Interdiffusion and Reactions between U-Mo and Zr at 650°C as a Function of Time

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Abstract

Development of monolithic U-Mo alloy fuel (typically U-10wt.%Mo) for the Reduced Enrichment for Research and Test Reactors (RERTR) program entails a use of Zr diffusion barrier to eliminate the interdiffusion-reactions between the fuel alloy and Al-alloy cladding. The application of Zr barrier to the U-Mo fuel system requires a co-rolling process that utilizes a soaking temperature of 650°C, which represents the highest temperature the fuel system is exposed to during both fuel manufacturing and reactor application. Therefore, in this study, development of phase constituents, microstructure and diffusion kinetics of U-10wt.%Mo and Zr was examined using solid-to-solid diffusion couples annealed at 650°C for 240, 480 and 720 hours. Phase constituents and microstructural development were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Concentration profiles were mapped as diffusion paths on the isothermal ternary phase diagram. Within the diffusion zone, single-phase layers of β -Zr and β -U were observed along with a discontinuous layer of Mo_2Zr between the β -Zr and β -U layers. In the vicinity of Mo_2Zr phase, islands of α -Zr phases were also found. In addition, acicular α -Zr and $\text{U}_6\text{Zr}_3\text{Mo}$ phases were observed within the γ -U(Mo) terminal alloy. Growth rate of the interdiffusion-reaction zone was determined to be $1.81 \times 10^{-15} \text{ m}^2/\text{sec}$ at 650°C, however with an assumption of a certain incubation period.

1. Introduction

The Reduced Enrichment for Research and Test Reactors (RERTR) program, now known as Global Threat Reduction Initiative (GTRI), is tasked with development and certification of low-enriched U-Mo fuels [1] for the research and test reactors around the world. For low-enriched fuels, higher U-density in the fuel meat is required to achieve the equivalent high-enriched uranium fuel [2]. In U-Mo fuel alloys, the alloying addition of Mo stabilizes the (bcc) γ -U phase with excellent irradiation behavior. The Mo has a wide solubility in γ -U, which allows for fuel customization, while satisfying the fissile-U densities required by various research and test reactors. Many investigations have been carried out to develop an understanding of the phase equilibria/thermodynamics [3-11] kinetics [11-13], mechanical properties [14,15], and irradiation behavior [16-21] for the binary U-Mo alloys. The U-Mo alloy fuel is considered for both dispersion and monolithic design [21]. Typically dispersion fuel contains U-density of approximately 8 g/cm³, while monolithic fuel contain that of approximately 15.6 g/cm³. The monolithic fuels have been reported to have a very positive performance during irradiation test in high-flux reactors [21].

The U-Mo alloys, typically containing 8 to 12 wt.% Mo for the RERTR applications, can undergo complex interdiffusion and reactions in contact with Al matrix or cladding, which can produce various phases with rapid growth kinetics [22-25] and undesirable irradiation behavior [16-18]. In monolithic fuels, AA6061, with nominal composition of, in wt.%, Al-1.0Mg-0.6Si-0.7Fe-0.25Zn-0.2Cu-0.2Cr-0.15Mn-0.15Ti, is commonly used to encase the U-Mo fuel to provide structural stability and to isolate the fuel. Interactions between the U-Mo and AA6061 take place at high temperature (450~650°C) during fuel plate manufacturing, and at lower temperature in reactor (well below 300°C), however possibly with irradiation-enhancement.

To reduce the overall kinetics and complexity of this diffusion interaction, Zr can be used as a diffusion barrier between the U-Mo fuel and AA6061 cladding [19,26,27]. Consequently, however, **interdiffusion and reactions** can occur between U-Mo and Zr, as well as Zr and AA6061 during the fuel plate fabrication. Typically these monolithic fuels are produced by the repeated co-rolling of Zr-laminated U-Mo fuel at soaking temperature reaching up to 650°C, **followed by** hot-isostatically pressing (HIP'ing) with AA6061 cladding at temperature ranging from 520 to 580°C. During co-rolling, it is estimated that the Zr laminated U-Mo fuel is exposed to the highest temperature of 650°C for approximately 2 to 3 hours.

Perez *et al.* [28] have reported microstructural development of U-10 wt.% Mo monolithic fuels in AA6061 cladding with Zr diffusion barrier. The γ -U(U-Mo), γ -UZr, Zr solid-solution and Mo_2Zr phases were observed between U-Mo and Zr. The $(\text{Al,Si})_2\text{Zr}$, $(\text{Al,Si})\text{Zr}_3$, $(\text{Al,Si})_3\text{Zr}$, and AlSi_4Zr_5 phase were observed between AA6061 and Zr. Park *et al.* [29] further examined phase constituents and microstructure changes as function of temperature (520, 540, 560 and 580 °C for 90 minutes) and duration (45~345 minutes at 560 °C) of hot-isostatic pressing (HIP) during fabrication. Jue *et al.* [30] also evaluated the HIP-bonded monolithic fuels with Zr diffusion barrier with emphasis on decomposition of U-Mo region, formation of Mo_2Zr precipitates and geometry-restricted processing defects associated with hot-rolling process.

To examine the details of **interdiffusion and reactions** between the U-10wt.%Mo (U10Mo) fuel and Zr diffusion barrier, diffusion couple experiments have been carried out at temperatures between 600 and 1000°C, in 100°C increments by Huang *et al.* [27]. According to Huang *et al.* [27], a negligible amount (i.e., less than the resolution of scanning electron microscope) of U10Mo/Zr interactions occurred at 600°C, while quantitative and qualitative analyses were carried out for couples annealed between 700° and 1000°C based on definite diffusion

interactions. According to Huang *et al.* [27], while the growth kinetics followed typical Arrhenius relation between 700° and 1000°C, lack of interaction at 600°C warranted a further investigation at temperature lower than 700°C. Furthermore from a RERTR applications perspective, an understanding of interdiffusion and reactions at 650°C is important, directly related to the co-rolling process, and starting microstructure for HIP.

In this study, the phase constituents and the growth of the interaction zone that develop between the U10Mo alloys and Zr at the co-rolling soaking temperature of 650°C were examined as a function of time using solid-to-solid diffusion couples. The couples were annealed at 650°C for 240, 480 and 720 hours to develop interaction regions with phase constituents observable by scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (XEDS). Details of microstructure and phase constituents were further examined by using transmission electron microscopy (TEM) for the couple annealed for 720 hours. Concentration profiles were determined by SEM-XEDS to construct semi-quantitative diffusion paths on the isothermal U-Mo-Zr phase diagram. For the couples annealed for 480 hours, variation in cooling rate (water-quench vs. furnace-cooling) was carried out to discern any difference, if any, in phase transformations.

2. Experimental Details

All metallurgical preparation and assembly of diffusion couples were carried out under an Ar atmosphere inside a glove box to minimize oxidation of the alloys. The U10Mo alloy and high-purity Zr (99.8%) were employed for the experiments. The U10Mo alloy was cast using high-purity depleted U and Mo via arc melting. They were melted three times to ensure the homogeneity and then drop-cast to form rods with ¼ inch (6.35mm) diameters. The as-cast rods

were then homogenized in an Ar atmosphere at 950°C for 96 hours. The U10Mo alloy was water-quenched in ice water after homogenization to retain the high temperature γ -phase. The homogeneity in composition, phase constituents, and microstructure of the alloys were examined by X-ray diffraction (XRD) on a RigakuTM DMAX-B and by scanning electron microscopy (SEM) on a ZeissTM Ultra 55 SEM equipped with X-ray energy dispersive spectroscopy (XEDS).

The U10Mo and Zr rods were sectioned into discs 6.35 mm in diameter and 3 mm in thickness. The faces of the U10Mo and Zr discs were metallographically polished with a final step using 1 μ m diamond paste. The polished surfaces were then placed in contact with each other, and held together by two clamping disks with stainless steel rods to form a jig. Jig assemblies were encapsulated in quartz capsules, and sealed under an Ar atmosphere after repeated vacuum (10^{-6} torr) and H₂ purge. Ta foil was placed inside the capsules prior to sealing to serve as an oxygen getter. All couples were annealed using a Lindberg/BlueTM three-zone tube furnace. Diffusion couples of U10Mo vs. Zr were annealed at 650°C for 240, 480 and 720 hours in order to develop large interdiffusion zones for feasible microstructural analyses. After annealing, the diffusion couples were quenched by breaking the quartz capsule in ice water. The process of water-quench typically takes approximately 10 seconds to complete: 6 seconds to pull the capsule from the center of the horizontal tube furnace to the end of the tube, 1 second to put the capsule in the water, and 3 seconds (after the steam clears-up) to break the capsule in the water. For an additional diffusion couple annealed for 480 hours, furnace cooling was carried out simply by turning off the furnace. All four diffusion couples were then mounted in epoxy, cross-sectioned, and polished with a final step using 1 μ m diamond paste for microstructural examination.

For each diffusion couple, SEM analysis was carried out to examine the quality of the diffusion bond, and measure the thickness of the interaction zone. The interaction zone thickness for each couple was determined by measuring the area of the zone in the SEM micrographs, and then by dividing the area by the zone's width. The growth constants, k , defined by the thickness, $Y = kt^{1/2}$, where t is the anneal time, were determined for each diffusion couple based on the assumption of parabolic growth. Compositional analysis of selected regions and/or phases was carried out by standard-less XEDS via SEM. Concentration profiles were also generated by SEM-XEDS. For the water-quenched diffusion couple after anneal for 720 hours, a few TEM samples were prepared using the focused ion beam (FIB) in-situ lift-out (INLO) technique. Selected area electron diffraction (SAED), XEDS and high angle annular dark-field (HAADF) were employed to examine the interdiffusion and reactions between U10Mo and Zr in detail.

3. Phase Constituents and Microstructure

Typical backscatter electron (BSE) micrographs from the U10Mo vs. Zr diffusion couples annealed at 650°C are presented in Figure 1. Figure 1(a), (b) and (c) are the BSE micrographs from water-quenched diffusion couples that were annealed for 240, 480, 720 hours, respectively. Figure 1(d) is the BSE micrographs from the diffusion couples annealed for 480 hours and furnace cooled. The interdiffusion and reaction in these couples resulted in similar microstructure with phase constituents. Based on BSE micrographs and XEDS analyses, phase constituents such as γ -U(Mo) solid solution (cI2), needle-like α -Zr (hP2) precipitates, Mo_2Zr (cF24), bcc β -Zr (cI2), and α -Zr (hP2) were identified as labeled in Figure 1.

Figure 2 presents a HAADF scanning TEM (STEM) micrograph from the region near the

interface between the γ -U(Mo) solid solution and β -Zr layer, where the discontinuous Mo_2Zr layer, needle-shaped α -Zr precipitates, blocky $\text{U}_6\text{Zr}_3\text{Mo}$ precipitates, and β -U layer were observed. Based on fast-Fourier transformation (FFT) of high-resolution TEM (HR-TEM) micrograph, from region (1) in Figure 2, the needle-shaped Zr precipitates were identified as α -Zr (hP2) surrounded in a matrix of γ -U(Mo) as presented in Figure 3. Figure 4 shows the SAED patterns collected from the region 2 in Figure 2 corresponding to the layers of β -Zr, Mo_2Zr and β -U. Occasionally within the β -U layer, small precipitates of α -Zr (hP2) were also observed as presented in Figure 5. Formation of the Mo_2Zr phase would deplete the Mo content from the U10Mo alloy, and can destabilize the γ -U(Mo) solid solution into the β -U with limited solubility for Zr. This would promote the formation of α -Zr precipitates upon cooling near the interface between the γ -U(Mo) solid solution and β -Zr layer since a two-phase equilibrium between the γ -U(Mo) and α -Zr does not exist at 650°C.

Aside from the stable Mo_2Zr and β -Zr phases, the microstructural development and phase formation presented can be a result of cooling after diffusion anneal. For example, analysis of blocky precipitates in region 3 of Figure 2 confirmed the presence of $\text{U}_6\text{Zr}_3\text{Mo}$ phase as presented in Figure 6. The $\text{U}_6\text{Zr}_3\text{Mo}$ phase, according to the ternary phase diagrams, should form at lower temperature during cooling. Figure 7 summarizes the phase constituents and microstructural development observed between the γ -U(Mo) solid solution and β -Zr layer in this study from the diffusion couples annealed at 650°C. Table I lists crystallographic information on phases identified within the interaction zone in this investigation. No significant variation in phase constituents was observed as a function of anneal time or cooling rate.

Onset of void formation during irradiation has been presented [19] few micrometers away from the fuel/barrier interface. Based on observation in this study, this location can correspond to the presence of U_6Zr_3Mo and needle-shaped α -Zr, and/or the interface between the γ -U(Mo) and β -U. Furthermore, the presence of β -U (possibly α -U with anneal at lower temperature of 520~580°C during subsequent HIP may adversely affect the irradiation behavior of the bonding between the U10Mo fuel and Zr diffusion barrier. Previous works [28-30] has noted several changes in the phase constituents including the presence of UZr_2 , after secondary anneal at lower temperature, with or without pressure, relevant to HIP (520~580°C), after the initial anneal at higher temperature (e.g., 650°C).

4. Concentration Profiles and Diffusion Paths

A concentration profile from the U10M vs. Zr diffusion couple, annealed at 650°C is presented in Figure 8, from the couple that was annealed for 720 hours and water-quenched. These profiles are very similar to those reported by Huang *et al.* [27], and other couples examined in this study also exhibited similar profiles regardless of cooling rate. The relative concentration of U and Mo clearly increases and decreases, respectively, within the U-10Mo alloy similar to the observation also reported by Huang *et al.* [27]. This is a favorable diffusional behavior for the barrier effectiveness of Zr to retain the U-density stability within the metallic fuel. However, it should be noted that the enrichment of U is accompanied by the depletion of Mo, presumably due to the formation of Mo_2Zr , and can alter the stability of γ -U(Mo) phase, as observed in study as a β -U layer.

Figure 9 shows the semi-quantitative diffusion paths estimated for the quenched and furnace-cooled diffusion couples annealed at 650°C for 480 hours. Despite the scatter due to the

presence of two-phase regions, compositions determined from the XEDS and the phase constituents identified (except for the α -Zr and $\text{U}_6\text{Zr}_3\text{Mo}$ precipitates upon cooling), the diffusion path constructed follows the ternary isotherm **approximately** with two-phase equilibrium between the γ -U(Mo) and Mo_2Zr , the β -U and Mo_2Zr , the β -Zr and Mo_2Zr , β -Zr and α -Zr. In all the diffusion couples, the two-phase region containing the γ -U(Zr) and Mo_2Zr equilibrium was not observed. However this may explain why α -Zr precipitates were observed, upon cooling to a room temperature, in the vicinity of Mo_2Zr phases. Although the concentration profiles determined via XEDS follow the ternary isotherm closely in a semi-quantitative manner, detailed analyses for the determination of diffusion coefficients and phase diagrams (i.e., solubility limits) **could not be** carried out due to the presence of non-planar interfaces, two-phase regions and precipitation of α -Zr. The β -Zr layer also did not exhibit any discernable concentration gradient.

5. Time- and Temperature-Dependence of **Interdiffusion and Reaction**

Thickness of the interaction zone was measured from the terminal ends of the U10Mo alloy and pure Zr, defined by $\partial C/\partial x = 0$, from the couples that were quenched after each anneal as reported in Table II and **Figure 10**. Assuming the initial thickness of zero, the growth of the **interaction** zone does not follow the parabolic growth as seen in **Figure 10**. In fact it does not follow any other time-dependence, $t^{1/n}$ where $n \geq 1$. However when the growth constant was determined just for the couples annealed at 650°C as a function of time in this study (i.e., assuming a certain incubation period, approximately 215 hours), a growth rate of $1.81 \times 10^{-15} \text{ m}^2/\text{sec}$ was determined as reported in Table II. Furthermore this analysis demanding the incorporation of “incubation” period, may be related to the Huang’s [27] observation of

“negligible” interaction in the same diffusion couple annealed at 600°C for 960 hours. Whether this incubation period is due to nucleation barrier for relevant phases (e.g., β -U and Mo_2Zr) or dissolution of native oxide should be investigated with a better understanding of experimental variables and thermo-kinetic description for nucleation and growth.

The growth constant determined at 650°C with an assumption of certain incubation period was plotted along with those determined at higher temperature by Huang *et al.* [27]. The temperature dependence of the growth constant for the interaction between U10Mo alloy and Zr at 650°C obeys the Arrhenius behavior of the activation energy close to what was previously determined by Huang *et al.* [27] at ~195 KJ/mole as reported in Table III and presented in Figure 11.

6. Discussion

In this investigation, U10Mo vs. Zr diffusion couples were annealed at 650°C for 240, 480 and 720 hours to examine the development of phase constituents and microstructure, and to quantify the growth kinetics of the interdiffusion-reaction zone. In all diffusion couples, including the one furnace-cooled after 480 hours of anneal, a thick layer of β -Zr and a thin layer of β -U were observed to develop. A discontinuous layer of Mo_2Zr was found between the β -Zr and β -U layers, and within the β -U layer, small α -Zr precipitates were found. Acicular α -Zr and blocky $\text{U}_6\text{Zr}_3\text{Mo}$ phases were also observed within the γ -U(Mo). The phase constituents and microstructural development are schematically summarized in Figure 7. While the complex diffusion microstructure was analyzed by TEM with small samples without any image analysis, the phase constituents followed the local phase equilibrium consistently with the ternary

isothermal phase diagram at 650°C, excluding the presence of α -Zr and U_6Zr_3Mo . These two phases appears to form during cooling, both water-quench and furnace-quench. There was no significant deviation in diffusion paths for the couples quenched in water and furnace-cooled after anneal for 480 hours. This similarity of phase constituents and concentration profiles between water-quenched and furnace-cooled samples indicates that the cooling-rate is not a significant factor that needs to be controlled during the co-rolling and HIP'ing of a monolithic fuel plate.

Phase constituents and microstructural development reported in this study are different from those previously reported by Perez *et al.* [28], Park *et al.* [29], and Jue *et al.* [30]. Notably the UZr_2 phase layer was not observed in this study. However, these previous studies have reported the phase constituents and microstructural development following the monolithic fuel plate processing: repeated soaking at 650°C and co-rolling followed by HIP, typically carried out at temperature (520~580°C) lower than 650°C. The ternary phase equilibrium for the U-Mo-Zr system changes drastically between this temperature range [10], and can produce changes in observed phase constituents and microstructure. This changes in observation as a function of temperature, either independently or sequentially, warrant fundamental investigations of interdiffusion and reaction in the U-Mo-Zr system between 650°C and 500°C, relevant to overall monolithic fuel plate processing.

The phase constituents, microstructure and concentration profile found in this study as a function of time, in general, agree well with the results reported by Huang *et al.* [27] for diffusion couples at high temperature. In particular, the diffusion couple annealed at 700°C by Huang *et al.* [27], with terminal Zr as the α -Zr, is very similar to the results obtained in this study. First, Zr is an excellent candidate for diffusion barrier between U-Mo fuel and Al cladding alloy

with an additional benefit of U uphill diffusion, which is reported by both Huang *et al.* [27] and this study. Second, the phase constituents and microstructure reported are also similar, although this study examined more details with TEM and SAED analyses for the Mo₂Zr, β -U, U₆Mo₃Zr and α -Zr phases distributed within the interaction zone.

Although the growth of the interaction zone required an assumption of a certain incubation period, the growth constant with diffusion couples annealed at 650°C for 240, 480, and 720 hours was calculated to be $k = 1.81 \times 10^{-15} \text{ m}^2/\text{sec}$. This, combined with those reported by Huang *et al.* [27], exhibited an excellent Arrhenius temperature-dependence with activation energy of 195.3 KJ/mole. However it should be noted that the diffusion work performed by Huang *et al.* [27] at 600°C for 960 hours showed negligible interdiffusion and reaction, and the current work supports that the interdiffusion and reaction between U10Mo and Zr is influenced by other factors, including the possible presence of an incubation period. To understand the nature of the incubation period, if any, a future investigation would require understanding of nucleation/growth of intermetallic layers and/or dissolution of native oxide scale (i.e., experimental procedure).

A future investigation with respect to the irradiation behavior should focus on the presence of α -Zr and β -U phases, based on this study. Preliminary research [19] on the irradiation behavior of U10Mo with a Zr diffusion barrier has indicated, by optical microscopy, possible void formation where these phases are located, i.e., a few micrometers away from the Mo₂Zr layer, towards the γ -U(Mo). This is the location where the β -U exists and the acicular α -Zr phase extends into the γ -U(Mo). Depletion of Mo from the γ -U(Mo) solid solution by the formation of the Mo₂Zr phase can destabilize the γ -U(Mo) into the β -U phase. While the γ -U has

complete solubility with Zr, the β -U phase has a very low solubility (and that for the α -U phase is even lower).

7. Summary

Development of phase constituents, microstructure and concentration profiles were investigated for U10Mo vs. Zr diffusion couples annealed as a function of time (240, 480 and 720 hours) at 650°C by using SEM and TEM. Thick and thin layers of β -Zr and β -U, respectively, were observed, while a discontinuous layer of Mo_2Zr was observed between β -Zr and β -U layers. Formation of the Mo_2Zr phase altered the local compositions and led to the development of β -U and α -Zr (upon cooling) phases nearby. In addition, acicular α -Zr and $\text{U}_6\text{Zr}_3\text{Mo}$ phases were observed within the γ -U(Mo). These observations were similar for all couples including the one that was furnace cooled after anneal at 650°C. In addition, these results were quite similar to a previous diffusion couple investigation at 700°C. Despite the development of a complex microstructure, the concentration profiles projected as semi-quantitative diffusion paths on an isothermal ternary phase diagram agreed in general to the composition-dependent phase equilibrium at 650°C. With an assumption of an incubation period, thickness for the zone of interdiffusion and reaction grew at a rate of $1.81 \times 10^{-15} \text{ m}^2/\text{sec}$ with an activation energy of 195 kJ/mole.

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Table I. Crystallographic information on relevant phases of this investigation

Phase	Pearson Symbol	Space Group
γ -U(Mo)	cI2	Im3m
β -U	tP30	P42/mnm
Mo ₂ Zr	cF24	Fd3m
β -Zr	cI2	Im3m
α -Zr	hP2	P63/mmc
U ₆ Zr ₃ Mo	cFX	Fm3m

Table II. Growth rate of diffusional interaction zone determined from U-10wt.% Mo vs. Zr diffusion couple annealed at 650°C followed by water-quench.

Temperature (°C)	Annealing time (hours)	Measured Thickness (μm)	Growth rate (m^2/s)
650	240	19.9 ± 5.1	1.81×10^{-15}
	480	61.0 ± 3.9	
	720	85.3 ± 1.0	

Table III. Growth rate of interaction zone of U-10wt.% Mo vs. Zr diffusion couples reported by Huang *et al.*[10] and this study

Temperature (°C)	Thickness (μm)	Annealing time (hours)	Growth rate (m ² /s)	Activation Energy (kJ/mole)
1000	1130	96	1.85×10^{-12}	195.3
900	990	240	5.76×10^{-13}	
800	650	480	1.22×10^{-13}	
650	See Table II		1.81×10^{-15}	

List of Figures

1. Backscattered electron micrographs from the water-quenched U - 10 wt.% Mo vs. Zr diffusion couples annealed at 650°C for (a) 240 hours, (b) 480 hours, (c) 720 hours. (d) The same couple annealed at 650°C for 480 hours followed by furnace-cooling.
2. High angle annular dark field STEM micrographs from the water-quenched U - 10 wt.% Mo vs. Zr diffusion couple annealed at 650°C for 720 hours. The three squares indicate sampling positions of the (1) α -Zr, (2) Mo_2Zr , β -U, and β -Zr, and (3) $\text{U}_6\text{Zr}_3\text{Mo}$ by selected area electron diffraction and high-resolution TEM.
3. From region (1) in Figure 2: (a) Bright field and (b) high-resolution TEM micrographs with the fast Fourier transformation analysis of needle-shaped α -Zr precipitate in the water-quenched U - 10 wt.% Mo vs. Zr diffusion couples annealed at 650°C for 720 hours.
4. From region (2) in Figure 2: selected area electron diffraction patterns from the (a) β -Zr, (b) Mo_2Zr and (c) β -U layers observed in the water-quenched U - 10 wt.% Mo vs. Zr diffusion couples annealed at 650°C for 720 hours.
5. From region (2) in Figure 2: (a) dark field and (b) high-resolution TEM micrographs of the α -Zr precipitates observed within the β -U layer formed in the water-quenched U - 10 wt.% Mo vs. Zr diffusion couples annealed at 650°C for 720 hours.
6. From region (3) in Figure 2: (a) dark field and (b) high-resolution TEM micrographs with the fast Fourier transformation analysis of $\text{U}_6\text{Zr}_3\text{Mo}$ precipitate within the U-Mo matrix from the water-quenched U - 10 wt.% Mo vs. Zr diffusion couples annealed at 650°C for 30 days.
7. A schematic diagram representing the phase constituents and microstructure of the interaction layers from the water-quenched U - 10 wt.% Mo vs. Zr diffusion couple annealed at 650°C for 720 hours.
8. Concentration profiles from the U - 10 wt.% Mo vs Zr diffusion couples annealed at 650°C for 720 hours and water-quenched.
9. Estimated diffusion paths from the U - 10 wt.% Mo vs. Zr diffusion couples annealed at 650°C for 480 hours after water-quench and furnace-cooling.
10. Thickness of the diffusional interaction zone as a function of time for the U - 10 wt.% Mo vs. Zr diffusion couples annealed at 650°C followed by water-quench.
11. Temperature dependence of growth constant determined from the U - 10 wt.% Mo vs Zr diffusion couples annealed at 1000, 900, 800 and 650°C.

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