recoil or diffusive jump, W atoms or precipitates become nearest neighbor atoms of other W atoms or surfaces of precipitates, the two bodies coalesce (again, the assumption of eq. (2)). All precipitates are assumed spherical. While the model is simple, we believe it includes the essential physical processes.

The results for the steady state sizes of precipitates are presented in Figure 11 (a)-(c) for three W concentrations, 1, 3, and 5 at.% W, and each using two starting conditions, solid solutions and two-phase alloys containing W precipitates with a diameter of 5.94 nm. These figures show rather clearly that the initial state of an alloy has little effect on the steady state size distribution of W precipitates. They also show that the average sizes of the steady-state precipitates are very comparable to the experimental values. Plotted in Figure 11(d), in addition, is the dose dependence of the solubility, in terms of

resistivity, of W in solution. For this plot, we have used eq. 1 to convert solubility to resistivity, assuming W atoms in clusters containing less than or equal to 5 atoms are in solution. The time constant obtained for the radiation-induced precipitation is notably quite similar to the experiments (see the inset in Figure 3), i.e., ~ 0.2 dpa. The steady-state solubilities found in this model are comparable to, but somewhat smaller than, those deduced from the resistivity experiments, as seen when comparing the value in Table 2 (0.61 at.%) to the value in Table 1 for the Cu-3.1 at.% W alloy (1.32 at.%). These simulation results are thus in good overall agreement with the experiments, both in terms of the qualitative trends and the quantitative values. In regard to the quantitative agreement, we checked the sensitivity of the precipitate size and solubility on our measured value of D_w^{irr} . As we reported above, the precipitate size was reduced from ~ 1.9 nm to ~ 1.5 nm when the irradiation temperature was lowered from RT to 80 K, and we speculated that this was due to a somewhat reduce value of D_w^{irr} . The results shown in Table 2 indeed show that a factor of two smaller diffusivity results in a reduction in precipitate size comparable to that found on irradiating at lower temperature. Similarly, as expected, the solubility increases with decreasing D_w^{irr} .

D_w^{irr}	1.05 nm ² /dpa	2.1 nm ² /dpa	4.2 nm ² /dpa
diameter	2.1 nm	2.7 nm	3.0 nm
solubility	.93 at%	.61 at%	.35 at%

Table 2: Average precipitate sizes and steady-state solubilities under irradiation for a Cu- 3at.%W alloy, when different D_w^{irr} values are used in the simulation.

Finally, to understand the low-temperature self organization process proposed here in more detail, we examined the effect of our assumption that W precipitates larger than the size of the melt zone are immobile. We emphasize that the model does not impose a limit on the maximum size of the W precipitates, but only on the mobility of large precipitates; i.e., precipitates can grow larger by the addition of mobile W atoms and small precipitates to the larger immobile precipitates. We thus

recalculated the size distribution for the 3-at.% W alloy but with condition limiting precipitate mobility extended to either 8 nm or to an indefinite size. In the case that precipitates up to 8 nm are mobile, the average steady state size of the W precipitates approximately doubles, from 2.7 nm to 5 nm, while for the unrestricted case, the final size of the precipitate becomes limited only by the size of the computational cell. We thus find that the size of the thermal spike is critical in limiting the precipitate size. As an aside, we note that the high temperature model of compositional patterning also allows for precipitate mobility, at least as implemented by KMC, but in that case diffusion of large precipitates has negligible effect on the patterning. We believe the difference in these two behaviors derives from the different dependencies of the precipitate mobility on precipitate size: in the solid state (i.e., under radiation-enhanced diffusion), the diffusivity of large precipitates varies as $1/d^4$ (or even more strongly with precipitate diameter, d) whereas in the (thermal spike) liquid, it varies as $1/d$. Thus diffusion of large particles can play a far stronger role in the liquid thermal spike than in the solid.

5. Conclusion:

This work has clarified several of the issues regarding the response of strongly immiscible alloys to energetic particle irradiation. Using the dilute Cu-W system as a model alloy for such systems, we find that under prolonged irradiation at low temperatures the microstructures reach a two-phase steady state whereby the size and density of W precipitates and the W solubility obtain fixed values on the order of nanometers. These values are governed by the specific thermochemical properties of the system and the irradiation particle, but they are independent of the initial microstructure of the system and they dependent only weakly on alloy concentration. The solubility of W in Cu matrix is raised many orders of magnitude above its equilibrium value at room temperature and even orders of magnitude larger than its solubility in the liquid at the melting temperature of Cu. Precipitate sizes remain about 2 nm. Irradiation of the multilayer Cu/W samples leads to W precipitation within the Cu layers and roughening of the Cu/W interface. It is found that the W layers remain continuous up to doses of ≈ 60 dpa when the Cu layer thickness is 100 nm, but they appear to becoming unstable at this dose when the Cu layer is 10 nm.

This suggests that thin multilayer structures of Cu-W will eventually transform to 3-dimensional structures, although the dose may be unattainably high. These observations can be rationalized by a model that includes a dynamical competition between ballistic recoil events and thermal spike diffusion. In this model, the finite length scale of the local thermal spikes is an essential requirement to reproduce the stabilization of finite size precipitates at steady state under irradiation.

Finally, in predicting how other nominally two- or multi- phase systems behave under low temperature irradiation, the key parameter found here is the chemical interdiffusion coefficient in the thermal spike, i.e., a combination of heat of mixing and tracer diffusivity, as ballistic recoil events do not vary significantly between different alloys when normalized by dpa. In the nano-ODS Fe based alloys mentioned above, for example, it has been reported that small precipitates are not stable when irradiated at low temperatures and that they tend to homogenize [41] . This can be rationalized by the present work since tracer diffusivities in thermal spikes in Fe are known to be the among the smallest in elemental metals [12].

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Figure captions:

Figure 1. Schematics showing the leaded chip carrier and the MgO substrate with sample pattern for the four-point electrical resistivity measurements. Five samples are deposited onto a single piece of substrate, labeled as ①-⑤. The grey square covering sample ①-④ is the irradiated area.

Figure 2. Electrical resistivity at RT as a function of W concentration for the as-grown samples (square symbols) and the samples irradiated to steady state (circular symbols)

Figure 3. Resistivity as a function of irradiation dose (at RT) for solid solution samples with different initial W concentration. The $\text{CuW}_{1.6}$ -ann sample is the reference sample that was not irradiated. The inset is the first-order derivation of the resistivity curve up to 1 dpa, showing the rate of resistivity change at the early stage of the irradiation experiment.

Figure 4. Evidence of steady state during irradiation. First irradiation was performed on a solid solution $\text{CuW}_{1.6}$ sample; afterward the sample was annealed at 600°C for 1 hour, and then the second irradiation was performed.

Figure 5. Resistivity as a function of irradiation dose (at RT) for multilayer samples with different Cu layer thicknesses, as specified in the legend (W layer thickness is constant at 10 nm).

Figure 6. (Left column) STEM-HAADF images showing irradiation-induced precipitate structure and (right column) precipitate (volume-averaged) size histograms in Cu-W alloys with different initial W solute concentration.

Figure 7. STEM-HAADF images showing: (a) W precipitates in 700°C annealed 3 at.% W alloy; (b) W precipitates of the alloy in (a) after being irradiated to ~ 55 dpa. Precipitate size histograms for the alloy after different treatments are shown in (c).

Figure 8. Bright field TEM images showing W layer morphology in the 100nm-Cu/10nm-W multilayer sample: (a) in the as-grown state; (b) after RT irradiation to ~ 60 dpa; (c) after post-irradiation annealing at 600°C .

Figure 9. Bright field (a) and STEM-HAADF (b) images showing W layer morphology in the 10nm-Cu/10nm-W multilayer sample: (a) in the as-grown state; (b) after RT irradiation to ~ 60 dpa.

Figure 10. Comparison of experimental results on Cu-layer resistivity in the multilayer samples during irradiation (solid lines) with the modeling results from solving diffusion equations (red dots).

Figure 11. (a): Steady-state precipitate size distribution (weighted by precipitate volume) from the KMC simulation for the Cu-1 at.% W alloy with two different initial structures: solid solution or having one 5.94nm W precipitate; (b): the same as (a), but for the Cu-3 at.% W alloy; (c): the same as (a), but for the Cu-5 at.% W alloy; (d): the rate of resistivity change with dose for the solid solutions during irradiation.

Graphical Abstract