Precipitate Stability in Cu-Ag-W System under High-Temperature Irradiation

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Abstract

The kinetics of precipitation was investigated in the ternary Cu alloy, $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ during irradiation with MeV Kr ions at elevated temperatures. The alloy was prepared as a solid solution by physical vapor deposition and then irradiated at room temperature to create a high density of nano-sized W precipitates. These precipitates served as effective sinks for point defects during subsequent elevated-temperature irradiation, suppressing radiation-enhanced diffusion. As a consequence the size of the Ag precipitates formed during elevated-temperature irradiation was stabilized below 20 nm, up to temperatures in excess of 300 °C, thus significantly extending the regime for “compositional patterning” above 175 °C, found for $\text{Cu}_{85}\text{Ag}_{15}$. For higher temperature irradiations (above 400 °C), the role of the W precipitates in stabilizing the size of the Ag precipitates switched from simply acting as point-defect sinks to serving as pinning sites for the Ag precipitates. At 500 °C, the average Ag precipitate diameter is ~ 30 nm compared to ~ 300 nm in the $\text{Cu}_{85}\text{Ag}_{15}$ binary alloy. Rate theory calculations and kinetic Monte Carlo simulations are employed to illustrate how this transition takes place.

Keywords: self-organization; radiation-enhanced diffusion; radiation-enhanced precipitation; radiation damage

Introduction

Nanostructured metal alloys have long been recognized for their excellent mechanical behavior for applications requiring high strength and hardness [1-4]. Recent attention in these materials has focused largely on controlling their stability at high temperatures, as they are inherently unstable to coarsening. A number of approaches have been taken to mitigate this problem, including grain boundary (GB) stabilization using GB doping [5, 6] or Zener pinning [7-9]. For multiphase alloys, different approaches are employed. These strategies typically rely on the general observation that in a dilute binary alloy the coarsening rate dR / dt of a precipitate of radius R scales with the solute diffusion coefficient, D_s , the solubility limit of the alloying element, X_{sat} , the precipitate matrix interface energy, γ , and the size distribution of the

precipitates, i.e., $\frac{dR}{dt} = \frac{2D_s \gamma W^2 X_{sat}}{kTR} \left(\frac{1}{\langle R \rangle} - \frac{1}{R} \right)$. Oxide-dispersion strengthened (ODS) alloys [10-

12] and core/shell-structured precipitate strengthened Al alloys illustrate this approach [13-17].

Alloys under irradiation present an even more challenging problem, since irradiation can greatly enhance both D_s and X_{sat} ; moreover the above expression for dR / dt may not even apply to this situation, as irradiation can drive materials away from equilibrium states [18]. One method proposed for stabilizing precipitate sizes during elevated-temperature irradiation, in fact, takes advantage of an intrinsic tendency of some alloys to self-organize when driven far from equilibrium, forming dimensionally stable patterns of composition on a nanometer length scale [19, 20]. A second possible approach for suppressing precipitate coarsening involves a Zener-like pinning mechanism. This possibility has been considered in soft materials and in computer simulations studies (of quenched disorder) [21-23], but not previously in an irradiation

environment. The present work examines the effectiveness of these mechanisms for stabilizing nanostructured metal alloys under elevated-temperature irradiation.

Two important irradiation-related processes in the coarsening of precipitates are radiation-enhanced diffusion (RED) and ion (beam) mixing (IM). In immiscible binary alloys, RED tends to accelerate phase separation, while IM tends to induce resolution of precipitates [24]. When the two mechanisms are of similar magnitude, a dynamical competition between these mechanisms can result in the development of unique steady-state microstructural morphologies [19, 24]. For example, during elevated-temperature irradiation, compositional patterning can occur in nominally two-phase alloys, whereby phase separation occurs on a very local (nanometer) length scale. Such patterning has been observed experimentally in binary two-phase alloys such as γ - γ' Ni-Al [25] and a series of moderately immiscible Cu based alloys, such as Cu-Ag, Cu-Fe, Cu-Co, etc. [26, 27]. Different models have been proposed to explain this behavior [19, 28, 29]; their main differences, as discussed in Ref. [30], arise mainly from how they treat ballistic mixing. More importantly, all of these models predict a maximum temperature, $T_{\max}$, for compositional patterning, above which the system will undergo coarsening until achieving macroscopic phase separation. This maximum temperature depends primarily on the relative rates of IM and RED. Attempts to increase $T_{\max}$ have thus focused on decreasing RED, since for given irradiation projectile and flux, little can be done to influence IM [31].

Previous work on Cu-based immiscible alloys has demonstrated that one method for decreasing RED is to use solutes with relatively small diffusion coefficients in Cu, relative to self-diffusion. Thus, $T_{\max}$ in systems like Cu-Mo and Cu-Nb is very high in comparison to systems like Cu-Ag and Cu-Fe [26]. Another possible means to suppress RED and thereby

increase $T_{\max}$ is to introduce a high density of unsaturable sinks into the alloy microstructure to reduce the supersaturation of point defects, as recently illustrated using kinetic Monte Carlo (KMC) simulations [32]. This work suggests, in fact, that for sink densities above a critical concentration, $T_{\max}$ increases to the temperature at which equilibrium vacancies begin to dominate the kinetics.

The second possibility for stabilizing precipitate sizes, Zener pinning, is commonly employed for controlling grain sizes or magnetic domain sizes, but we are unaware of comparable work on controlling precipitate sizes during thermal aging or during irradiation. We point out that the use of Zener pinning for controlling precipitate size is intrinsically different from traditional Zener pinning, since the composition field is a conserved order parameter for the former, but grain orientation and magnetization are non-conserved order parameters for the latter. This point will be revisited in the discussion section. While the control of precipitate size during irradiation through compositional patterning and Zener-like pinning both rely on additions of stable nanoparticles we emphasize that these two mechanisms result in distinctly different kinetic behaviors. The first relies on a dynamical competition between IM and RED, which leads to a *microstructural steady state*, whereas the second simply adds a kinetic barrier to coarsening.

The experimental procedure employed here for creating a nanoparticle-stabilized alloy begins with first forming a solid solution of $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ using physical vapor deposition. By irradiating the alloy with energetic particles at room temperature, the alloy undergoes *selective precipitation* whereby the W atoms come out of solution to form nano-sized precipitates, while Ag atoms remain in solution. As described elsewhere [13, 26] this process is a consequence of the extreme immiscibility of W in Cu, whereas Ag is only moderately immiscible in Cu. Thus W precipitates out in the thermal spike phase of energetic displacement cascades, whereas Ag does

not. The W precipitates, moreover, are particularly effective for the present experiments as they are themselves highly stable against coarsening in Cu at temperatures below $\approx 0.8T_m$ (T_m = melting temperature) [33]. The Cu-Ag-W system was selected for this study since the heats of mixing of the binary alloy systems obey $\Delta H_{Ag-W}^m > \Delta H_{Cu-W}^m > \Delta H_{Cu-Ag}^m > 0$, and therefore the Ag precipitates should not wet the W precipitates at elevated temperatures, but rather nucleate between them. The heats of mixing for these binary systems are provided in Table 1. In the results section we show that with the irradiation-induced 1-3 nm sized W precipitates, T_{max} for compositional patterning can be increased during MeV Kr ion irradiation from 175 °C, which is found for the Cu-Ag binary alloy [26], to over 300 °C in the ternary alloy. Above 300 °C the Ag precipitates grow to a size at which direct interaction of Ag precipitates and W nanoprecipitates is possible, and the pinning effect of the W nanoprecipitates then becomes relevant.

Table 1. Heat of mixing for equiatomic alloys.

	Cu-Ag	Cu-W	Ag-W
ΔH^{mix} (kJ/mol)	6 [34]	33 [35]	65 [35]

Experimental Procedure

$Cu_{83.5}Ag_{15}W_{1.5}$ thin film alloys were grown on oxidized Si wafers at room temperature using three independent DC magnetron sputtering sources. The base pressure in the sputtering system was $\sim 3 \times 10^{-8}$ torr, and the operation pressure during growth was $\sim 2.1 \times 10^{-3}$ torr Ar. The film thickness was chosen to be ≈ 300 nm, with a 2-3 nm W capping layer deposited at the top surface of the film to prevent preferential sputtering of the alloying elements and Ag segregation to the surface at elevated temperatures. The samples were subjected to various irradiation treatments at

different temperatures. The irradiations were performed using 1.8 MeV Kr^+ ions, as this irradiation condition leads to reasonably uniform defect production across the thickness of the film, with the maximum variation across the film being less than 30% [36]. The dpa rate was 1.77×10^{-2} dpa/s for the room-temperature (RT) irradiations and 1.33×10^{-2} dpa/s for the irradiations at elevated-temperature; these conditions limit the beam heating to less than 10 °C. The sample thicknesses and compositions were obtained using Rutherford backscattering spectrometry (RBS). All samples were studied using X-ray diffraction (XRD) to obtain information about phase evolution and solubility. Transmission electron microscopy (TEM) was used to obtain complete size distributions of the Ag precipitates, the average size of the W nanoprecipitates, and the grain sizes of the Cu matrix. The average precipitate sizes in this work represent volumetric averages. The statistical analysis of precipitate sizes includes measurements on hundreds of precipitates obtained from multiple TEM/STEM images. The open-source software ImageJ was used to outline the individual precipitates and measure their areal projections. The effective diameters of the precipitates were then calculated by treating the precipitates as spheres.

Scanning electron microscopy (SEM) was used to examine the surface condition of the samples after the different treatments to ensure that the internal structure of the samples had not changed due to any surface related processes. Selected samples were examined by TEM using a JEOL 2010 LaB₆ microscope for general bright field (BF), selected area diffraction (SAD) and dark field (DF) imaging. Additional characterization was performed using a JEOL 2200FS Cs-corrected Scanning TEM (STEM) with a high-angle-annular-dark-field (HAADF) detector for Z-contrast imaging. All TEM observations were performed at a voltage of 200 kV.

Experimental results

Figure 1 shows XRD θ - 2θ scans on the as-grown sample and on samples following various thermal/irradiation treatments. The scan on the as-grown sample shows only the Cu (111) peak, which is shifted from that of pure Cu due to the Ag and W in solution, and broadened by the small grain size. After room-temperature irradiation, there is a slight shift of Cu (111) to higher angle due to W precipitation, but since the Ag remains in solution, the shift is small. The precipitation of W is not observed directly in the XRD profiles, but this is due to the low concentration and small sizes of the W nanoprecipitates. It is also observed that the Cu peak narrows; this arises from an increase in the Cu grain size during irradiation. Upon further irradiation at elevated temperatures, Ag precipitation is clearly evidenced by the emerging (111) peak of the Ag-rich phase and the additional shift of Cu-rich phase. Both peaks shift closer to (111) positions of the corresponding pure phases as the irradiation temperature is increased. For the higher temperature irradiated samples, a small overshift of the Cu (111) peak to an angle higher than that of pure Cu is seen; this is a consequence of residual strain developed in the Cu film during cooling, as the thermal expansion coefficient of Cu is larger than that of the Si substrate. When calculating the solubility listed in Table 2, the peak positions are adjusted according to the calculated residual strain [37]. The Ag precipitate sizes and the Cu grain sizes can also be determined from the XRD data using the Scherrer equation, however, since the XRD results reflect mainly the heavily twinned structure of the film in the growth direction, this measure of the grain size is inaccurate. Plane view TEM shows that the average Cu grain size normal to the growth direction after room-temperature irradiation is ~ 200 nm, and thus comparable to the film thickness. Ag precipitate sizes were obtained using both XRD and TEM; these results are reported in Table 2.

Table 2. Solubilities and Ag precipitate sizes from XRD and TEM measurement of $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ after various treatments. The Ag solubility in copper matrix is calculated based

on the Linde table [38]. W has been assumed to precipitate out of the matrix without interfering with the Ag phase, and has little effect in the peak analysis here.

	RT irr	RTirr + 200 °C irr	RTirr + 300 °C irr	RTirr + 400 °C irr	RTirr + 500 °C irr
Ag solubility in Cu (at.%)	15	5.9	1.2	0.2	0
Cu solubility in Ag (at.%)		6.4	4.6	1.9	4.3
Ag precipitate size from XRD (nm)		3.6 (± 0.5)	8.7 (± 0.2)	21.2 (± 0.3)	33.8 (± 0.5)
Ag precipitate size from TEM (nm)		1.8 (± 0.5)	9.3 (± 0.5)	13.8 (± 0.6)	32.7 (± 0.9)

Figure 2(a) is a micrograph showing the precipitates in the $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ samples after RT irradiation. Only W atoms precipitated while Ag atoms remained in solution. The diameters of these W precipitates are on average ~ 1 nm. High-resolution TEM analysis (see Supplementary Figure S1) shows the orientation relationship between the precipitates and the matrix being Bain type, the same as reported previously for other Cu-based alloy systems containing small W precipitates [13, 39]. The precipitate concentration (in atomic fraction) C_p is $\sim 3 \times 10^{-4}$, however, this will be discussed in more detail below.

Following the RT irradiation, the samples were irradiated a second time at elevated temperatures. In this case Ag begins to precipitate, and owing to the extremely high heat of mixing between Ag and W, the Ag precipitates nucleate between the W precipitates. Figure 2(b) and 2(c) show the microstructures of samples after irradiation to a dose of $2.0 \times 10^{16} \text{ cm}^{-2}$ at 200 °C and 250 °C, respectively (denoted in the following as the 200 °C and the 250 °C samples). The presence of Ag precipitates is confirmed by the Moiré fringes in the BF TEM micrographs, as shown in Figure 2(b)-inset and 2(c). The Moiré fringe spacing measured in these figures is ~ 1.6 nm, which corresponds to Ag {200} // Cu {200}, indicating a cube-on-cube orientation relationship. No combination of W and Cu planes yields a beat frequency corresponding to this

value. An accurate determination of the Ag precipitate size in the 200 °C sample is difficult due to the problem of distinguishing the W and Ag precipitates, as both types of precipitate are quite small; however an upper limit of 1.8 nm can be placed on the average Ag precipitate size. Since smaller precipitates are harder to distinguish, they are more likely to be undercounted, and so the true average size is less than 1.8 nm. For the 250 °C sample, the average Ag precipitate size is $\approx$ 6.7 nm. The size distribution of these Ag precipitates will be discussed in more detail below (see Figure 6), where it is compared with results for higher-temperature irradiations.

Figure 3 shows BF images of samples irradiated at RT, followed by 300 °C irradiation (denoted as the 300 °C sample hereafter) to a dose of (a) $2.0 \times 10^{16} \text{ cm}^{-2}$ and (b) $4.0 \times 10^{16} \text{ cm}^{-2}$. Again the coexistence of Ag and W precipitates is observed; the Ag precipitates are easily identified by the Moiré fringes. Note that the images in Figure 3(a) and 3(b) are remarkably similar, despite the factor of two difference in irradiation dose. This suggests that the microstructure has reached a steady state (i.e. patterning) by a dose of $2.0 \times 10^{16} \text{ cm}^{-2}$. The average size of the Ag precipitates in these samples is now 9.3 nm; additional details will be provided below in Figure 6. Unlike the 200 °C and 250 °C samples, the Ag precipitates in the 300 °C sample are now running into the W precipitates and becoming engaged by them. An example is shown in Figure 3(a)-inset where a Ag precipitate, indicated by the Moiré fringes, is surrounded by the much smaller W precipitates. We point out that even though the average precipitate size of the Ag precipitates increases somewhat with temperature between 200 °C and 300 °C, the precipitates are nevertheless in *steady state* at each temperature. This conclusion, which is in agreement with theoretical predictions [19], was further confirmed by a second set of experiments. In these experiments, the RT pre-irradiated samples were first irradiated at some high temperature and then again at a somewhat lower temperature. Two such irradiation

sequences were performed: RT + 300 °C + 200 °C and RT + 400 °C + 300 °C. It was observed that the final, lower-temperature, irradiation always tended to bring the microstructure to a state with smaller Ag precipitates, as if the sample was only irradiated at this lower temperature. Results from these experiments can be found in Supplementary Figure S2 and Figure S3.

Returning attention to the two-step irradiations, i.e., RT + high temperature, we next raised the 2nd-step irradiation temperatures to 400 °C and 500 °C, each with two doses, $2.0 \times 10^{16} \text{ cm}^{-2}$ and $4.0 \times 10^{16} \text{ cm}^{-2}$. Figure 4 shows micrographs for the sample irradiated at 400 °C to the lower dose: (a) shows a Z-contrast STEM image, and (b) a BF TEM image. Notably the grain boundaries do not appear to be preferred sites for Ag precipitation, in contrast to the small W precipitates. The average size of the Ag precipitates after the lower dose irradiation is 13.8 nm. A closer examination of the precipitates reveals that similar to the 300 °C sample, the Ag precipitates are surrounded by small W precipitates, as shown in Figure 4(b). TEM characterization of the higher-dose sample (see Supplementary Figures S4 (a) and S5) shows that the Ag precipitates are now coarsening, with a volume averaged diameter increasing to 28.0 nm.

Figure 5 shows two Z-contrast images of a pre-irradiated sample irradiated at 500 °C to $2.0 \times 10^{16} \text{ cm}^{-2}$. The average Ag precipitate size has increased to 32.7 nm. In Figure 5(b), a string of W precipitates clearly marks the Cu grain boundary. Similar to the other specimens, the grain boundaries do not appear to be preferred precipitation sites for Ag, and in the grain interior Ag precipitates are always surrounded by W precipitates. The higher-dose sample was also characterized by TEM (see Supplementary Figures S4(b) and S5), which yielded an average Ag precipitate size of 48.7 nm.

Figure 6 summarizes the results for the sizes of both Ag and W precipitates in samples irradiated at different temperatures to the dose of $2.0 \times 10^{16} \text{ cm}^{-2}$. Corresponding information for

the samples irradiated to the dose of $4.0 \times 10^{16} \text{ cm}^{-2}$ can be found in Supplementary Figure S5. Figure 6(a) shows the size distributions of the Ag precipitates; as discussed above, the peak in the distribution shifts to larger sizes as the 2nd-step irradiation temperature increases, and the width broadens. Figure 6(b) plots the average diameter of the W precipitates and their corresponding interspacing, also as a function of the 2nd-step irradiation temperature. The W precipitate interspacing, which will be important for analyzing the caging effect, was calculated from average size of the W precipitates (TEM data in Table 2), assuming negligible W solubility in the matrix after irradiation (this assumption can result in a small underestimation in the spacing, $\sim 25\%$, which we neglect here [40]). Notice that the W precipitate size (and interspacing) increases with irradiation temperature; this slow coarsening of W precipitates had been observed previously in a $\text{Cu}_{90}\text{W}_{10}$ binary alloy [33]. If the W precipitates were to form a simple cubic lattice, for example, the largest Ag precipitate that could be contained without enveloping any W precipitates is $\sqrt{3} \times \text{interspacing}$; this dimension thus defines a “caging limit”.

The volume-averaged sizes of the Ag precipitates after irradiation to the dose of $2.0 \times 10^{16} \text{ cm}^{-2}$ are plotted as a function of the 2nd-step irradiation temperature in Figure 6(c) (solid line). The dotted line in this figure represents the caging limit; it crosses the line for the average Ag precipitate size at $\sim 350 \text{ }^\circ\text{C}$. Below $300 \text{ }^\circ\text{C}$, the Ag precipitates are smaller than the W precipitate interspacing and consequently they do not interact significantly with the W precipitates, while above $400 \text{ }^\circ\text{C}$ the Ag precipitates impinge on the W precipitates, as was illustrated in Figure 4(b) and Figure 5(b). For comparison, data from Ref. [26] for the average Ag precipitate sizes in irradiated $\text{Cu}_{85}\text{Ag}_{15}$ *binary* alloys, irradiated to a dose of $4 \times 10^{16} \text{ cm}^{-2}$, are also included in Figure 6(c). The compositional patterning regime and the macroscopic phase separation (coarsening)

regime for this binary alloy are labelled in the plot, showing clearly the much higher maximum temperature for compositional patterning in the ternary alloy system.

Discussion

We have shown that by introducing a high density of nm-sized W precipitates into dilute Cu-Ag alloys, coarsening of the Ag precipitates can be strongly suppressed. The W precipitates play different roles depending on the irradiation temperature. Below 300 °C the W precipitates serve primarily as sinks for point defects, and this leads to an extension of the compositional patterning regime in the Cu-Ag system. Above this temperature, the Ag precipitates grow to a size comparable to the interspacing between W precipitates, and direct interaction between the two kinds of precipitates is expected. In this case, Ag precipitates are pinned by the more immobile W precipitates and coarsening is largely suppressed. We next quantitatively analyze these two mechanisms.

The first step in evaluating the role of W precipitates on compositional patterning is determining the radiation-enhanced diffusion coefficient of Ag in Cu as a function of temperature [41]. As discussed in the Introduction, compositional patterning results from a competition between RED, causing precipitate coarsening, and IM, leading to precipitate dissolution. The important variable for patterning is the ratio of the radiation-enhanced diffusion coefficient, D_{Ag}^{RED} , to the rate of relocating atoms in ballistic events. Since the latter is nearly independent of temperature, we consider the effect of the W precipitates on D_{Ag}^{RED} . For relatively dilute Cu-Ag alloys, we are specifically interested in the quantity $D_{Ag}^{RED} = d_v^{Ag} \cdot C_v$, where d_v^{Ag} refers to the partial diffusivity of Ag in Cu by a vacancy mechanism [42] and C_v is the vacancy concentration during irradiation. Since Ag is oversized in Cu, we neglect Ag mobility by an

interstitial mechanism. Following Refs. [43, 44] we write the rate equation for the vacancy concentration as:

$$\frac{\partial C_v}{\partial t} = \xi_{FM} K_{NRT} - \frac{4\pi r_{iv}}{\Omega} (D_i + D_v) C_i C_v - \frac{4\pi r_p}{\Omega} \xi_p D_v C_v C_p - \frac{3\pi^2}{L^2} \xi_{gb} D_v C_v, \quad (1)$$

where K_{NRT} is the production rate of point defects in terms of displacements per atom per second, dpa/s (calculated within the NRT model [45] using SRIM [36]); Ω is the atomic volume; D_i is the interstitial diffusivity; D_v is the vacancy diffusivity; C_i is the interstitial concentration; C_p is the precipitate density; r_{iv} is the recombination distance for a vacancy and an interstitial; r_p is the capture radius of the precipitates for defects; L is the average grain size; ξ_{FM} is the fraction of freely migrating defects; ξ_p is the sink efficiency of the precipitate/matrix interface; ξ_{gb} is the sink efficiency of the grain boundaries. All concentrations refer to atomic fractions. Note that the concentration of equilibrium vacancies is small for $T < 300$ °C ($C_v^{thermal} = 8.5 \times 10^{-12}$ at 300 °C) and thus ignored in this temperature regime. Before determining whether recombination or annihilation at sinks is more important, we assess the ratio R of defects annihilating at precipitate/matrix interfaces versus at grain boundaries, which is the ratio of third and fourth term in Eq. (1). Using the values, $K_{NRT} = 1.33 \times 10^{-2}$ dpa/s, $\xi_{FM} = 0.01$ [46], $L = 200$ nm, $\Omega = 1.2 \times 10^{-23}$ cm³, $C_p = 3 \times 10^{-4}$, $r_{iv} = 0.6$ nm [47], $r_p = 0.5$ nm, $E_i^{mig} = 0.12$ eV, $E_v^{mig} = 0.72$ eV [48], we obtain $R \approx 200 \frac{\xi_p}{\xi_{gb}}$. Assuming that the sink efficiency of W precipitate/matrix

interfaces is comparable to that of grain boundaries, we expect that most of the defects will annihilate at the W precipitates. Note that the Ag precipitate/matrix interfaces may also serve as sinks once the Ag precipitates form, but since they grow quickly, their number density soon

becomes far smaller than that of the W precipitates, and therefore their contribution is neglected. The relative strength of the second term (recombination) compared with the third term (sink elimination) in right-hand-side of Eq. (1) thus determines whether the system is in the recombination or sink-limited regime.

Rate theory predicts that at the cross-over between recombination and sink elimination regime, the point defect recombination fraction is roughly 1/3 (see Ref. [32] for details). With this criterion and assuming that the W precipitate/matrix interface is an ideal sink, i.e., $\xi_p = 1.0$, we find that when the irradiation temperature is greater than ≈ 50 °C, the system enters the sink elimination regime at steady state. In contrast, if we consider a system without the W precipitates, the transition temperature is ≈ 200 °C. Recall that the maximum temperature of compositional patterning for the Cu₈₅Ag₁₅ binary alloy under Kr⁺ irradiation is 175 °C [26]. Therefore, for the binary system, the transition from patterning to macroscopic phase separation occurs at a temperature lower than that for the transition from the recombination-limited to sink-limited regimes. This is significant since, as we will now show, when the transition temperature from recombination-limited to sink-limited kinetics is lower than the transition temperature from patterning to macroscopic phase separation, the patterning regime will persist up to the temperature at which equilibrium vacancies dominate the kinetics.

For dilute Cu-Ag alloys, D_{Ag}^{RED} can be written as

$$D_{Ag}^{RED} = d_{Ag}^v C_v = \frac{d_{Ag}^v}{d_{Cu}^v} d_{Cu}^v C_v,$$

where d_{Ag}^v and d_{Cu}^v are the partial diffusion coefficients of Ag and Cu in the Cu matrix, both via a vacancy mechanism [42]. In the sink-elimination regime, the steady state vacancy concentration is

$$C_v = \frac{\xi_{FM} K_0 \Omega}{4\pi r_p \xi_p C_p D_v} \propto D_v^{-1},$$

As pointed out in Ref. [32], $D_v \approx d_v^{Cu} C_{Cu}$, since the Ag concentration in the matrix is low. Taking advantage of the relationship $d_{Cu}^v = d_v^{Cu}$ [42], the Ag diffusivity becomes $D_{Ag}^{RED} \propto \frac{d_{Ag}^v}{d_{Cu}^v}$. Figure 7(a)

shows the temperature dependence of the ratio $\frac{d_{Ag}^v}{d_{Cu}^v}$ obtained by taking the ratio of the tracer diffusion coefficients of Ag and Cu in a Cu matrix [49]. For the temperature range of interest (below 300°C), D_{Ag} is only weakly dependent on temperature. Accordingly, the steady-state precipitate size remains nearly constant as the irradiation temperature increases, in agreement with Figure 6(c). We note that the experiments in fact show that the precipitate size increases slowly with increasing temperature in the patterning regime, in contrast to the slow decrease in D_{Ag} calculated in Figure 7(b). This difference, however, is very small and can be caused by a number of possibilities. For example, we have assumed that ξ_{FM} (the fraction of freely migrating defects) is independent of temperature, but past work has shown that ξ_{FM} increases slowly with temperature [50]. Such details are beyond the scope of this work.

At higher temperatures (≥ 400 °C), the interactions between the Ag precipitates and the W nanoprecipitates become significant, as indicated in Figure 6(c) by the line for the caging limit crossing the line representing Ag precipitate size. At 400 °C, with $C_p = 2.9 \times 10^{-5}$ and

$r_p = 1.1$ nm, the irradiation-induced and equilibrium vacancy concentrations are becoming comparable [51, 52]. This indicates that the role of W precipitates as defect sinks is becoming less important. Our experiments reveal, however, that coarsening is slow in comparison to binary $\text{Cu}_{85}\text{Ag}_{15}$ at both 400 °C and 500 °C, as shown from Figure 6 and the Supplementary Figure S5(a) for those temperatures. In addition, TEM images, as pointed out above, show a direct interaction between W precipitates and Ag precipitates. These observations suggest that the W precipitates can now serve as pinning sites. We have estimated the energy barrier for de-pinning using KMC simulations; by de-pinning we mean the Ag precipitates overgrow the W precipitates. Details regarding the KMC algorithm can be found in Ref. [53]. In this set of simulations, a ternary A - B - C system was constructed to mimic the Cu-Ag-W system (A -Cu, B -Ag, C -W): the pair-wise ordering energies were set to be $\omega_{AB} = 0.0553\text{eV}$, $\omega_{AC} = 2\omega_{AB} = 0.1106\text{eV}$ and $\omega_{BC} = 3\omega_{AB} = 0.1659\text{eV}$, so as to reproduce $\Delta H_{Ag-W}^m > \Delta H_{Cu-W}^m > \Delta H_{Cu-Ag}^m > 0$; the vacancy migration energies were set as $\Delta E_{VA} = \Delta E_{VB} = 0.8\text{eV}$ and $\Delta E_{VC} = 1.8\text{eV}$, which leads to much slower diffusion of C in A , compared to that of A and B , again similar to the Cu-Ag-W system. The tracer diffusivity of W in Cu is not well known, but we assume it is similar to that of other refractory elements in Cu, which is very small (for example, for Ir $D \sim 2 \times 10^{-18} \text{ cm}^2/\text{s}$ at 500°C in Cu, whereas for Ag in Cu $D \sim 4 \times 10^{-14} \text{ cm}^2/\text{s}$ [54]). The simulation cell contains 64^3 atoms and initially 12 C particles are placed symmetrically on a spherical surface, serving as pinning sites. A single B precipitate is placed at the center of the sphere and the matrix contains a supersaturation of B solutes. The system is then annealed at $T = 0.055 \text{ eV}$ (365 °C) until the system reaches a *quasi*-steady state. We estimate the energy barrier for de-pinning by measuring the solubility of B at the end of the simulation for increasing sizes of the B precipitate, until the B precipitate overgrows the W pinning sites. The diffusion of C particles and the solubility of C in

A are negligible. Figure 8(a) shows the results of these simulations, here plotting the solubility of B as a function of the precipitate radius r . Shown for comparison is the solubility of B in absence of C pinning particles; this latter curve fits well with the Gibbs-Thomson equation (solid line). The fitting gives an equilibrium solubility of 2.39×10^{-3} , which is very close to the value obtained from a grand canonical simulation for the A - B binary system, 2.48×10^{-3} . It is significant that for the system with pinning, the solubility first decreases with the size of the B precipitates, following the Gibbs-Thomson relationship. When the B precipitates begin to contact the C particles, however, the solubility increases and the Ag precipitate bows out between the C particles, as shown in Figure 8(b). Eventually the precipitate overcomes the barrier to envelop the C particles and continues growing; the solubility then decreases again, returning to a level close to that for the binary system.

Quantitatively, the free energy difference between the pinned and un-pinned system is at a maximum when the size of the B precipitate corresponds to the highest point in the solubility bump, $n \approx 15000$ atoms:

$$\Delta E = nkT(\ln C_{max} - \ln C_{G-T}) = nkT \ln \frac{C_{max}}{C_{G-T}} \approx 15000 * 0.055 \text{eV} * \ln \frac{3.25 \times 10^{-3}}{2.95 \times 10^{-3}} \approx 80 \text{eV},$$

Where C_{max} refers to the solubility at the highest point in the barrier and C_{G-T} refers to the solubility in the binary system following the Gibbs-Thomson relationship. In real systems it is nearly impossible to overcome such a huge barrier by evaporation-condensation mechanism for coarsening, which explains why the nanometer sized Ag precipitates in the Cu - Ag - W system are so stable even at 500°C . We emphasize that the above considerations refer to thermal coarsening. The slow coarsening observed in the experiments occurred during irradiation and is most likely

due to mobility of the W nanoprecipitates during elevated-temperature irradiation and not de-pinning.

Conclusion

In this study we demonstrated a remarkable stability of Ag precipitates in the Cu-Ag-W system under high temperature ion irradiation, owing to the presence of a high density of 1-3 nm W precipitates formed under room-temperature irradiation. The role of the W precipitates is different for different regimes: in moderate temperature regime (≤ 300 °C), they serve as defect sinks which lead to an extension of the compositional patterning regime under irradiation to higher temperatures compared to binary Cu-Ag system; in high temperature regime (≥ 400 °C), they serve primarily as pinning sites to stop the growth of Ag precipitates. Between 300 °C and 400 °C both mechanisms are at play. Rate theory reveals that the W clusters as sinks lower the temperature for the defect kinetics to enter the sink elimination regime from 200 °C to 50 °C, which, based on the theory of dynamic phase diagram by Enrique and Bellon, extends the patterning regime to much higher temperatures. KMC simulations of the pinning phenomenon show that the energy barrier for de-pinning is extremely high so the microstructure is stabilized at nano-scale. The results from this study add feasibility in engineering materials for advanced nuclear reactor applications.

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Figure Captions

Figure 1. XRD scans for $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ in the as-grown state as well as subjected to various treatments (color online). The ion dose for RT irradiation is $2.7 \times 10^{16} \text{ cm}^{-2}$ and for irradiation at elevated temperatures is $2.0 \times 10^{16} \text{ cm}^{-2}$.

Figure 2. Micrographs showing the precipitates in the $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ samples after various irradiation treatments: (a) RT irradiation only; (b) RT irradiation followed by 200 °C irradiation; (c) RT irradiation followed by 250 °C irradiation. (a) and (b)-main are high-resolution Z-contrast STEM images and (b)-inset and (c) are BF TEM images. Coexistence of W (small) and Ag (large) precipitates is observed in (b) and (c). Moiré fringes are used to identify the Ag phase, as illustrated in (b)-inset and (c). The ion dose for RT irradiation is $2.7 \times 10^{16} \text{ cm}^{-2}$ and for irradiation at elevated temperatures is $2.0 \times 10^{16} \text{ cm}^{-2}$.

Figure 3. BF TEM images showing the precipitates in the $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ samples after RT irradiation followed by 300 °C irradiation to a dose of (a) $2.0 \times 10^{16} \text{ cm}^{-2}$ and (b) $4.0 \times 10^{16} \text{ cm}^{-2}$. Ag precipitates are identified by the Moiré fringes. The inset in (a) is a high-resolution TEM image showing the caging of a Ag precipitate by W precipitates.

Figure 4. Micrographs showing the precipitates in the $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ sample after RT irradiation followed by 400 °C irradiation to a dose of $2.0 \times 10^{16} \text{ cm}^{-2}$: (a) a Z-contrast STEM image showing the precipitation in several grains with the arrows pointing to grain boundaries (the few very dark features are analyzed as Kr-stabilized voids); (b) a BF TEM image showing the coexistence of the Ag precipitates (large) and W precipitates (small) and the caging of Ag precipitates by W precipitates.

Figure 5. Z-contrast micrographs showing the precipitates in the $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ sample after RT irradiation followed by 500 °C irradiation to a dose of $2.0 \times 10^{16} \text{ cm}^{-2}$: (a) showing precipitation across an entire grain; (b) showing a Ag precipitate being caged by W precipitates near a grain boundary triple junction.

Figure 6. Statistical information on precipitates of samples being RT irradiated and then irradiated at various temperatures for a dose of $2.0 \times 10^{16} \text{ cm}^{-2}$: (a) histograms of Ag precipitates; (b) average W precipitate sizes and W precipitate interspacing vs. the highest irradiation temperature; (c) average Ag precipitate size vs. irradiation temperature for $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ and $\text{Cu}_{85}\text{Ag}_{15}$ [26], as well as the “caging limit” (for definition see text) vs. temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 7. (a) The ratio of partial diffusivities of vacancies via exchanging with Ag and with Cu in a Cu matrix, in the dilute limit. (b) The rate theory approximation of irradiation-enhanced Ag diffusivity and the thermal diffusivity in Cu as a function of inverse temperature

Figure 8. (a) Solubility of *B* measured for the system with 12 *C* pinning particles (black squares) and without (red dots). The line is the fitting using Gibbs-Thomson equation. (b) A slice of the microstructure at the end of the simulation of the system at the highest point in the solubility bump, showing a pinned *B* precipitate developing positive and negative curvatures. The large positive curvature leads to the high solubility. Red: *A* atoms; Blue: *B* atoms; Yellow: *C* atoms.

(For interpretation of the references to color, the reader is referred to the web version of this article.)

Figure 1

Figure 2(a)

Figure 2(b)

Figure 2(c)

Figure 3(a)

Figure 3(b)

Figure 4(a)

Figure 4(b)

Figure 5(a)

Figure 5(b)

Figure 6(a)

Figure 6(b)

(b)

Figure 6(c)

(c)

Figure 7(a)

Figure 7(b)

Figure 8(a)

(a)

Figure 8(b)

(b)