Radiation effects on interface reactions of U/Fe, U/(Fe+Cr), and U/(Fe+Cr+Ni)

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ABSTRACT

We study the effects of radiation damage on interdiffusion and intermetallic phase formation at the interfaces of U/Fe, U/(Fe+Cr), and U/(Fe+Cr+Ni) diffusion couples. Magnetron sputtering is used to deposit thin films of Fe, Fe+Cr, or Fe+Cr+Ni on U substrates to form the diffusion couples. One set of samples are thermally annealed under high vacuum at 450°C or 550°C for one hour. A second set of samples are annealed identically but with concurrent 3.5 MeV Fe⁺⁺ ion irradiation. The Fe⁺⁺ ion penetration depth is sufficient to reach the original interfaces. Rutherford backscattering spectrometry analysis with high fidelity spectral simulations is used to obtain interdiffusion profiles, which are used to examine differences in U diffusion and intermetallic phase formation at the buried interfaces. For all three diffusion systems, Fe⁺⁺ ion irradiations enhance U diffusion. Furthermore, the irradiations accelerate the formation of intermetallic phases. In U/Fe couples, for example, the unirradiated samples show typical interdiffusion governed by Fick's laws, while the irradiated ones show step-like profiles influenced by Gibbs phase rules.

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A. Introduction

Understanding fuel-cladding interactions is important for reactor design and reactor safety. For fission reactors, both nuclear fuels and the fuel cladding experience significant microstructural and dimensional changes during use. Damage cascades created by neutron recoils and fission products lead to the formation of voids, precipitates, dislocations, pores, and phase transitions. Eventually, the original spacing between the fuel and cladding gap is closed and intermetallic phases begin to form. These compounds are often mechanically fragile. These interactions with the fuel degrade the fuel cladding and increase the chances of a cladding failure in which coolants may penetrate into fuels through a cracked cladding surface. Fuel-cladding interactions have been intensively studied during the past decades by using bulk diffusion couples prepared by bonding U or U-Pu fuel materials with fuel cladding materials such as stainless steels 304, 346 and Incoloy 800 [1-4], with major focus on identifying the intermetallic phases formed and studying the kinetics of the interdiffusion.

Among the various alloys considered for fuel cladding material for fast reactors are ferritic/martensitic steels with Cr additions, which are known to have good swelling resistance and thermal shock resistance [5,6]. Fe-Cr alloys are also considered as the primary structural materials in the first wall and blanket structure for fusion reactors [7,8]. In particular, Fe-Cr alloys have been the bases of various steels explored by several countries, including EUROFER9 [9], F82H [10], JLF-1 [11], CLAM [12], TK-181 [13], and 9Cr-2WVTa [14]. Driven by the need to understand alloy compatibility with the nuclear fuel in fission reactor applications, many studies have used bulk diffusion couples involving pure Fe, Fe-Cr, and Fe-Cr-Ni alloys. Several intermetallic phases for U-Fe and U-Ni couples have been identified [15]. The U and Ni binary system forms U_6Ni , U_7Ni_9 , U_5Ni_7 , UNi_2 , and UNi_5 phases. The U and Fe system only forms two phases, UFe_2 and U_6Fe . No intermetallic phases are observed for the U and Cr system. When U is bonded with a Fe-Ni-Cr alloy, alloying atoms can substitute to form ternary and higher phases, including $U(Fe,Ni,Cr)_2$, $U_6(Fe,Ni,Cr)_2$, $U_6(Fe,Ni)$ and $U_2(Fe,Ni)$ [16].

Bulk diffusion couple studies involving U generally have issues from poor bonding and interface oxidation. Oxidation can initially block interdiffusion and reaction at the alloy/U interface, resulting in an inhomogeneous interaction as evidenced by forming very rough interface zones and/or the observation of a delay to start interdiffusion. Poor bonding results in cavity and crack formation and is another primary reason for large interface variations. Furthermore, bulk diffusion couple approaches are not ideal to study radiation effects on interdiffusion, since diffusion zone changes, if there are any, are difficult to measure with high roughness. The evaluation of radiation effects at high damage levels is even more difficult. For

accelerator based ion irradiation experiments, the penetration depth of ions of MeV energy is a few microns, which limits the interface area available to study the effect of irradiation in bulk diffusion couples, which must be irradiated over a cross section after bonding. The result is that data analysis from bulk diffusion couples is challenging with these combined issues from limited depths, cross sectional analysis, and interface roughness.

In this study, we use physical vapor deposition to deposit thin films of Fe, Fe+Cr, and Fe+Cr+Ni, on depleted U substrates. One advantage of the thin film deposition approach over traditional diffusion couples is that film is highly uniform, and the film thickness is not influenced by micro-scale substrate roughness. The second advantage is that film atoms are deposited on the substrate one by one, without forming cavity and empty space like mechanical bonding. A third advantage is that Ar ion bombardment can be used in-situ to remove surface oxides and form a clean alloy/U interface. The fourth advantage comes from the feasibility in data analysis. With Rutherford backscattering spectrometry (RBS) analysis [17], the interdiffusion of substrate and film atoms into each other can be characterized with minimal effects from substrate roughness. The energy of RBS analysis beam at the interface is determined by the film thickness only, which avoids lateral mixing of data from portions of the originally polished interphase at different heights. The thin film approach also makes it possible to study the interdiffusion kinetics at short time periods, before forming interface compounds. This is important since the diffusion kinetics are expected to be different in different phases. For example, previous studies using diffusion couples have shown an abnormal uphill diffusion of U in UNi_2 phase [16]. Due to complexity of 5f actinides, the accurate description of the diffusion kinetics of uranium, even in simple metal systems, is challenging. While predictions can be made using quantum mechanics-based models, these continue to need validation from experiments.

B. Experimental procedures

The samples employed for this investigation consist of physical vapor deposited (sputtered) Fe and Fe-alloy thin films on depleted uranium (DU) substrates. The DU substrates are prepared from a cast rod produced by triple arc melting. The melt is drop cast to form the rod with a approximate diameter of 4 mm. All subsequent handling and metallographic preparation of the DU is carried out in a glove box under an Ar atmosphere to minimize oxidation and eliminate contamination. The DU rod is sectioned into disks of about 3 mm in thickness, and their surfaces are metallographically prepared down to 1200 grit SiC paper with ethanol as a non-oxidizing lubricant. All DU substrates are stored and transported in inert container until the insertion into the deposition chamber. The Fe (99.9%), Fe-20wt.%Cr, and Fe-

20wt.%Cr-20wt.%Ni alloy are acquired from ACI Alloys, Inc. in disk target form, 50.8 mm in diameter. The complete chemical analyses of these targets are carried out, and the compositions are reported within $\pm 0.3\%$ with O, H, and N as main impurities, each less than 200 ppm.

The depositions are carried out using AJA International A2800 6-gun physical vapor deposition (sputtering) system. The main chamber provides a low base pressure, less than 2.8×10^{-7} Torr, for all processing. The DU substrates, initially transported in acetone, is secured in the deposition carrier using double-sided tape, transferred quickly to the load lock, and pumped down to 5×10^{-5} Torr. This procedure of loading the DU substrates takes less than 1 minute to complete. For all the depositions, the substrates are pre-cleaned in the deposition chamber by a 50 Watt RF (~ 240 volt Ar ion bombardment) plasma at a pressure of 10 ~ 15 mTorr to fully remove any surface oxide that may have formed. For all of the depositions, targets are at full power for 60 seconds prior to the shutter opening, and the substrate RF pre-clean overlap the shutter opening by 10 seconds. The depositions are carried out at 200 Watt DC power to the target, a pressure of 4 mTorr of Ar, flowing at 20 standard cubic centimeters per minute, and for time of 150 to 300 minutes, as needed to achieve the desired film thickness of 1 micrometer.

The film thickness is chosen to be thick enough to allow U interdiffusion with the alloy film without influences from film surfaces. On the other hand, it must be thin enough that RBS analysis beam is able to penetrate through the film and film-substrate interface without significant beam energy variation (straggling) that would result in a degraded depth resolution of the compositional information. The irradiations by 3.5 MeV Fe^{++} ions are performed using a 1.7 MeV tandemron accelerator. The to-be-irradiated samples and control samples are loaded in the same chamber and on the same heating stage to insure that both types of samples experienced the same annealing. The only difference in the procedure is that the control samples are not exposed to the Fe^{++} ion beam. The annealing temperatures are 450 and 550 °C, selected based on the fact the fuel-cladding interface temperature is about 400 to 430 °C for a typical pressured water reactor. The ion beam is collimated through an aperture of 4mm in diameter and scanned over an area of 1cm $\times$ 1cm of the thin film diffusion couple samples. The beam current is controlled to be ~ 200 nA. The chamber was maintained at a high vacuum, better than 5×10^{-7} Torr, during the experiment. A thermocouple is installed on the backside of the sample to record sample temperature and used as feedback to automatically adjust the heater power to maintain the designed temperature. In addition, an infrared camera is used to monitor the surface temperature of the samples. Upon irradiation, the temperature of front surfaces is found to increase only $\sim 2^\circ\text{C}$ higher than the backside. This small increase justifies ignoring the beam heating effect in the analysis of the data. After Fe^{++} ion irradiation, the RBS analysis is carried out by using a 2 MeV He^+ ion beam obtained from the same accelerator. The

RBS analysis beam current is about 10 nA and the accumulated charge for each analysis is about 4×10^{-6} coulomb. A semiconductor solid state detector of 15 keV energy resolution is positioned at 165° away from the beam incident direction and used to collect the RBS spectra. The solid angle of the detector is 0.0008 sr. The RBS spectra are simulated by using SIMNRA code [18]. The simulations considers both electronic energy loss straggling based on Chu's theory [19,20], and the plural scattering effect based on dual scattering approximation [21].

C. Results

Figure 1 plots the calculated displacements per atom (dpa) as a function of depth into the sample for Fe/U thin film diffusion couple, obtained by using SRIM code [22]. The position of the Fe/U interface is determined by the Fe layer thickness of 480 nm, calculated from the Fe atomic area density (from RBS measurement) and the bulk Fe atomic density of 8.48×10^{22} atoms/cm³. The dpa calculations use the default displacement energies of 25 eV for both Fe and U atoms. The damage calculations use the Kinchin-Pease model instead of full damage cascade model since the latter has been reported to suffer from dpa overestimation [23]. After the irradiation by $9 \times 10^{15}/\text{cm}^2$ 3.5 MeV Fe⁺⁺ ions, the accumulated damage at the U/Fe interface reaches about 10 dpa in the Fe side, and about 20 dpa in the U side. The dpa difference between each side of the interface is caused by the differences of cross sections for displacement creation between U and Fe. The SRIM calculated sputtering yield is 1.3 atom per Fe ion. Thus, the total loss of deposited Fe layer thickness due to the irradiation is only ~ 1.4 nm, which is ignored in the diffusion analysis. The density of Fe ion implants is calculated to peak at a depth of 1 μm from the surface, which is about 0.6 μm below the U/Fe interface. At the interface region, the density of Fe implants is about $3 \times 10^{19}/\text{cm}^2$, which is about 0.04% of the Fe atomic density and 0.06% of the U atomic density, hence the direct compositional contribution of the irradiation can also be ignored in analysis of the Fe/U interdiffusion. One interesting feature in Fig. 1 is the presence of dpa drops at Fe/U interface. The cause of the drop is complicated. The drop at Fe side is due to the lack of Fe damage cascade contribution from deeper region due to discontinuity of the film, while the drop at U side is an artifact from SRIM code. The code uses free flying distance concept for fast calculations under full damage cascade mode. Hence there are no collisions within the first free flying distance, starting from the Fe/U interface.

Figure 2 compares the RBS spectra obtained from all three diffusion systems with or without ion irradiation as deposited and annealed at temperatures of 450°C and 550°C for 1 hour. U has large atomic mass (238) and its spectra are well separated from that of the other elements. The atomic masses of the

other elements (Cr at 52, Fe at 56, and Ni at 59) are close to each other, and their individual contributions to the RBS spectra are not separable. The backscattered He ion beam from Fe at the film's exterior surface contributes to yield front close to channel number 400. A bare U substrate without film deposition should contribute to a yield front close to channel number 500. However, He ion energy loss after traveling through the alloy film's thickness reduces the He ion energy when scattered from U atoms. This shifts the major (substrate) portion of the U signal to the lower channel regions, with the extent of shift determined by the as-deposited alloy film thickness. For all spectra, signals with channel number >400 are contributed by U diffusion tails within the alloy thin film towards the exterior surface (channel number 500 for U). In other words, the diffusion tails of U in the films cause signals separated from the Fe signals. Based on the height difference of U diffusion tails, it is easy to reach conclusions that in all irradiated samples (denoted by red color), U diffusion is enhanced when compared with unirradiated samples (denoted by green color).

The red and green curves in both Fig. 2(b-2) and (c-2) show a sharp peak at a channel close to 500, which means that a significant fraction of U reach Fe (or Fe-Cr alloy) exterior surface and begin to accumulate in the plane of the surface, achieving a concentration (atoms/cm²) higher than that of the planes in the Fe alloy layer below the surface. This can occur when the Fe alloy film thickness becomes insufficient, comparable or less than the mean diffusion length of the U atom. Due to this accumulation, no further attempts are made to extract diffusivities from 550°C annealed/irradiated U/(Fe+Cr) and U/(Fe+Cr+Ni) diffusion couple data due to complexity of modeling the interdiffusion with this boundary condition.

For the SIMNRA fitting, the U diffusion profiles are divided into approximately 20 layers, with the deepest layer corresponding to the pure U substrate. The U diffusion tails close to the film surface are simulated first since the RBS spectra provide excellent separation of the Fe and U compositional information in this region. Then the U concentrations are incrementally calculated for deeper layers. The sensitivity of RBS is a function $\sim Z^2$, and hence the technique has very high accuracy in measuring U compositions. For example, for U diffusion tails near the film surface, any normalized composition change above 0.001 can lead to noticeable RBS yield changes. To illustrate the ability of the RBS spectra to correctly provide compositional information in the region of U and Fe overlap, figure 3 compares the simulated spectra with experimental data, wherein different simulation spectra are shown to indicate possible changes in the U concentration of $\pm 10\%$. The inset shows the U concentration profile extracted from 450°C irradiated U/Fe. The pair of arrows in the inset mark the points after upshifting (+10%) and downshifting (-10%). Even if only one point is shifted by this small amount, the change that would be

observed in the RBS spectrum is readily apparent, as denoted by the two red curves, which deviate significantly from the experimental data (gray squares).

C.1 U/Fe

Figure 4 and 5 compare the experimentally obtained (squares) and simulated (solid line) RBS spectra from U/Fe thin film diffusion couples annealed at 450°C and 550°C, respectively. Figure 4a is the data and fit from analysis of the as-deposited U/Fe couple before annealing. Figures 4b and 4c correspond to 450°C annealing, without or with concurrent Fe ion irradiation, respectively. Figure 5a and 5b correspond to 550°C annealed sample without and with concurrent ion irradiation, respectively.

Figure 6 summarizes the RBS spectra simulations in terms of the U and Fe composition profiles from the exterior film surface downwards for the Fe/U couples annealed at 450°C. Fig. 6a is for annealing only, and 6b is for the irradiated annealing. Fig. 6c compares these two U profiles, plotted in log scale to highlight the difference at low U concentration regions. The radiation induced diffusion enhancements are small but noticeable. The He ion energy loss is determined by the atomic areal density of the film penetrated by the He ion beam, therefore the RBS simulation can only give the thickness as $N \times d$, whereas N is atomic density and d is the film depth. The thickness zero corresponds to the film surface. The simulated spectra for the as-deposited film are not provided here, simply because the U and Fe distributions are sharp step profiles without any mixing or preexisting interdiffusion. The U and Fe penetrations into each other are smooth and there is no step-like profile observed, suggesting that Gibbs phase rule does not play a role yet. The thermal budget is high enough to cause significant interdiffusion but still low enough to avoid interfacial intermetallic compound formation. Otherwise, two steps corresponding to U_6Fe in U side and UFe_2 in Fe side will form.

The data calculated from the 550°C annealed Fe/U diffusion couples are shown in figure 7. Figure 7a and 7b show the extracted U and Fe profiles from unirradiated and irradiated samples, respectively, and these two U profiles are further compared in Fig. 7c. At the higher temperature 550°C, interdiffusion is greater, and the radiation effect is stronger, as shown by larger profile difference in Fig. 7c. One important finding is that ion irradiation accelerates the formation of intermetallic phases. As marked by the arrow in Fig. 7c, the irradiated U profile begins to show a transition towards a step-like distribution at a U concentration of ~ 0.8 , while the unirradiated U profile follows a smoother interdiffusion distribution. Further evidence of diffusion behavior difference can be found from the derivatives of two U profiles. As shown in Fig. 8a for 550°C unirradiated sample, the derivative of the U profile reaches a single peak at

the location of the Fe/U interface. In contrast, Fig. 8b shows that the derivative of the U profile for the 550°C irradiated sample has two peaks. The local minimum between two peaks, as marked by the arrow, corresponds to the U profile shoulder region marked in Fig. 7c. Note that the arrow position is in the U-rich side of the profile, hence the phase formed is likely to be U_6Fe or its precursor. Both U profiles and their derivatives approach to zero at the film surface, suggesting that the U diffusion is not influenced by presence of the exterior surface and there is no uphill diffusion or surface segregation.

The calculations of interdiffusion coefficients include the following two steps. First, the position of the Matano planes, x_0 , is calculated by

$$\int_{C_U^{-\infty}}^{C_U^{+\infty}} (x - x_0) dC_U = 0 \quad [1]$$

where C_U is the U concentration at position x . $C_U^{-\infty}$ (=0 at the film surface) and $C_U^{+\infty}$ (=1 at deep depth within the U substrate) are the U concentrations at the two terminal ends of the diffusion system. Second, the concentration dependent U diffusivities are calculated by

$$\tilde{D}(C_U^*) = -\frac{1}{2t} \frac{\int_{C_U^{-\infty}}^{C_U^*} (x - x_0) dC_U}{(dC_U/dx)_{C_U^*}} \quad [2]$$

where C_U^* is the U concentration for which the diffusivity is to be determined. It has been shown that $\tilde{D}$ values can be scattered due to small fluctuations of dC_U/dx , and one mathematical treatment to minimize such fluctuations is to use Spline method to smoothen the experimental data [24], which can be readily done as an interpolation option, as provided in commercial software OriginPro 8 (OriginLab, Northampton, MA).

Figure 9 compares the extracted U interdiffusion coefficients as a function of U concentrations. In general, U diffusivities decrease with increasing U concentrations. The lines are used to guide the comparisons. For 450°C, the effects of ion irradiation are small but noticeable with approximately a 25% diffusivity enhancement. For 550°C, the irradiation enhancement is about 40%. For both irradiated and unirradiated samples, comparing the 450°C anneal to that at 550°C, the U interdiffusion coefficients (at U concentration <0.4) change by only a factor of ~2. This suggests a small activation energy of ~0.2eV if the interdiffusion coefficients follow an Arrhenius temperature dependence. At 550°C, the U rich region (U concentration >0.4) has large interdiffusion coefficients which deviate from the straight line trend of the low U concentration region. This region has not only a higher $\tilde{D}$ enhancement but also higher $\tilde{D}$ activation energy after ion irradiation. However, we cannot exclude the possibility that data for the U rich region is influenced by the phase formation since Eq.[2] is invalid when the flux is not proportional to the concentration gradient.

C.2 U/(Fe+Cr)

Figure 10 shows the RBS spectra and corresponding spectra simulation for the U/(Fe+Cr) diffusion couples for the as-deposited (Fig. 9a), 450°C annealed (Fig. 9b) and 450°C annealed and irradiated (Fig. 9c) conditions. All simulated spectra agree well with experimental results. The analysis excludes the 550°C data since significant U diffusion at this temperature leads to surface U segregation (as shown in Fig. 2(b-2)). Figure 11 compares the U and Fe+Cr composition profiles obtained through RBS spectra simulations. As shown in Fig. 11a, in contrast to U/Fe diffusion samples, step-like distributions at the interface reaction region are clearly observed in U/(Fe+Cr). Due to the convolution of the Fe and Cr compositional information (due to close atomic masses) and the fact that the diffusion couple is not in a near-equilibrium condition for this annealing time, it is not possible to identify the phases formed. A similar step-like profile is also observed in the irradiated sample, as shown in Fig. 11b. The comparison in Fig. 11c further shows that ion irradiation causes a longer diffusion tail beyond the region where the intermetallic phases are formed. No additional analysis on the interdiffusion coefficient is performed since Eq. [2] becomes invalid.

The U and Cr binary system has no interface compound formation, while U and Fe can form UFe_2 and U_6Fe phases [25]. But adding Cr into U/Fe system may change the U-Fe phase formation. Previous studies on diffusion couples made of U-Zr and Fe, and of U-Zr and Fe-Cr suggest such complexity [26]. Cr diffuses slowly in U side, thus leading to a Cr rich layer at the interface. With Cr, a single layer of U_6Fe forms in (U+Zr)/(Fe+Cr) couples. Without Cr, such a single layer is not observed in the U-Zr/Fe couples. This suggests that Cr addition can influence the formation certain phases [26]. Furthermore, although Cr does not form a UCr_2 binary compound, it can substitute Fe to form $\text{U}(\text{Fe}_{1-x}\text{Cr}_x)_2$ [27].

C.3 U/(Fe+Cr+Ni)

Figure 12a-c compare the experimental and simulated RBS spectra for U/(Fe+Cr+Ni) diffusion samples as deposited, unirradiated at 450°C, and annealed and irradiated at 450°C, respectively. Figure 13a and b show the elemental profiles extracted from RBS spectral simulations without and with Fe^{++} ion irradiation at 450°C, respectively. There is no step like feature observed in Fig. 13a, suggesting that the no intermetallic phase forms in this diffusion couple. For the sample with ion irradiation (Fig. 13b), the profile shows a slight deviation from a typical interdiffusion curve near the Matano plane (the straight

line), which can be caused by either phase formation or a changed diffusivity across the Matano plane. Figure 13c compared the U profiles and the evidence of irradiation enhanced interdiffusion is obvious.

Figure 14 shows the extracted interdiffusion coefficients of U at 450°C for the U/(Fe+Cr+Ni) diffusion couples. The concentration dependence of the coefficients suggests a transition from one trend to another, at the position close to the Matano plane. At low U concentration region (<0.5), or in the Fe+Cr+N side, the interdiffusion coefficients are less sensitive to U concentration. The data for the irradiated sample is not plotted and compared, due to the concern that new phases may have formed.

D Discussion

Neutron and ion irradiation enhance diffusivities primarily through changing two key parameters, one is diffusion frequency and the other is diffusion length, as expressed by $D = \lambda d^2$ where λ is the time rate of successful diffusion events and d is the mean migration distance in one diffusion event. As most metals diffuse through vacancy diffusion mechanisms, λ is primarily determined by two factors: the likelihood of finding a vacancy nearby a given atom and the energy barrier that must be overcome for an atom to occupy the vacancy site. Under annealing without ion irradiation, the likelihood of finding a vacancy on a given site is determined by equilibrium vacancy numbers, or the formation energies of vacancies. Under ion irradiation, supersaturated point defects are introduced through nuclei-nuclei collisions, resulting in athermally enhanced λ by $\lambda \propto \bar{C}_V / C_V^*$, where $\bar{C}_V$ and C_V^* are mean vacancy concentration and equilibrium vacancy concentration, respectively [28]. Irradiation is unlikely to significantly change d , since the dissociation of one atom-vacancy pair, which represents the ending of one diffusion event, is determined by vacancy binding energy. Irradiation can manipulate d only when tracer atoms diffuse through complicated mechanisms such as dissociative diffusion mechanism in which one diffusion event must be ended by occupying an empty site.

A strong diffusivity dependence on U concentration is expected. Under thermal annealing conditions, the vacancy formation energy, the vacancy binding energy (energy required to dissociate a mobile atom-vacancy pair), and migration energy of atoms are all expected to change when alloy composition is changed. Under ion irradiation conditions, the U concentration difference may influence the following parameters: the cross section of nuclear stopping, the threshold energy of displacement creation, energy barrier for interstitial-vacancy recombination, and the kinetics of defect clustering. These parameters determine the time evolution of point defect concentrations and hence the defect mediated diffusion.

When incident Fe ions penetrate through the substrate-film interface, nuclei-nuclei scattering may result in two kinds of damage; one is recoil mixing and the other is damage cascade mixing [29]. Recoil mixing refers to the long range atomic relocation due to knock on events. The damage cascade mixing refers to the formation of a high density of point defects featuring with a vacancy-rich core and interstitial-rich shell. The damage cascade creation is followed by defect recombination, local energy equilibrium and thermal spike formation [29]. Both long range recoil mixing and short range cascade mixing will help atom transport at the interface, particularly if the interface has a thin oxidation layer which might otherwise effectively block the interdiffusion at an early stage of annealing.

A collision-displaced target atom will not diffuse, if it follows vacancy diffusion mechanism and if there is no vacancy nearby. From this consideration, the diffusion enhancement due to irradiation is largely due to the supersaturated point defect populations, which increase the chances of atoms to move. On the other hand, the average diffusivity, or the average defect number, is a result of complicated defect reactions at elevated temperatures. Under a simplified picture in which only defect creation, interstitial-vacancy recombination, and defect annihilation at grain boundaries are considered, the vacancy density will first increase linearly with time, then reach saturation [30]. This means that the irradiation enhancement effects are likely dependent on time. At a later stage when phase formation occurs, the time dependence of defect densities are even more complicated, as these phases begin to influence defect clustering through their defect sink properties.

Radiation is expected to promote intermetallic phase formation. The high temperature, high pressure, and stoichiometry deviations associated with damage cascades can promote phase formation by either lowering the nucleation energy barrier or by reducing the critical temperature required by phase transition. Furthermore, the defect clusters, such as edge dislocations, can act as preferred nucleation sites for new phases to form.

The interdiffusion is contributed by the sum of bulk diffusion and grain boundary diffusion. Due to relatively lower migration energy barriers at grain boundaries, grain boundary diffusion dominates low temperatures. At a high temperature with higher defect densities, bulk diffusion becomes dominant. For the present study, we believe that grain boundary diffusion plays an important role in mass transport because of the relatively lower temperatures used. Since grain boundaries act as defect sinks and boundary defect numbers expect to be at the equilibrium value even under ion irradiation [30], diffusion at a grain boundary is less affected by radiation damage. But radiation enhanced bulk diffusion can increase the mass transport from bulk to grain boundaries. Therefore the overall diffusivity is still

sensitive to radiation damage at low temperatures. The diffusivity enhancement expects to be larger at higher temperature when bulk diffusion becomes dominant.

The study shows that interdiffusion behaviors of U/Fe and U/(Fe+Cr+Ni) are similar and both show certain resistance to interface phase formation. In a comparison, U/(Fe+Cr) is less resistant. We hypothesize that resistance difference is relevant to vacancy diffusions, as reflected by swelling difference between Fe, Fe+Cr, and Fe+Cr+Ni. Earlier studies have shown that adding Cr in Fe alloys enhances swelling but adding Ni reduces swelling [31]. There are certain competing effects between Cr and Ni for influencing defect migration.

The finding that ion irradiation can speed up interface compound formation may be valuable to the development of phase field theory. The phase field theory predicts phase changes based on energy minimization. However, how to apply this theory, developed under basic assumption of equilibrium conditions, to describe nonequilibrium process is still unclear. A simple diffusion system, such as U/Fe, may serve to aid the development of phase field modeling.

E Conclusion

Our study shows that U/Fe has minimal interdiffusion when compared with other two systems U/(Fe+Cr) and U/(Fe+Cr+Ni). For example, at 450°C, the U interdiffusion coefficient for U/Fe at a normalized U composition of 0.4 is about $2 \times 10^{-14} \text{ cm}^2/\text{s}$, and this coefficient increases to $1 \times 10^{-13} \text{ cm}^2/\text{s}$ in U/(Fe+Cr+Ni) diffusion couples. Among all three systems, U/(Fe+Cr) most rapidly forms an intermetallic phase at the U/alloy interface. After one hour annealing at 450°C, step-height like elemental distributions are clearly visible.

All three diffusion systems show radiation enhanced diffusion. The radiation enhancement at 450°C are ranked, from low to higher, as $\text{U/Fe} < \text{U/(Fe+Cr)} < \text{U/(Fe+Cr+Ni)}$. Furthermore, it is clear that ion irradiation can promote intermetallic phase formation. For U/Fe couples irradiated at 550°C, the U interdiffusion begins to develop step- like features. In comparison, such feature is not observed in unirradiated U/Fe.

The present study shows that the role of radiation damage must be considered for development of a predictive ability to describe fuel-cladding interactions and interface reactions. The study also shows that feasibility of using the thin film deposition and RBS analysis for such studies.

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Figure 1 SRIM calculations of dpa (left y axis) and Fe implant (right y axis) depth distributions in Fe/U after irradiation by 3.5 MeV Fe ions to a dose of $9 \times 10^{15}/\text{cm}^2$.

Figure 2. RBS spectra of (a) U/Fe, (b) U/(Fe+Cr), and (c) U/(Fe+Cr+Ni) samples as-deposited (black), after annealing only (green), or after annealing with concurrent 3.5 MeV Fe ion irradiation (red). The left column has spectra obtained from samples annealed at a temperature of 450°C and the right column is that from an anneal at 550°C.

Figure 3 Sensitivity testing for the RBS spectra fitting. The gray squares are experimentally obtained RBS spectrum from 450°C irradiated U/Fe diffusion couple. The dark line is the best fit simulation of the experimental spectrum. The blue triangles in the inset are the U profile extracted from the best fit simulation. The red squares in the inset refer to two points shifted away from the best fit simulation by $\pm 10\%$. This shifting leads to the deviation of the simulated spectra from experimental data shown by the two red curves in the figure.

Figure 4 RBS spectra of (a) an as-deposited U/Fe sample, and (b) a U/Fe sample after annealing at 450°C for 1h, and (c) a U/Fe sample after annealing with concurrent 3.5 MeV Fe ion irradiation at 450°C for 1h. The squares correspond to experimentally obtained spectra and the solid lines correspond to the simulated spectra.

Figure 5. RBS spectra of U/Fe samples (a) after annealing at 550°C for 1h, and (b) after annealing with concurrent 3.5 MeV Fe ion irradiation at 550°C for 1h. The squares correspond to experimentally obtained spectra and the solid lines correspond to the simulated spectra.

Figure 6. The U and Fe profiles extracted from spectral simulations. (a) Fe/U after annealing at 450°C for 1h; (b) Fe/U after annealing and concurrent 3.5 MeV Fe ion irradiation at 450°C for 1h; and (c) the comparison of U profiles with or without ion irradiation.

Figure 7. The U and Fe profiles extracted from the RBS spectra simulations. (a) Fe/U after annealing at 550°C for 1h; (b) Fe/U after annealing and concurrent 3.5 MeV Fe ion irradiation at 550°C for 1h; and (c) the comparison of U profiles with or without ion irradiation.

Figure 8. The derivative of U composition profile of a U/Fe sample (a) annealed at 550°C without irradiation and (b) annealed at 550°C with ion irradiation.

Figure 9. The interdiffusion coefficients of U/Fe samples, determined from profiles obtained through RBS spectra fitting. Comparison are made for 450°C and 550°C anneals

Figure 10. The RBS spectra of (a) an as-deposited U/(Fe+Cr) sample, and (b) a U/(Fe+Cr) sample after annealing at 450°C for 1h, and (c) a U/(Fe+Cr) sample after annealing with concurrent 3.5 MeV Fe ion irradiation at 450°C for 1h. The squares correspond to experimentally obtained spectra and the solid lines correspond to simulated spectra.

Figure 11. The U and Fe/Cr profiles extracted from RBS spectra simulations of U/(Fe+Cr) samples. (a) After annealing at 450°C for 1h; (b) after annealing and concurrent 3.5 MeV Fe ion irradiation at 450°C for 1h; and (c) the comparison of U profiles with or without the ion irradiation.

Figure 12. RBS spectra of (a) an as-deposited U/(Fe+Cr+Ni) sample, and (b) a U/(Fe+Cr+Ni) sample after annealing at 450°C for 1h, and (c) a U/(Fe+Cr+Ni) sample after annealing with concurrent 3.5 MeV Fe ion irradiation at 450°C for 1h. The squares correspond to experimentally obtained spectra and the solid lines correspond to simulated spectra.

Figure 13. The U and summed Fe+Cr+Ni profiles extracted from spectral simulations of U/(Fe+Cr+Ni) samples. (a) After annealing at 450°C for 1h; (b) after annealing and concurrent 3.5 MeV Fe ion irradiation at 450°C for 1h; and (c) the comparison of U profiles with or without the ion irradiation.

Figure 14. The interdiffusion coefficients of U/(Fe+Cr+Ni) samples, determined from profiles obtained through RBS spectral fitting.