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Diffusion And Reaction In Selected Uranium Alloy System

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DIFFUSION AND REACTION IN SELECTED URANIUM ALLOY SYSTEMS

by

KE HUANG
B.S. Harbin Institute of Technology (HIT), China, 2007

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Materials Science and Engineering in the College of Engineering and Computer Science at the University of Central Florida, Orlando, Florida

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Major Professor: Yongho Sohn
ABSTRACT

U-Mo metallic fuels with Al alloys as the matrix/cladding are being developed as low enriched uranium fuels under the Reduced Enrichment for Research and Test Reactor (RERTR) program. Significant interactions have been observed to occur between the U-Mo fuel and the Al alloy during fuel processing and irradiation. U-Zr metallic fuels with stainless steel claddings have been developed for the generation IV sodium fast reactor (SFR). The fuel cladding chemical interaction (FCCI) induced by the interdiffusion of components was also observed. These interactions induce deleterious effects on the fuel system, such as thinning of the cladding layer, formation of phases with undesirable properties, and thermal cracking due to thermal expansion mismatches and changes in molar volume.

The interaction between the fuel and the cladding involves multi-component interdiffusion. To determine the ternary interdiffusion coefficients using a single diffusion couple, a new method based on regression via the matrix transformation approach is proposed in this study. This new method is clear in physical meaning and simple in mathematical calculation. The reliability and accuracy of this method have been evaluated through application to three case studies: a basic asymptotic concentration profile, a concentration profile with extrema and a smoothed concentration profile with noise. Generally, this new method works well in all three cases.

In order to investigate the interdiffusion behavior in U-Mo alloys, U vs. Mo diffusion couples were assembled and annealed in the temperature range of 650 to 1000°C. The interdiffusion microstructures and concentration profiles were examined via scanning electron
microscopy (SEM) and electron probe microanalysis (EPMA), respectively. Interdiffusion coefficients and activation energies were calculated as functions of temperature and Mo composition. The intrinsic diffusion coefficients of U and Mo at the marker composition were also determined. The activity of U and the thermodynamic factor of the U-Mo alloy have been calculated using the ideal solution, the regular solution, and the subregular solution models based on the molar excess Gibbs free energy of the U-Mo alloy. The calculated intrinsic diffusivities of U and Mo along with the thermodynamic factor of the U-Mo alloy were employed to estimate the atomic mobilities and the vacancy wind effects of U and Mo according to Manning’s description.

To explore potential diffusion barrier materials for reducing the fuel cladding chemical interaction between the U-Mo fuel and the Al alloy matrix/cladding, the interdiffusion behavior between U-Mo alloys and Mo, Zr, Nb and Mg were systematically studied. U-10wt.%Mo vs. Mo, Zr and Nb diffusion couples were annealed in the temperature range from 600 to 1000°C. A diffusion couple between U-7wt.%Mo and Mg was annealed at 550°C for 96 hours. SEM and transmission electron microscopy (TEM) were applied to characterize the microstructure of the interdiffusion zone. X-ray energy dispersive spectroscopy (XEDS) and EPMA were utilized to examine the concentration redistribution and the phase constituents. For the U-Mo vs. Mo diffusion couples, the interdiffusion coefficients at high Mo concentrations ranging from 22 to 32 at.%Mo were determined for the first time. In the U-Mo vs. Zr diffusion couples, the Mo₂Zr phase was found at the interface. The diffusion paths were estimated and investigated according to the Mo-U-Zr ternary phase diagram. Thermal cracks and pure U precipitates were found within the diffusion zone in the U-Mo vs. Nb system. The growth rate of the interdiffusion zone
was found to be lower by about $10^3$ times for Zr, $10^5$ times for Mo and $10^6$ times for Nb compared to those observed in the U-10wt.%Mo vs. Al or Al-Si systems. For the diffusion couple of U-Mo vs. Mg, the U-Mo was bonded very well to the Mg and there was negligible diffusion observed even after 96 hours annealing at 550°C.

For a more fundamental understanding of the complex diffusion behavior between U-Zr fuels and their stainless steel claddings, U vs. Fe, Fe-15wt.%Cr and Fe-15wt.%Cr-15wt.%Ni diffusion couples were examined to investigate the interdiffusion behaviors between U and Fe and the effects of the alloying elements Cr and Ni. The diffusion couples were annealed in the temperature range from 580 to 700°C for various times. Two intermetallic phases, U₆Fe and UFe₂, developed in all of the diffusion couples with the U₆Fe layer growing faster than the UFe₂ layer. For the diffusion couples of U vs. Fe, extrinsic growth constants, intrinsic growth constants, integrated interdiffusion coefficients and activation energies in each phase were calculated. The results suggest that U₆Fe impeded the growth of UFe₂, and the boundary condition change caused by the allotropic transformation of U played a role in the growth of the U₆Fe and UFe₂ layers. The reasons why U₆Fe grew much faster than UFe₂ are also discussed. The additions of Cr and Ni into Fe affected the growth rates of U₆Fe and UFe₂. The solubility of Cr and Ni in U₆Fe and UFe₂ were determined, and it was found that Cr diffused into U more slowly than Fe or Ni.
This work is dedicated to my parents and wife.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor, Dr. Yong-Ho Sohn for his support, guidance and patience; and I would also like to extend my thanks to my committee members: Dr. Helge Heinrich, Dr. Kevin Coffey, Dr. Linan An, and Dr. Chengying Xu. I would also like to express my thanks to all my fellow students at the Laboratory of Materials and Coatings for Extreme Environment (MCEE) and to the engineers, faculty and staff members at the Advanced Materials Processing and Analysis Center (AMPAC) and the MMAE department. Especially, I appreciate Miss Ashley Ewh and Judith Dickson, who did the final reviewing and formatting. Finally, I would like to thank my family and friends for always being there for me.
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<tr>
<td>ATR</td>
<td>Advanced Test Reactor</td>
</tr>
<tr>
<td>DU</td>
<td>Depleted Uranium</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron Probe Microanalysis</td>
</tr>
<tr>
<td>FCCI</td>
<td>Fuel Cladding Chemical Interaction</td>
</tr>
<tr>
<td>LEU</td>
<td>Low-Enriched Uranium</td>
</tr>
<tr>
<td>HEU</td>
<td>High-Enriched Uranium</td>
</tr>
<tr>
<td>RERTR</td>
<td>Reduced Enrichment for Research and Test Reactor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SFR</td>
<td>Sodium Fast Reactor</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TTT</td>
<td>Time-Temperature-Transformation</td>
</tr>
<tr>
<td>XEDS</td>
<td>X-ray Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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CHAPTER ONE: INTRODUCTION

1.1 General Background

Metallic nuclear fuels are a very important type of nuclear fuel with many advantages including high thermal conductivity, passive safety, ease of fabrication and recyclability [1-3]. However, the fissile materials uranium (U) or uranium-plutonium (U-Pu) alloys cannot be used as commercial nuclear fuels directly because of their low melting points. In order to increase the melting point and phase stability of metallic fuels under irradiation, alloying elements, such as zirconium (Zr), molybdenum (Mo), titanium (Ti), and chromium (Cr) are added into U or U-Pu alloys [1].

U-Mo alloys are being developed for use as low-enriched uranium (LEU, $^{235}$U content less than 20 wt.%) fuels under the Reduced Enrichment for Research and Test Reactor (RERTR) program [4, 5]. Historically, research and test reactors employed high-enriched uranium (HEU, $^{235}$U content higher than 20 wt.%) to obtain high intensity neutron flux. To avoid nuclear proliferation, all of the research and test reactors worldwide are expected to be converted from using HEU fuels to LEU fuels. The RERTR program was initiated by Argonne National Lab (ANL) U.S. in 1978 [4, 5], and has been developed into an international cooperation program to study the technology of converting HEU to LEU. Because the enrichment of $^{235}$U in LEU is lower than HEU, a higher density of U isotopes in the fuel is required to meet the critical density of $^{235}$U for maintaining the chain reaction.

Two types of U-Mo fuels, dispersion and monolithic configurations, are being developed as new LEU fuels with high U densities up to 16 g U cm$^{-3}$. For the dispersion fuel design, U-Mo
alloy particles are dispersed in an Al-alloy matrix and assembled between an Al alloy cladding. In the monolithic fuel design, the U-Mo plate is directly laminated between an Al alloy cladding. Schematics of these two fuel systems are presented in Figure 1.

![Schematics of dispersion (a) and monolithic (b) U-Mo alloy fuel configurations.](image)

Aluminum is selected as the matrix material due to its low neutron absorption [4] and high thermal conductivity. Alloying with Mo satisfies the requirement of high U density and also retains the U alloy in the metastable \( \gamma \) phase in which best irradiation performance can be achieved at relatively low operation temperatures. In addition, U-Mo based alloys show the best compatibility with aluminum matrices compared to other alloying elements, such as zirconium and niobium [4]. Metallurgical interactions can occur between the U-Mo fuels and Al alloy during processing and irradiation due to interdiffusion [6-8]. The microstructure and intermediate phases in the interaction zone have been studied in the literature [9-12]. A typical fuel-cladding
chemical interaction (FCCI) zone is shown in Figure 2 [12]. These reaction products can decrease the thermal conductivity of the fuel and cause cracks due to thermal expansion mismatch and molar volume change.

![Image of interdiffusion zone](image)

Figure 2 Interdiffusion zone developed in U-10wt.%Mo vs. Al diffusion couple annealed at 550°C for 1 hour [12].

U-Zr alloys have been developed as fuels for sodium fast reactors (SFR) because of their unique compatibility with stainless steel claddings [1]. The sodium fast reactor, one of the generation IV nuclear reactor designs, employs fast neutrons as a source and liquid sodium as a coolant. This is an attractive design because of its highly efficient use of nuclear fuels and its minimization of long-lived actinide waste production. This is due to the fact that fast neutrons can convert $^{238}$U and long-lived transuranic elements, which are commonly considered as nuclear waste in thermal neutron reactors, into nuclear fuel to generate power. In the SFR system, the U-
Zr alloy fuel rods are encapsulated into stainless steel cladding to avoid releasing fuels and radiation. A schematic of a metallic U-Zr fuel rod with sodium bond is presented in Figure 3 [13].

![Figure 3 Schematic of a metallic U-Zr fuel rod with sodium bond [13].](image)

Under irradiation, the fuel rod swells and makes contact with the cladding because of thermal expansion and fission product accumulation. The fuel cladding chemical interaction (FCCI), due to interdiffusion of components, has deleterious effects on the system because it thins the cladding and produces phases with relatively low melting points. The U-Zr system has
been studied since the late 1960s, and the interaction between the U-Zr and Fe alloys has been well documented in the literature [14-18]. In most cases, the interaction zone shows a complex multi-layer structure with intermetallic compound precipitates (shown in Figure 4 [17]).

Figure 4 BSE micrograph of the reaction zone from the U-23at.%Zr vs. Fe diffusion couple annealed at 650°C [17].

FCCI is a very complex process involving multiple phases and multiple components. Although the microstructures and phase constituents of the FCCI in U-Zr based fuels with stainless steel claddings and U-Mo based fuels with Al alloy claddings have been studied extensively, the fundamental diffusion parameters in these systems were rarely reported. In this study, solid-to-solid isothermal diffusion studies in selected binary, ternary and quaternary systems of uranium were carried out to investigate the interdiffusion process quantitatively, and to explore potential barriers or non-reacting materials to reduce the FCCIs.
1.2 Motivation

Interaction between the fuel and matrix/cladding is a common phenomenon which has deleterious effects on the fuel system, including thinning of the cladding layer, formation of phases with undesirable properties, decreasing the thermal conductivity, and causing thermal cracking due to a thermal expansion mismatch and molar volume change. For safety concerns, it is critical to understand the complex FCCI and provide an engineering solution to prevent or reduce it.

To help clarify the diffusional processes in the U-Mo-Al system and develop models that can provide insight for the advancement of U-Mo metallic fuels, the interdiffusion behavior in U-Mo alloys must be clearly understood. In order to reduce the interdiffusional reactions between the U-Mo fuel and Al matrix/cladding, the addition of alloying elements (e.g., Zr or Nb into the U-Mo fuel and Si into the Al cladding) has been investigated [9, 19, 20]. Another approach for preventing the reactions in the monolithic fuel design is to insert barrier materials between the U-Mo fuel and Al alloy cladding; whereas, for the dispersion fuel design the Al matrix is replaced with a non-reacting matrix.

Refractory metals such as Mo, Zr, and Nb could be good candidates to be applied as a barrier layer, since the diffusion of U in the refractory metals is slow [21, 22] and their melting points and thermal conductivities are high [23]. Each of the above metals has unique desirable properties for barrier applications. Zirconium is a viable option since the neutron absorption rate is fairly low (0.185 barn) [23] and the fabrication of the Zr barrier is compatible with the current hot rolling process adopted by Idaho National Laboratory (INL) [24]. Mo may also be a promising barrier material for the U-Mo fuel system since Mo maintains a simple binary system
between the fuel and barrier. According to the binary Mo-U phase diagram [25], only one solid solution forms above 600°C, while only an intermetallic phase exists below 600°C. The maximum composition of Mo in the U solid solution or intermetallic phase is approximately 37 at.%. Therefore, the compositional variation in the U-10wt.%Mo fuel due to interdiffusion with the Mo barrier is less than 15 at.%. The effect of the interdiffusion reaction on the fuel composition is hence minimized. Nb was chosen because only a solid solution with U forms based on the binary Nb-U phase diagram [25], and it forms less intermetallic phases with Al as compared to Zr and Mo [26].

Mg could be an excellent candidate as a non-reacting matrix for the dispersion fuel design or as a barrier layer for the monolithic fuel design because there is negligible solubility and no intermetallic compounds identified based on the binary Mg-U and Mg-Mo phase diagrams [25]. Therefore, there should be no reactions between the U-Mo fuel and Mg matrix. Mg has a low neutron absorption coefficient and high thermal conductivity similar to those of Al [23]. Moreover, interactions between Mg matrix and Al alloy cladding were observed to be insignificant during the hot rolling process at 275°C [27]. For potential application of Mo, Zr, Nb and Mg as barrier materials, the interdiffusion behaviors between them and U-Mo alloys have to be understood.

The reactions between U-Zr and stainless steel in sodium fast reactors have been studied extensively [14-17, 28-30]. However, most of the studies focused on the microstructural evolution and phase constituents. No quantitative reaction diffusion studies between U and Fe have ever been reported. In order to help understand the complex FCCIs between U-Zr alloy fuels and stainless steel claddings as well as to quantitively analyze the effects of alloying additions (such
as Zr, Cr and Ni), the diffusion behavior in these systems has to be documented to form a base line for further investigations. Moreover, the reaction mechanisms between U and Fe and the effects of the allotropic transformation of U on the reactions are also interesting from a scientific point of view.

Fuel cladding chemical interactions involve multi-component diffusion. A set of \((n-1)^2\) interdiffusion coefficients is required to describe the diffusion process in an \(n\)-component system. In a ternary system, only two components are independent (e.g., component 1 and 2), and four coefficients, \(\bar{D}_{11}^3\), \(\bar{D}_{12}^3\), \(\bar{D}_{21}^3\), and \(\bar{D}_{22}^3\), are typically determined by two independent diffusion couples with a common intersection composition. To extract more information from a single diffusion couple, Dayananda [31] and Bouchet [32] proposed new methods based on the integration of diffusion fluxes and the numerical inverse approach to determine the four coefficients using one diffusion couple, respectively. The details about these two methods will be introduced in section 2.6. In Dayananda’s method [31], the moment, \((x-x_0)^n\), is introduced into the diffusion flux calculation and creates more equations to determine the four ternary coefficients. However, this moment can actually enlarge the uncertainty. Furthermore, when analyzing ternary diffusion coefficients in a linear concentration range, this method was proven to be unstable. In Bouchet’s method [32], the interdiffusion coefficients are determined by an iterative procedure which minimizes the difference between the experimental and the calculated profiles from estimated coefficients via “trial and error” techniques. This method is complex in computation and time consuming. To overcome these weaknesses, a new method based on a transferring matrix approach is proposed to determine ternary diffusion coefficients over selected
ranges in the diffusion zone from a single experimental concentration profile. This method is clear in physical meaning and straightforward in computation.

1.3 Objectives

Based on the above statement, four main objectives were set in this study. They were: (1) determination of the interdiffusion behavior in U-Mo alloys, (2) investigation of the interdiffusion behavior in the U-Mo vs. Mo, Zr, Nb and Mg systems to explore their potential application as barrier materials or non-reacting matrices, (3) quantitative examination of reactions between pure U and Fe, Fe-Cr or Fe-Cr-Ni alloys to form a baseline for better understanding of the complex reaction between U-Zr fuels and stainless steel claddings, and (4) development of a new method to determine ternary interdiffusion coefficients using a single diffusion couple. To achieve these objectives, the following tasks were identified and the corresponding work was carried out.

1. To understand the interdiffusion behavior in U-Mo alloys by investigating diffusion couples of U vs. Mo.
2. To understand the interdiffusion behavior between U-Mo alloys and Mo by investigating diffusion couples of U-10wt.%Mo vs. Mo.
3. To understand the interdiffusion behavior between U-Mo alloys and Zr by investigating diffusion couples of U-10wt.%Mo vs. Zr.
4. To understand the interdiffusion behavior between U-Mo alloys and Nb by investigating diffusion couples of U-10wt.%Mo vs. Nb.
5. To understand the interdiffusion behavior between U-Mo alloys and Mg by investigating diffusion couples of U-7wt.%Mo vs. Mg.

6. To understand the interdiffusion behavior between U and Fe and explore the effects of the allotropic transformation of U on the reactions by investigating diffusion couples of U vs. Fe.

7. To understand the influence of alloy elements Cr and Ni on the reactions between U and Fe by investigating diffusion couples of U vs. Fe-15wt.%Cr and U vs. Fe-15wt.%Cr-15wt.%Ni.

8. To develop a new method for the determination of the ternary diffusion coefficients based on a matrix transformation approach using a single diffusion couple and to evaluate the reliability and accuracy of this new method.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray energy dispersive spectroscopy (XEDS) and electron probe microanalysis (EPMA) were applied to analyze the microstructure, phase constituents and concentration profiles of the interdiffusion zones. Based on these results, the interdiffusion fluxes, interdiffusion coefficients, integrated interdiffusion coefficients, growth constants, and activation energies can be calculated. Diffusion paths in ternary systems can also be constructed and examined according to the ternary isothermal phase diagrams. In selected diffusion couples, the intrinsic diffusion coefficients at the marker plane compositions can be determined and utilized to estimate tracer diffusivities, atomic mobilities and vacancy wind effects.
CHAPTER TWO: LITERATURE REVIEW

2.1 Reduced Enrichment for Research and Test Reactors (RERTR)

Nuclear power plays an important role in energy production. Research and test reactors are used for the purpose of irradiation studies or as neutron sources rather than for power generation [5]. The neutrons produced by a research reactor are used for neutron scattering, non-destructive testing, analysis and testing of materials, production of radioisotopes, research, public outreach and education. Historically, to obtain high density neutron fluxes, HEU fuels such as UO$_x$ or UAl$_x$ dispersed in an Al alloy matrix were used [4, 5, 33]. In HEU fuels, the content of the $^{235}$U isotope is greater than 20 wt.%. Aluminum alloys were selected for use as the inner matrix because of their low neutron absorption rate and high thermal conductivity.

To prevent proliferation of nuclear materials, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) program was created in 1978 [4]. The mission of this program is to develop technologies to convert research and test reactors from the use of HEU to LEU fuels, consistent with the U.S. policy to eventually eliminate the use of HEU fuels in civilian nuclear programs worldwide [5]. As uranium enrichment is decreased, the uranium density in the fuel must increase to maintain the net fissile ($^{235}$U) atomic density of the fuel. The RERTR program has gained a great deal of interest and support from other countries and has subsequently developed into a multi-national program [11]. Specifically, the active international partners include the CNEA in Argentina, AECL in Canada, CEA in France, TUM in Germany, KAERI in Korea, and VNIIM, RDIFE, IPPE, NCCP and RIARR in Russia [11]. In 1987, this development work, involving great efforts of international cooperation, resulted in the qualification of several
dispersion fuels with significantly increased densities: UAl$_x$-Al at 2.3 g U cm$^{-3}$, U$_3$O$_8$-Al at 3.2 g U cm$^{-3}$, and U$_3$Si$_2$-Al at 4.8 g U cm$^{-3}$ [4]. This great achievement could convert 90% of the research and test reactors around the world to using LEU fuels.

In order to convert the remaining highest flux reactors in the world, LEU fuels with densities of 8-10 g U cm$^{-3}$ are required [5]. Since the volume loading of dispersed fuel particles is limited to 55% under the current fabrication process, the density of fuel particles should be greater than 14.5 g U cm$^{-3}$ [5]. Only two types of fuel are suitable for this high uranium density requirement: metallic uranium with a low alloying content and U$_6$M intermetallics where M indicates a metal element such as Fe or Mn. The observation that U$_6$Fe and U$_6$Mn intermetallic fuels tended to break-away swell during irradiation suggested these were not desirable candidates for future investigation [5]. Therefore, uranium alloys are the only choice for very high density fuel designs. Based on previous knowledge, $\gamma$-phase uranium alloys exhibit superior irradiation performance relative to $\alpha$-phase uranium alloys; therefore, $\gamma$-uranium stabilized by alloying additions was studied. Irradiation testing of various stabilized $\gamma$-uranium alloys, including U-Mo, U-Mo-Pt, U-Mo-Ru, U-Mo-Sn, and U-Nb-Zr, suggests that U-Mo based alloys are the best candidates [5]. The U-Mo alloy fuels with Al matrices or claddings will be discussed later in detail.

2.2 U-Mo Fuel and Its Reactions with Matrix/Cladding

U-Mo based alloys were chosen as candidates for very high density fuel designs because they have better performance under irradiation compared to other uranium alloys. Post irradiation examination revealed that the U-Zr-Nb alloy fuels exhibited a large fuel thickness
increase caused by both extensive fuel-matrix reactions and break-away swelling [5]. However, U-Mo alloys with at least 6 wt.% Mo performed quite well up to 70% burnup.

The equilibrium Mo-U phase diagram is shown in Figure 5 [25]. There is an allotropic transformation between α-U and β-U at 668°C and between β-U and γ-U at 776°C. The crystal structure of α-U is orthorhombic with a Pearson symbol of cI2. The solubility of Mo in α-U is less than 1 at.%. The β-U phase, which has a tetragonal crystal structure with a Pearson symbol of tP30, exhibits a very small solubility of less than 1 at.% Mo. In the γ-U phase, the solubility of Mo increases up to 37 at.% with a body centered cubic structure (cI2). At about 600°C, decomposition of $\gamma \rightarrow \gamma'+\alpha$ occurs, where the $\gamma'$ phase is $U_2Mo$ and has a tetragonal, tI6, crystal structure. The addition of alloying elements (i.e., Mo, Zr, Ti) stabilizes the $\gamma$ phase and delays the decomposition of $\gamma \rightarrow \gamma'+\alpha$ at low temperatures [34]. Repas [34] reported the isothermal transformation kinetics for four uranium-based alloys: U-8wt.%Mo, U-10wt.%Mo, U-8wt.%Mo-1/2wt.%Ti, and U-8wt.%Mo-1wt.%Ti, and developed the Time-Temperature-Transformation (TTT) diagram for U-Mo alloys at Mo compositions of 8 and 10 wt.%.
The thermodynamics of U-Mo alloys have been studied extensively [35-39], but there are discrepancies in some of the previously reported results. In Berche’s work [35], the $\alpha_U$ calculated using the CALPHAD method was compared to the values obtained from the equations of Vamberskii [38], which were derived from emf measurements. There was an inexplicable disparity between the values determined by the two methods. The molar excess Gibbs free energy for the formation of U-Mo alloys, $\Delta G^E$, which relates to $\alpha_U$ or $\alpha_{Mo}$, was given by Parida [39] in polynomial form as a function of U composition for the $\alpha$, $\beta$, $\gamma$ and liquid phases based on the data reported by Brewer [36].

Figure 5 Equilibrium phase diagram of Mo-U [25].
To achieve a high density of uranium isotopes, there are two types of fuel designs for U-Mo alloys which are the dispersion and monolithic configurations [33]. For the dispersion fuel design, U-Mo alloy particles are dispersed in an Al alloy matrix and assembled between an Al alloy cladding. In the monolithic fuel design, a U-Mo plate is laminated between an Al alloy cladding directly. A schematic of these two fuel systems is presented in Figure 1.

For both designs, metallurgical interactions can occur between the U-Mo fuels and Al alloy cladding during processing and irradiation due to interdiffusion [6-8]. Representative dispersion and monolithic U-Mo fuels both before and after annealing are presented in Figure 6 [12]. These reactions have deleterious effects on the system, such as thinning of the cladding layer, formation of phases with relatively low melting points, and thermal cracking due to a thermal expansion mismatch and molar volume change. The reaction products can also decrease the thermal conductivity of the fuel [33].

Extensive studies [12, 20, 40-46] have been carried out to investigate the complex interactions between U-Mo alloys and Al or Al alloys. Meyer [6] studied the in-pile FCCI behavior of U-Mo dispersion fuels under irradiation. U-Mo fuels with Mo content ranging from 4 to 10 wt.% were tested in the Advanced Test Reactor (ATR) at a fuel temperature of approximately 65°C and burnups from 40 to 70%. In general, fuels with molybdenum contents of 6 wt.% or more showed stable in-reactor fission gas behavior, exhibiting a distribution of small, stable gas bubbles. Moderate fuel particle swelling was observed and it decreased with increasing alloy content. Fuel particles with a lower molybdenum content of 4 wt.% performed poorly, exhibiting extensive fuel-matrix interaction and the growth of relatively large fission gas
bubbles. Fuel particles with 4 to 6 wt.% molybdenum reacted more rapidly with the aluminum matrix than those with higher alloy content.

Figure 6 SEM of U-Mo dispersion fuel before annealing (a) and after annealing (b) and U-Mo monolithic fuel before annealing (c) and after annealing (d) [12].

To study the interdiffusion behavior between U-Mo fuels and Al or Al alloy claddings in detail without the influence of irradiation, diffusion couples of U-Mo vs. Al and U-Mo vs. Al alloy were examined [9, 10, 44, 46-49]. Perez [9] reported the interaction microstructures and phase constituents developed in the diffusion couples of U-7wt.%Mo, U-10wt.%Mo and U-12wt.%Mo vs. pure Al annealed at 600°C for 24 hours, and U-7wt.%Mo, U-10wt.%Mo and U-12wt.%Mo vs. Al-2wt.%Si and Al-5wt.%Si annealed at 550°C for 20 hours. In the ternary U-Mo-Al diffusion couples annealed at 600°C for 24 hours, the interdiffusion microstructures contained finely dispersed UAl₃, UAl₄, U₆Mo₄Al₄₃ and UMo₂Al₂₀ phases while the average composition throughout the interdiffusion zone remained approximately constant at 80 at.% Al. The addition of Si in Al significantly reduced the thickness of the interdiffusion layers. The
formation of \((U,Mo)(Al,\text{Si})_3\), with relatively large solubilities for Mo and Si, was observed along with \(\text{UMo}_2\text{Al}_{20}\). However, the \(\text{U}_6\text{Mo}_4\text{Al}_{43}\) and \(\text{UAi}_4\) phases were not observed in the U-Mo vs. Al-Si diffusion couples.

Many studies have been carried out in order to reduce the reaction between U-Mo alloys and Al or Al alloys. For U-Mo dispersion fuels, the addition of Zr into the U-Mo fuel and Si into Al has been considered. Park [19] conducted diffusion tests between U-7Mo-\(x\)Zr and Al-\(y\)Si (\(x=0, 1, 2, 4\) wt.\% and \(y=0, 2, 5\) wt.\%) at 580 and 600°C. It was observed that the \(\gamma\)-phase U-7Mo-Zr alloys with more than 2 wt.\% Zr decomposed faster than the U-7Mo alloys. The addition of Zr into U-7Mo and Si into Al reduced the interaction layer growth rates. However, Zr additions to U-Mo were most effective in reducing the overall interdiffusion rates when combined with Si additions to Al.

Another approach of decreasing the interaction is to replace the Al alloy matrix with a non-reacting matrix. Mg is an excellent candidate since there is negligible solubility and no intermetallic compound readily identified based on the binary phase diagrams of Mg-U and Mg-Mo [25]. Mg has a low neutron absorption coefficient and high thermal conductivity similar to that of Al [23]. Moreover, the reaction between Mg and Al alloy is insignificant during the improved hot rolling process at 275°C reported by Wiencek [27]. In Wiencek’s work, U-2wt.\%Mo and U-10wt.\%Mo fuel particles were dispersed into a Mg matrix and assembled between Al 6061 alloy claddings. After hot rolling at 415°C, the fuel was bonded well. Significant reactions had occurred between the Mg matrix and Al alloy cladding. However, very little or no reaction between the fuels and Mg matrix was observed even after 420 hours.
annealing at 400°C. The reaction between the Mg matrix and Al alloy cladding had been reduced effectively using the improved hot rolling technique at a lower temperature of 275°C.

For the U-Mo monolithic design, refractory element barriers (i.e., Mo, Zr, Nb) are being considered for application between the fuel and Al alloy cladding to impede the FCCI. Perez [8] documented the microstructure of an as-processed U-10wt.%Mo monolithic fuel plate in an Al 6061 alloy matrix with a Zr diffusion barrier. Multiple phases including α-U, Mo₂Zr, UZr₂, U-Zr solid solution, and a Zr rich phase were observed at the interface of U-Mo and Zr. The interface between the Al 6061 alloy cladding and Zr barrier consisted of four layers including (Al, Si)₂Zr, (Al, Si)Zr₃, (Al, Si)₃Zr and AlSi₄Zr₅.

2.3 Sodium Fast Reactor (SFR)

The sodium fast reactor (SFR) is one of the Generation IV nuclear reactor designs with the aim of creating significant improvements in economics, safety, sustainability, and proliferation resistance [50]. The SFR applies high energy fast neutrons as a neutron source and liquid sodium as a coolant, which increases the efficiency of using U isotopes and minimizes nuclear waste [50]. In thermal reactors ²³⁵U is used as a fission material to generate energy. Of the naturally occurring U approximately 99.3% is in the form of ²³⁸U isotopes, which are useless for power generation purposes. However, when fast neutrons hit ²³⁸U atoms there is a high likelihood that they are absorbed and a new atom, ²³⁹Pu, is produced. ²³⁹Pu is a new fissile material and can be used to generate power. This process is called breeding if more fissile material is produced than is consumed for the production of energy. The breeding process in SFRs can increase the efficiency of U utilization by 60 times [51]. At the same time, the fast neutrons in fast reactors make it possible to use or transmute certain long lived isotopes that
cannot be used in thermal reactors, and thus normally become part of the thermal reactors’ waste burner and minimize the production of nuclear waste [1, 52].

The history and current status of SFR development have been reviewed in the literature [1-3, 50-55]. Fast reactor research and technology development programs started in a number of countries in the 1940s and early 1950s. The U.S. was the first to construct an operational fast reactor, with Clementine becoming critical in 1946 [51]. SFRs were developed steadily and reached their peak in the 1980s. Thereafter, there was a gradual decline in fast reactor activities in most developed countries throughout the 1990s [51]. The main reasons included adequate uranium resources, high operation and maintenance costs, safety concerns and proliferation risks [1, 51, 52, 56]. Currently, Germany and the United Kingdom have abandoned their breeder reactor development programs. The U.S. is considering the fast reactor as a nuclear waste burner. France and Japan consider fast reactors as an ultimate justification for the reprocessing of spent fuel; however, there is no follow-up breeder reactor planned in France for at least a decade, and the funding for SFRs is also decreasing in Japan. Russia and India are building demonstration breeder reactors since both countries lack uranium resources [51].

The very high energy densities necessary in a fast reactor core require either a very efficient means of heat transfer or the use of highly refractory core and coolant materials. Thus, metallic fuels (i.e., U-Zr based alloys) with high thermal conductivities and U oxide fuels with high melting points are being developed for SFRs [50]. To achieve a high thermal conductivity and a low influence on fast neutrons, a liquid metal was selected as a coolant. Sodium is an excellent coolant because of its relatively low melting temperature (98°C), low-capture cross-
section of neutrons, low abundance of troublesome fission products, good flow characteristics, and good compatibility with existing fuels and structural materials [50].

Uranium alloy fuels have many advantages including high thermal conductivities, passive safety, and ease of fabrication and recyclability [1-3]. The addition of alloying elements into uranium enhances the dimensional stability under irradiation, allows the alloy solidus and liquidus temperatures to be tailored toward values desired for fabrication and operation, and reduces the fuel-cladding interdiffusion. The first SFR used metallic fuel because it was easy to fabricate. There was no gap between the fuel and cladding in the original design. It was not successful due to large swelling of the fuel caused by fission gas accumulation and thermal expansion. Large amounts of swelling caused fuel failure at only 3% burnup [1]. To solve this problem, a large gap was introduced between the fuel and cladding (shown in Figure 3 [13]). High thermal conductivity was achieved by filling this gap with a liquid sodium bond. At the same time, a gas plenum was designed for the top of the fuel. Under irradiation, the fuel swells due to fission gas accumulation. When the fuel swelling reaches about 30%, the gas bubbles begin to interconnect and can escape from the fuel and enter the gas plenum. This maintains a low stress between the fuel and cladding [1]. A burnup of 20% can be routinely reached by this new design [1].

Historically, uranium alloys including U-Zr, U-Mo, U-Cr, and U-5Fs (Fs is designated as the symbol for fissium which contains 2.4 wt.% Mo, 1.9 wt.% Ru, 0.3 wt.% Rh, 0.2 wt.% Pd, 0.1 wt.% Zr, 0.01 wt.% Nb) have been developed for SFRs [1]. More recent interest has shifted to U-Pu-Zr alloys because of their fabrication, reprocessing, and compatibility with stainless steel claddings.
2.4 U-Zr Fuel and Reactions with Claddings

As stated above, U-Zr alloys were selected as the fuels for SFRs because their high thermal conductivity, passive safety, ease of fabrication and recyclability [1-3]. More importantly, the addition of Zr exhibits the best compatibility with stainless steel claddings compared to other alloying elements. The content of zirconium in the fuel is limited to about 10 wt.% since too much Zr increases the liquidus temperature and would cause difficulty in fabrication. On the other hand, insufficient Zr concentration would not maintain phase stability and hence would not impede the interaction with the cladding [1].

The U-Zr alloy and phase diagram were studied in the literature [57-64]. The previously presented phase diagrams are in good agreement and one is presented in Figure 7 [25]. There are three allotropic phases in U as mentioned above. The allotropic transformation between α-Zr and β-Zr occurs at 863°C. With an hexagonal (hP2) structure, α-Zr has a solubility of U less than 0.4 at.%. However, β-Zr, with a bcc (cI2) structure, forms a complete solid solution with U. At temperatures below 606°C, the δ- UZr2 phase, which has an hP3 structure and solubility range from 63 to 78 at.%Zr, forms between α-U and α-Zr, [59]. The thermodynamic properties of U-Zr were also assessed by Kurate [58]. The Gibbs free energies of the solid solution and compound phases in the U-Zr system were calculated through an optimization procedure based on both the experimental thermochemical and phase diagram data.
When the U-Zr fuel swells and contacts the stainless steel cladding, metallurgical reactions can occur at the interface at high temperature [1]. The FCCIs between U-Zr alloys and stainless steels have been studied extensively, including U-Zr vs. Fe [14, 17, 29], U-Zr vs. Fe-Cr [17, 29], U-Zr vs. Fe-Ni [29], U-Zr vs. Fe-Cr-Ni [29] and U-Zr vs. stainless steel (e.g., D9, 316, HT9) [18, 28, 65]. The observations made in these previous studies are summarized in Table 1. In most cases, the interaction zone shows a complex multi-layer structure with various intermetallic compounds. However, there are some discrepancies among these studies regarding the development of the reaction zones.
Table 1 Interactions between U-Zr alloys and Fe alloys.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>Reference</th>
<th>Annealing Temperature (°C)</th>
<th>Interaction Zone*</th>
<th>Phases in the Interaction Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Zr vs. Fe</td>
<td>[29]</td>
<td>700</td>
<td>S</td>
<td>UFe₂/ Zr rich/ Zr depleted</td>
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<tr>
<td></td>
<td>[14]</td>
<td>650</td>
<td>L</td>
<td>UFe₂/ U₆Fe+UFe₂/ ZrFe₂/ U₆Fe+ZrFe₂/ U₆Fe+ε/ U+λ.</td>
</tr>
<tr>
<td></td>
<td>[17]</td>
<td>635, 650, 700, 715</td>
<td>L</td>
<td>UFe₂/ U₆Fe+UFe₂ at 635 and 650 °C or UFe₂+ZrFe₂ at 700 and 715 °C/ ZrFe₂/ U₆Fe+χ / U₆Fe+ε / U+ε / U+λ,</td>
</tr>
<tr>
<td>U-Zr vs. Fe-Cr</td>
<td>[29]</td>
<td>700</td>
<td>S</td>
<td>UFe₂/ Zr rich/ Zr depleted</td>
</tr>
<tr>
<td></td>
<td>[17]</td>
<td>680, 700, 715</td>
<td>L</td>
<td>Cr-rich/ UFe₂/ U₆Fe/ U₆Fe+ZrFe₂/ U₆Fe+χ / U₆Fe+ε / U+ε / U+λ.</td>
</tr>
<tr>
<td>U-Zr vs. Fe-Ni</td>
<td>[29]</td>
<td>700</td>
<td>L</td>
<td>UFe₂/ ZrFe₂/ U₆Fe+(Zr,U)₂(Fe,Ni)/ U+(Zr,U)₂(Fe,Ni)</td>
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<tr>
<td>U-Zr vs. Fe-Cr-Ni</td>
<td>[29]</td>
<td>700</td>
<td>L</td>
<td>UFe₂/ ZrFe₂/ U₆Fe+(Zr,U)₂(Fe,Ni,Cr)/ U+(Zr,U)₂(Fe,Ni,Cr)/</td>
</tr>
<tr>
<td>U-Zr vs. D9</td>
<td>[65]</td>
<td>700</td>
<td>L</td>
<td>UFe₂/ZrFe₂/ U₆Fe+(Zr,U)₂(Fe,Ni)/ U+(Zr,U)₂(Fe,Ni)/ U+(U,Zr)₂(Fe,Ni,Cr)</td>
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<td>U-Zr vs. 316</td>
<td>[65]</td>
<td>700</td>
<td>L</td>
<td>similar to D9</td>
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<tr>
<td>U-Zr vs. HT9</td>
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<td>700</td>
<td>S</td>
<td>UFe₂/ Zr rich/ Zr depleted</td>
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<tr>
<td>U-Zr vs. HT9</td>
<td>[18]</td>
<td>700, 730</td>
<td>S</td>
<td>(U rich+HT9)/ UFe₂/ Zr rich/ Zr depleted</td>
</tr>
</tbody>
</table>

*S: small diffusion zone
L: large diffusion zone

For diffusion couples between U-Zr and pure Fe, Ogata [14] and Nakamura [17] reported that multiple layers formed in the interdiffusion zone including UFe₂, a mixture of UFe₂ and U₆Fe or ZrFe₂, ZrFe₂, U₆Fe+χ, U₆Fe+ε, U+ε, and U+λ. The χ, ε, and λ phases are ternary compounds and their compositions are U-32Zr-50Fe, U-(33-50)Zr-33Fe and U-(21-25)Zr-6Fe (in at.%), respectively. UFe₂ and U₆Fe include less than 3 at.% and 2 at.% Zr, respectively, and
ZrFe$_2$ contains approximately 10 at.% U. However, only UFe$_2$ and a Zr rich phase were observed in the reaction zone of the U-Zr vs. Fe diffusion couple analyzed by Keiser [29]. The thickness of the interaction zone in Keiser’s study [29] was much smaller than those reported by Ogata [14] and Nakamura [17].

Nakamura [17] documented that the addition of Cr into Fe did not change the microstructures with partial substitution of Cr for Fe. The diffusion of Cr into the U-Zr side was slower than that of Fe; some Cr remained in the Fe-Cr side of the reaction zone and a Cr-rich phase formed adjacent to the unreacted Fe-Cr alloy [17]. Cr was detected in the UFe$_2$, ZrFe$_2$, and $\chi$ phases, but not in the U$_6$Fe, $\varepsilon$, $\lambda$, U phases [17]. However, in the same system of U-Zr vs. Fe-Cr, negligible interdiffusion occurred and only UFe$_2$ and a Zr rich phase were observed at the interface in Keiser’s study [29]. The addition of Ni into Fe enhanced the interaction between the U-Zr and Fe alloy because the interaction zone in the system containing Ni in the Fe alloy was much larger as compared to that of the pure Fe case [29].

The interaction between U-Zr alloys and stainless steels were also reported [18, 28, 65]. In Keiser’s study [65], significant interdiffusion occurred between U-Zr and stainless steels D9 and 316. However, a Zr rich phase and thin reaction zone were observed between U-Zr and HT9 stainless steel [65]. The significant difference between HT9 and D9 or 316 stainless steels is that HT9 contains negligible amounts of Ni. Lee [18] reported a similar result to Keiser regarding the reaction between U-Zr and HT9. Hofman [1, 28] carried out a large number of diffusion tests between U-Zr and HT9, D9, and 316 stainless steels and the found experimental data to be inconsistent.
The discrepancy in the observations of extensive and insignificant diffusion occurring may be caused by the Zr rich layer at the interface. Hofman [1, 28] suggested that the delta phase (i.e., UZr_2 with Zr solubility of 63-78 at.%) in the U-Zr alloy decomposed into Zr rich and Zr depleted phases and that the Zr rich phase formed a uniform layer at the interface. This Zr rich layer acted as a barrier layer to impede further diffusion. It was observed that the Zr rich layer existed in diffusion couples with short reaction zones [18, 29, 65]; however, it was not found in diffusion couples with large reaction zones [14, 17]. Hofman [1, 28] found that the Zr rich layer contained approximately 20-30 at.% of interstitial elements (oxygen, carbon, nitrogen). These interstitial impurities were thought to have come from environmental contamination or the initial alloys. The exact reason for the development of this Zr rich layer has not yet been determined.

2.5 Diffusion in Selected Uranium Alloy Systems

Interdiffusion, tracer diffusion, and self diffusion studies regarding the U-Mo system have previously been conducted [21, 22, 66-71]. Adda [67] determined the interdiffusion coefficient and activation energy of the U-Mo solid solution in the composition and temperature range of 2 to 26 at.% Mo and 850 to 1050°C, respectively. However, the results showed an unusual trend in the interdiffusion coefficients and activation energy [67]. The diffusion coefficients reported by Adda showed a convex variation between N_{Mo} = 0.05 and 0.1, while the activation energy increased to a maximum at N_{Mo} = 0.1 and then decreased. Lundberg [66] reported experimental data for the interdiffusion coefficient and phase diagram in the temperature range of 1127 to 1252°C from analysis of compatibility experiments in which UO_2 was decomposed by lithium in closed molybdenum capsules. In the study, U decomposed from
UO₂ penetrated into the Mo capsule. The intermediate U₂Mo phase formed in this temperature range, contrary to the prediction based on the currently accepted equilibrium U-Mo phase diagram [25]. The solubility of U in Mo was determined to be about 1 at.% in this temperature range, while the solubility range of U in the U₂Mo phase was reported to be 63.6 to 69.2 at.% at 1127°C, 62 to 70 at.% at 1177°C, and 63.6 to 87.1 at.% at 1252°C. The composition independent interdiffusion coefficients at 1127, 1177 and 1252°C were determined to be 3.6 x 10⁻¹⁵, 4 x 10⁻¹⁴ and 2 x 10⁻¹⁴ m²/s, respectively. Since these interdiffusion coefficients involved three phases including Mo, U₂Mo and liquid U, they were only very rough estimations which could explain why the interdiffusion coefficient at 1252°C was reported to be lower than that at 1177°C.

Self diffusion coefficients of U in the γ, β, and α phases have been reported by Adda [68-70]. The pre-exponential factors and activation energies for self diffusion of U were determined to be 1.80 x 10⁻⁷ m²/s and 115 kJ/mole for the γ phase [68], 1.35 x 10⁻⁶ m²/s and 176 kJ/mole for the β phase [69] and 2.00 x 10⁻⁷ m²/s and 167 kJ/mole for the α phase [70], respectively. The tracer diffusion of U in other metals including Mo, Zr, Ti, Nb, V, Ta and W [21, 22] and tracer diffusivities of metals including Fe, Ni, and Cr into U [72] have also been reported. Additionally, Adda observed a decrease in the tracer diffusion coefficient of U in γ-U with the addition of Mo [68, 71].

The interdiffusion coefficients in U-Zr alloys have also been experimentally determined by Adda [73], Ogata [74] and Akabori [75]. Above the temperature of 950°C, Adda [73] measured the interdiffusion coefficients in the U-Zr solid solution and obtained the pre-exponential factors and the activation energies for a wide range of alloy compositions. Ogata measured interdiffusion coefficients in the temperature range of 700 to 950°C and composition
range of 10 to 95 at.% Zr [74]. The interdiffusion coefficients measured at temperatures lower than 950°C showed a notable depression in the Zr concentration range of 20 to 40 at.%, which was determined to be caused by the decrease in the thermodynamic factor in that composition range. The interdiffusion behavior in the δ-UZr₂ phase of U-Zr alloys was studied by Akabori [75] in the composition and temperature range of 67 to 75 at.% Zr and 500 to 600°C, respectively.

2.6 Ternary Diffusion Coefficient Calculation Methods

Multi-component diffusion plays an important role in alloy systems because it is related to a number of phenomena and applications, such as diffusion bonding, heat treatment, oxidation, phase transformation and surface modification. The interdiffusion behavior in an n-component alloy system is described by \((n-1)^2\) independent interdiffusion coefficients based on Onsager’s formalism of Fick’s law [76, 77]. Therefore, in a ternary system, four concentration-dependent interdiffusion coefficients, two main and two cross-coefficients, are required. In order to experimentally determine these coefficients, some classical methods including the Boltzmann-Matano method [78, 79], the improved Sauer-Freise analysis [80], and the “square root diffusivity” method [81] have been developed. Many other efforts [82-89] have been carried out to investigate ternary diffusion. Bouchet [32] provided a comprehensive review of the common methods to determine ternary coefficients in the literature. Typically, two independent diffusion couples whose diffusion paths intersect are needed to determine the coefficients at the common concentration. To study the composition dependence of the interdiffusion coefficients, a large series of diffusion couples is therefore required.
The four coefficients can also be extracted based on one diffusion couple’s concentration profile. Under the assumption that the coefficients are composition-independent, an analytical solution method (also called error function method) [90] can be applied. However, this method is restricted to diffusion occurring only within a small concentration range [31]. To determine composition-dependent coefficients, Dayananda [31] and Bouchet [32] proposed new methods based on the integration of the diffusion flux and a numerical inverse approach, respectively.

In order to extract more information from a single diffusion couple, Dayananda and Sohn [31] developed a method (referred to as the “DASO” method) to calculate a local average diffusion coefficient over a selected interval. They applied the local average interdiffusion coefficient, \( \bar{D}_{ij} \), to replace the composition-dependent \( \tilde{D}_{ij} \) and yield Onsager’s formalism as Eq. (1) [31]:

\[
\tilde{J}_i = -\bar{D}_{i,1} \frac{dC_1}{dx} - \bar{D}_{i,2} \frac{dC_2}{dx} \quad (i = 1 \text{ or } 2)
\]

where \( \tilde{J}_i \) and \( C_i \) are the interdiffusion flux and concentration of component \( i \), respectively.

Using the Boltzmann-Matano method, the interdiffusion flux can be calculated using [91]:

\[
\tilde{J}_i = \frac{1}{2t} \int_{C_i^{\pm \infty}}^{C_i^*} (x - x_0) dC_i \quad (i = 1 \text{ or } 2)
\]

where \( C_i^{\pm \infty} \) is the composition of component \( i \) at one of the terminal ends, \( C_i^* \) is the concentration of component \( i \) at the point which the interdiffusion flux is being determined, and \( t \) refers to the annealing time. Here \( x_0 \) is the Matano plane and is defined by [91]:

\[
\int_{C_i^{\pm \infty}}^{C_i^*} (x - x_0) dC_i = 0 \quad (i = 1 \text{ or } 2)
\]
To create the necessary equations for determining the unknown diffusion coefficients, Dayananda and Sohn [31] proposed the integration flux method wherein both sides of Eq. (1) are multiplied by \((x-x_0)^m\) \((m = 0,1,2\ldots)\) and then integrated over the same interval \((x_1, x_2)\) to yield a set of equations that can be created by varying the value of \(m\) to obtain:

\[
\int_{x_1}^{x_2} \bar{J}_i(x) \cdot (x-x_0)^m \, dx = -\overline{D}_{i1}^3 \int_{C_1(x_1)}^{C_1(x_2)} (x-x_0)^m \, dC_1 - \overline{D}_{i2}^3 \int_{C_2(x_1)}^{C_2(x_2)} (x-x_0)^m \, dC_2 \quad (i=1 \text{ or } 2)
\]  

(4)

When \(m = 0\), Eq. (4) can be expressed as:

\[
\int_{x_1}^{x_2} \bar{J}_i(x) \, dx = \overline{D}_{i1}^3[C_1(x_1) - C_1(x_2)] + \overline{D}_{i2}^3[C_2(x_1) - C_2(x_2)] \quad (i=1 \text{ or } 2)
\]  

(5)

When \(m = 1\), and after substituting Eq. (2), Eq. (4) yields:

\[
\int_{x_1}^{x_2} \bar{J}_i(x) \cdot (x-x_0) \, dx = 2t \overline{D}_{i1}^3 \left[\bar{J}_1(x_1) - \bar{J}_1(x_2)\right] + \overline{D}_{i2}^3 \left[\bar{J}_2(x_1) - \bar{J}_2(x_2)\right] \quad (i=1 \text{ or } 2)
\]  

(6)

Solving the system of equations obtained by combining Eqs. (5) and (6) leads to the determination of the four \(\overline{D}_{ij}^3\) coefficients in a ternary system. It is also possible to apply this method to systems with more components by varying the value of \(m\) to create more equations. This method has been used to analyze the Re-Al-Ni [92, 93], Ni-Cr-X (X=Al, Si, Ge, or Pd) [94], Ni-Al-X (Cr, Fe, Nb or Ti) [95], and Ni3Al-M ternary systems [96]. In order to obtain an independent relationship between Eq. (5) and Eq. (6) for the determination of the four coefficients, the interval \((x_1, x_2)\) must be selected in non-linear portions of the concentration profile (i.e. \(\partial C/\partial x \neq \text{constant}\)). When the concentration profile is approximately linear in the middle region of the interdiffusion zone, the calculated \(\overline{D}_{ij}^3\) may not be accurate and hence
cannot be considered reliable [31]. On the other hand, the moment, \((x-x_0)^m\), in Eq. (4) makes the concentration profiles near the terminal end more significant than the data near the Matano plane, \(x_0\), especially when \(m\) is a large value. However, the uncertainty of the experimental data near the terminal ends is larger than that of the data in the middle region. Therefore, the moment, \((x-x_0)^m\), actually enlarges the uncertainty of the experiments. In some cases, the calculated \(\overline{D}_3\) shows relatively large errors [32].

A numerical inverse method (referred to as the “BOME” method) was proposed by Bouchet and Mevrel [32] to calculate the ternary coefficients using a single diffusion couple. The procedure is based on the minimization of the difference between the profiles calculated by a finite difference scheme and the experimental profiles via “trial and error” techniques. There are some issues that need attention as the author indicated. First of all, in order to get stable and accurate \(\tilde{D}^3\) values, particular attention must be paid to smoothing of the experimental data and the initial value inputs. Secondly, from a mathematical standpoint, the best calculated \(\tilde{D}^3\) values may have no physical meaning. In addition, the computing process is complex and time consuming (12 hours for each diffusion path).
CHAPTER THREE: ANALYTICAL FRAMEWORK

Different diffusion coefficients and parameters are applied to describe the diffusion phenomena with varying initial and boundary conditions, intermetallic phases, and number of components. The various cases and analytical methods involved in this study are reviewed here including (1) binary solid-to-solid diffusion with concentration gradients; (2) binary solid-to-solid diffusion without concentration gradients (i.e., stoichiometric (line-) intermetallic compound existing in the diffusion zone); and (3) ternary and multi-component solid-to-solid diffusion.

3.1 Binary Solid-to-Solid Diffusion with Concentration Gradients

In a binary system, only one interdiffusion coefficient is required to describe the interdiffusion process. If the molar volume can be assumed to not vary significantly within the alloy composition, then Vegard's law applies, which means that the total volume of the diffusion couple does not change during the diffusion process. Under this assumption, the simple Boltzmann-Matano analysis described in [91] can be applied to determine the interdiffusion flux and Matano plane position using Eqs. (2) and (3). The interdiffusion coefficient can be calculated using Eq. (7) and the concentration profile of component A or B:

\[
\tilde{D}(C_i^*) = -\frac{\tilde{J}(C_i^*)}{(dC_i/dx)_{C_i^*}} = -\frac{1}{2t} \int_{C_i^*}^{C_i} (x - x_0) dC_i
\]

\[(i = A \text{ or } B) \quad (7)\]
The interdiffusion flux can also be determined using the Sauer-Freise method, which takes into account the molar volume variation during the interdiffusion process. Another advantage of this method is that it avoids the determination of the Matano plane. A normalized concentration variable $Y_i$ is introduced as:

$$Y_i = \frac{C_i - C_i^{-\infty}}{C_i^{+\infty} - C_i^{-\infty}} \quad (i=A \text{ or } B) \quad (8)$$

The interdiffusion flux can then be obtained using Eq. (9):

$$J_i = \frac{V^*_m}{2t} (C_i^{+\infty} - C_i^{-\infty})[(1 - Y_i^*) \cdot \int_{-\infty}^{x} \frac{Y_i}{V_m} \, dx + Y_i^* \cdot \int_{x}^{+\infty} \frac{1 - Y_i}{V_m} \, dx] \quad (i=A \text{ or } B) \quad (9)$$

where $V_m$ is the molar volume and the superscript “*” indicates values at the location where the interdiffusion flux is being determined.

In a diffusion process, each component may diffuse intrinsically at a different rate. This results in the movement of the marker plane (also called the Kirkendall plane), which is the original interface of the diffusion couple. The marker plane moving velocity, $v_K$, can be expressed by Eq. (10), where $x_K$ is the marker plane position after annealing time $t$.

$$v_K = \frac{1}{2t} (x_K - x_0) \quad (10)$$

The intrinsic diffusion coefficient of component $i$, $D_i$, at the marker plane is related to $v_K$ and the interdiffusion coefficient, $\tilde{D}$, by Eqs. (11) and (12) as shown below:

$$v_K = (D_A - D_B) \frac{dC_A}{dx} \quad (A \neq B) \quad (11)$$
\[ \tilde{D} = C_A D_B + C_B D_A \]  

(12)

Combining Eqs. (10), (11) and (12) yields the intrinsic diffusion coefficients of \( A \) and \( B \), \( D_A \) and \( D_B \), at the marker plane.

The intrinsic diffusivity of each component, \( D_i \), can also be determined directly by Heumann’s method [97] expressed by:

\[ D_i = \frac{1}{2t} \frac{A_i}{\left( \frac{dC_i}{dx} \right)_{x=x_k}} \quad (i=A \text{ or } B) \]  

(13)

where \( A_i \) is the cumulative intrinsic flux of component \( i \) at the marker plane, which can be determined from the corresponding areas under the concentration profile of component \( i \).

If \( D_i \) in a binary system is known, the tracer diffusivity (\( D^*_i \)), atomic mobility (\( \beta_i \)) and vacancy wind effect (\( \Psi_i \)) of component \( i \) can be determined based on the random alloy model developed by Manning [98]. \( \Psi_i \) is a parameter describing the effect of the vacancy flux on the diffusion of component \( i \). The intrinsic diffusivity, \( D_i \), is related to its respective tracer diffusivity, \( D^*_i \), through Eq. (14):

\[ D_i = D^*_i \Phi \Psi_i \quad (i=A \text{ or } B) \]  

(14)

where \( \Phi \) is the thermodynamic factor of the alloy, which can be calculated by:

\[ \Phi = \frac{d \ln(a_i)}{d \ln(N_i)} \quad (i=A \text{ or } B) \]  

(15)

where \( a_i \) represents the thermodynamic activity of component \( i \). The vacancy wind terms, \( \Psi_i \), are given by Eq. (16) [98]:
\[
\Psi_A = 1 + \frac{2N_A(D_A^* - D_B^*)}{\alpha(N_A D_A^* + N_B D_B^*)} \quad (A \neq B)
\]  \hspace{1cm} (16)

where \( N_{A or B} \) refers to the atomic fraction of the respective component \( A \) or \( B \) and \( \alpha \) is a structure-dependent parameter (e.g., 7.15 for fcc, 5.33 for bcc, 3.77 for sc, and 2 for diamond cubic). The atomic mobility, \( \beta_i \), can be determined from its respective \( D_i^* \) using the relation:

\[
D_i^* = \beta_i k T \quad (i=A \text{ or } B)
\]  \hspace{1cm} (17)

where \( k \) is the Boltzmann constant and \( T \) is the temperature in Kelvin.

### 3.2 Binary Solid-to-Solid Diffusion without Concentration Gradients

In some cases, intermetallic phases or compounds may form in the interdiffusion zone. The methods described above can be used if the solubility range in the intermediate phase is relatively large. However, it is not appropriate to apply them when the homogeneity range in the phase is narrow since the error of the calculated interdiffusion coefficients may be large due to uncertainty in the concentration gradient. Heumann [97] extend the Boltzmann-Matano method to intermediate phases with a narrow homogeneity range. An equation was derived to determine the interdiffusion coefficient for the average concentration within a phase under an assumption of a linear concentration profile in the intermediate phase. Wagner [99] also developed a similar equation under the condition that the interdiffusivities are composition independent in the intermediate phase.

However, in a stoichiometric (line-) intermetallic compound with a negligible concentration gradient, the interdiffusion coefficient in the phase cannot be calculated since the
concentration gradient is nearly zero, which causes the interdiffusion coefficient to approach infinity. New diffusion parameters including integrated interdiffusion coefficients \( \tilde{D}^\text{int}_i \) [99, 100] and two kinds of growth constants [99], extrinsic \( (K_i) \) and intrinsic \( (K_{ii}) \), can be applied to describe the diffusion process. The integrated interdiffusion coefficient, \( \tilde{D}^\text{int}_i \), of component \( i \) in a selected range \( (x_1, x_2) \) is defined as [100]:

\[
\tilde{D}^\text{int}_i = -\int_{x_1}^{x_2} \tilde{J}_i \, dx = \int_{C_i(x_1)}^{C_i(x_2)} \tilde{D}_i \, dC_i \quad (i = AorB)
\] (18)

Assuming that the \( \nu \) phase is a line compound, ranging from \( x^{(\nu)^-} \) to \( x^{(\nu)^+} \), the thickness of the \( \nu \) phase can be defined as \( \Delta x^{(\nu)} = x^{(\nu)^+} - x^{(\nu)^-} \). Because there is no concentration gradient in the \( \nu \) phase, the interdiffusion flux through the \( \nu \) phase is constant according to Eq. (2) or (9). Selecting the interval \( (x_1, x_2) \) through the \( \nu \) phase, the integrated interdiffusion coefficient of component \( i \) through phase \( \nu \), \( \tilde{D}^\text{int,}(\nu)_i \), defined by Eq. (18), can be simplified to:

\[
\tilde{D}^\text{int,}(\nu)_i = -\tilde{J}^{(\nu)}_i \cdot \Delta x^{(\nu)} \quad (i = AorB)
\] (19)

Wagner [99] also provided an equation to calculate the integrated interdiffusion coefficient as:

\[
\tilde{D}^\text{int,}(\nu)_i = \frac{(N_i^{(+\nu)} - N_i^{(-\nu)})(N_i^{(+\nu)} - N_i^{(-\nu)})}{(N_i^{(+\nu)} - N_i^{(-\nu)})} \times \left[ \frac{(\Delta x^{(\nu)})^2}{2t} \right] + \frac{\Delta x^{(\nu)}}{2t} \left[ \frac{N_i^{(+\nu)} - N_i^{(-\nu)}}{N_i^{(+\nu)} - N_i^{(-\nu)}} \times \int_{-\infty}^{+\nu} \frac{V_m^{(\nu)}}{V_m}(N_i - N_i^{(-\nu)}) \, dx \right] + \frac{\Delta x^{(\nu)}}{2t} \left[ \frac{N_i^{(+\nu)} - N_i^{(-\nu)}}{N_i^{(+\nu)} - N_i^{(-\nu)}} \times \int_{+\nu}^{+\nu} \frac{V_m^{(\nu)}}{V_m}(N_i^{(+\nu)} - N_i) \, dx \right]
\] (20)

which is equivalent to Dayananda’s equation [100] when the molar volume remains constant.
It should be noted that the integrated interdiffusion coefficient of a specific phase \( \nu \), \( \tilde{D}_{i}^{\text{int,(v)}} \), as defined in Eqs. (19) and (20), is a material constant and must therefore remain the same in all diffusion couples in which the phase forms [99, 101]. However, the parabolic growth constant of the \( \nu \) phase is not a material constant and may vary in diffusion couples with different terminal ends. Therefore, in solid-to-solid diffusion couples, two kinds of parabolic growth constants, first kind (extrinsic) \( K_{I}^{(v)} \) and second kind (intrinsic) \( K_{II}^{(v)} \), are employed to describe the diffusion process in the \( \nu \) phase [99]. Assuming the \( \nu \) phase forms in a diffusion couple with pure components as terminal ends (a diffusion couple of the first kind, \( N_{i}^{-\infty} = 0, N_{i}^{+\infty} = 1 \)), the first kind parabolic growth constant, \( K_{I}^{(v)} \), is defined as:

\[
K_{I}^{(v)} = \left[ \frac{(\Delta x^{(v)})^2}{2t} \right]_{N_{i}^{-\infty} = 0, N_{i}^{+\infty} = 1}
\]  

(21)

Inserting Eq. (21) into Eq. (20) yields Eq. (22), which correlates \( \tilde{D}_{i}^{\text{int,(v)}} \) and \( K_{I}^{(v)} \).

\[
\tilde{D}_{i}^{\text{int,(v)}} = \int_{N_{i}^{(v)}}^{N_{i}^{(v)}} \tilde{D} dN_{i} = N_{i}^{(v)} \times (1 - N_{i}^{(v)}) K_{I}^{(v)} + \frac{(1 - N_{i}^{(v)})}{2t} \int_{-\infty}^{d_{e}} \frac{V_{m}}{V_{m}} N_{i} \, dx + N_{i}^{(v)} \int_{d_{e}}^{+\infty} \frac{V_{m}}{V_{m}} (1 - N_{i}) \, dx
\]  

(22)

Alternatively, the \( v \)-th phase can also form in a diffusion couple with its neighboring phases, \((v-1)\) and \((v+1)\), as terminal ends (a diffusion couple of the second kind \( N_{i}^{-\infty} = N_{i}^{(v-1)} \), \( N_{i}^{+\infty} = N_{i}^{(v+1)} \)) and the second kind of parabolic growth constant, \( K_{II}^{(v)} \), can be expressed using the same equation with different boundary conditions:
\[ K_{II}^{(v)} = \left[ \frac{(\Delta x^{(v)})^2}{2t} \right]_{N_i^{(v)}=N_i^{(v-1)}, N_i^{(v)}=N_i^{(v+1)}} \]  

(23)

where \( N_i^{(v-1)} \) and \( N_i^{(v+1)} \) are the atomic fraction of component \( i \) in the neighboring phases \((v-I)\) and \((v+I)\). In diffusion couples of the second kind, the integral terms in Eq. (22) vanish. One obtains,

\[ \tilde{D}_{I}^{int.(v)} = \frac{(N_i^{(v)} - N_i^{(v-1)})(N_i^{(v+1)} - N_i^{(v)})}{(N_i^{(v+1)} - N_i^{(v-1)})} \times [K_{II}^{(v)}]_{N_i^{(v)}=N_i^{(v-1)}, N_i^{(v)}=N_i^{(v+1)}} \]

(24)

\( K_{II}^{(v)} \) is a “true” growth constant and can be related to the intrinsic diffusion in the phase.

In contrast, values of \( K_{I}^{(v)} \) are determined by the properties of all phases involved in the diffusion process [99]. Both \( K_{I}^{(v)} \) and \( K_{II}^{(v)} \) are related to \( \tilde{D}_{I}^{int.(v)} \) by Eqs. (22) and (24). Since \( \tilde{D}_{I}^{int.(v)} \) is a material constant for the \( v \) phase, the terms on the right side of Eqs. (22) and (24) are equal, and \( K_{II}^{(v)} \) can be obtained from \( K_{I}^{(v)} \).

3.3 Ternary and Multi-component Solid-to-Solid Diffusion

The interdiffusion behavior in an \( n \)-component alloy system is described by \((n-1)^2\) independent interdiffusion coefficients based on Onsager’s formalism of Fick’s law [76, 77]. In a ternary system, four concentration-dependent interdiffusion coefficients, two main and two cross-coefficients, are required. These interdiffusion coefficients can be determined using the methods introduced in section 2.6 based on concentration profiles. The new method developed in this study can also be applied to calculate the diffusion coefficients. Unfortunately, the ternary or multi-component systems investigated in this study did not develop single-phase concentration profiles for determination of interdiffusion coefficients due to the existence of large precipitates.
(e.g., U-Mo vs. Zr), cracks at the interface (e.g., U-Mo vs. Nb), no concentration gradients, or thin diffusion zones (e.g., U vs. Fe-Cr). Alternatively, diffusion paths and parabolic growth rates of the interdiffusion zones were applied to analyze the observations made in this study.

3.4 Arrhenius Relation

Because diffusion is a thermally activated process, both diffusion coefficients and intermetallic growth constants should obey the Arrhenius relation, which describes the temperature dependence as:

\[
A = A_0 \exp \left( -\frac{Q}{RT} \right)
\]

(25)

where \( A \) can be a diffusion parameter (such as \( \tilde{D}_{i} \), \( \tilde{D}_{int} \), \( K_{i}^{(v)} \) and \( K_{II}^{(v)} \) etc.), \( A_0 \) is the pre-exponential factor, \( Q \) is the activation energy, and \( R \) is the molar gas constant with a value of 8.31 J/mol-K. Following the determination of the \( A \) values at different temperatures, \( A_0 \) and \( Q \) can be determined, which are very important to study the temperature dependence of \( A \) and to predict the value of \( A \) over an appropriate temperature range.
CHAPTER FOUR: EXPERIMENTAL DETAILS

4.1 Alloy Preparation

Uranium containing alloys including pure U, U-7wt.%Mo, U-10wt.%Mo and non-uranium containing alloys of Mo, Zr, Nb, Mg, Fe, Fe-15wt.%Cr and Fe-15wt.%Cr-15wt.%Ni were used for these experiments. Since $^{238}\text{U}$ and $^{235}\text{U}$ have the same chemical properties, depleted uranium (DU) was used in this study. Pure U and U-Mo alloy rods were cast using high-purity DU and Mo via arc melting at Idaho National Laboratory (INL). They were melted three times to ensure homogeneity and then drop-cast to form rods of 6.35 mm in diameter. Mo, Zr, Nb, Mg and Fe rods of 99.99% purity and Fe-15wt.%Cr, Fe-15wt.%Cr-15wt.%Ni alloys were acquired from a commercial source (Alpha-Aesar™). The homogeneity in composition, phase constituents and microstructure of the alloys were examined via x-ray diffraction (XRD, Rigaku™ DMAX-B) and scanning electron microscopy (SEM, Zeiss Ultra-55) equipped with X-ray energy dispersive spectroscopy (XEDS).

4.2 Diffusion Couple Assembly and Annealing

All metallographic preparations and the assembly of diffusion couples were carried out under an Ar atmosphere inside a glove box to minimize oxidation of the alloys and avoid contamination of lab facilities. The glove box was setup to maintain an inert atmosphere by feeding argon through an inlet on the rear bottom of the box and pumping the air though an outlet at the center top of the box as shown in Figure 8. An inert atmosphere can be achieved by balancing the feeding and pumping rate.
All the pure metal or alloy rods were cut into 3mm-thick disks. The disk surfaces, which would become the interface of the diffusion couple, were metallographically ground using 240, 600, 800, and 1200-grit SiC papers and final polished down to 1 µm using diamond paste. To avoid oxidation of the alloy disks, the grinding process employed non-oxidizing lubricant (i.e., high purity ethanol). Since pure uranium oxidizes easily, all the U disks were immersed momentarily into nitric acid (1:1 volume with distilled water) before assembling the diffusion couples to remove the oxide layer on the surface. The prepared surfaces were then placed in contact with each other and held together by two clamping disks with stainless steel rods to form a jig as shown in Figure 9. Al$_2$O$_3$ disks were employed between the alloy disks and the steel clamping disks to prevent any interaction between them. Each couple assembly was wrapped with Ta-foil and encapsulated in a quartz capsule that was sealed under high vacuum ($10^{-6}$ torr) or Ar atmosphere after repeated vacuum and pure H$_2$ flushing operations. Finally, the couples were annealed using a Lindberg/Blue™ three-zone tube furnace. Annealing times and temperatures for each of the diffusion systems are presented in Table 2.
After annealing, the diffusion couples were quenched by breaking the quartz capsule in cold water. Each diffusion couple was then mounted in epoxy, cross-sectioned, and polished down to 1 µm for microstructural examination and compositional analysis.
Table 2 Annealing temperature and time for diffusion couples investigated in this study.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>Temperature (°C)</th>
<th>Temperature (K)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U vs. Mo</td>
<td>1000</td>
<td>1273</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1173</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1073</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>923</td>
<td>360</td>
</tr>
<tr>
<td>U-10wt.%Mo vs. Mo (U-21.6at.%Mo vs. Mo)</td>
<td>1000</td>
<td>1273</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1173</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1073</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>873</td>
<td>960</td>
</tr>
<tr>
<td>U-10Mo vs. Zr (U-21.6at.%Mo vs. Zr)</td>
<td>1000</td>
<td>1273</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1173</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1073</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>873</td>
<td>960</td>
</tr>
<tr>
<td>U-10Mo vs. Nb (U-21.6at.%Mo vs. Nb)</td>
<td>1000</td>
<td>1273</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1173</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1073</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>873</td>
<td>960</td>
</tr>
<tr>
<td>U-7Mo vs. Mg (U-15.7at.%Mo vs. Mg)</td>
<td>550</td>
<td>823</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>853</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>615</td>
<td>888</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>923</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>680</td>
<td>953</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>96</td>
</tr>
<tr>
<td>U vs. Fe</td>
<td>600</td>
<td>873</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>923</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>96</td>
</tr>
<tr>
<td>U vs. Fe-15wt.%Cr (U vs. Fe-15.9at.%Cr)</td>
<td>600</td>
<td>873</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>923</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>96</td>
</tr>
<tr>
<td>U vs. Fe-15wt.%Cr-15wt.%Ni (U vs. Fe-16.0at.%Cr-14.2at.%Ni)</td>
<td>600</td>
<td>873</td>
<td>240</td>
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<tr>
<td></td>
<td>650</td>
<td>923</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>973</td>
<td>96</td>
</tr>
</tbody>
</table>
4.3 Diffusion Couple Characterization

The bonding condition and interdiffusion microstructure of the diffusion couples were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM analysis was performed using a Zeiss Ultra-55 field emission SEM equipped with XEDS. Details of the interface were further examined using an FEI/Tecnai™ F30 300 keV TEM equipped with a Fischione™ high angle annular dark field (HAADF) detector and XEDS. Site-specific specimens were prepared using an FEI TEM200 Focus Ion Beam (FIB) in situ lift-out (INLO) technique. Initially, a Pt layer was deposited onto the selected area of interest to protect the surface of the sample from the accelerated Ga-ion beam. The high energy Ga beam was utilized to mill material creating a trench on both sides. The edges of the sample were then milled leaving only a small bridge of material so that the sample remained attached to the bulk alloy. A W omni-probe was then lowered in and Pt-welded to the bridge connecting the sample and the bulk alloy. The partially attached edge of the specimen was then milled completely to release the sample. The W omni-probe, with the TEM specimen still welded to it, was then lifted away from the stage and lowered toward a slotted copper TEM grid.

Chemical composition analyses were performed via X-ray energy dispersive spectroscopy (XEDS) and electron probe microanalysis (EPMA). Standardless semi-quantitative XEDS equipped on the SEM and TEM was applied to obtain a rough chemical composition of each phase, a concentration profile across the interface, and elemental mapping. To quantitatively determine an accurate composition in the diffusion zone, EPMA (JEOL™ Superprobe 733) was employed to obtain the concentration profiles from selected couples utilizing a point-to-point scan with a 3-10 μm step size and an accelerating voltage of 20 kV. The
pure metals, DU, Mo, Zr, Nb, and Fe, were used as standards to calibrate the EPMA instrument before every measurement. The intensities of the U-Mα, Mo-Lα, Zr-Lα, Nb-Lα and Fe-Kα X-rays were converted to compositions using a ZAF correction technique. Two independent measurements were conducted for each couple with excellent agreement. The average concentration profiles obtained from the two EPMA measurements were curve fitted using the nonlinear curve-fitting tool in Origin™. These fitted concentration profiles were used for quantitative analysis.
CHAPTER FIVE: RESULTS

5.1 New Method for Determining Ternary Diffusion Coefficients

As mentioned in the literature review (section 2.6), the available methods for determination of ternary diffusion coefficients have some weaknesses or limitations. In this study, a new method has been developed to determine the diffusion coefficients using a single diffusion couple based on Onsager’s formalism and a linear algebra transformation. This method avoids the negative influence of the moment \((x-x_0)^m\) in the DASO method [31]. Initial input values of \(\tilde{D}_{ij}^3\) are not required and the calculation process is more straightforward and simple unlike the BOME method [32]. This new method is introduced in section 5.1.1 and its accuracy and reliability are evaluated using three case studies in section 5.1.2. The three case studies include a basic asymptotic concentration profile, a concentration profile with uphill diffusion and extrema, and a concentration profile with noise. It was found that the new method works well in all of the three cases.

5.1.1 Analysis of New Method for Determining Ternary Diffusion Coefficients

In the studied interval \((x^1, x^2)\), \(\tilde{D}_{ij}^3\) is considered as composition-independent \(\bar{D}_{ij}^3\). Arbitrary points \((x_1, x_2, ..., x_n)\) are selected in the interval \((x^1, x^2)\) and Onsager’s formalism, presented in Eq. (1), is built at each point as:
\[ \mathcal{J}_i \big|_{x_i} = -\overline{D}_{i,1} \frac{dC_1}{dx} \big|_{x_i} - \overline{D}_{i,2} \frac{dC_2}{dx} \big|_{x_i} \]

\[ \mathcal{J}_i \big|_{x_2} = -\overline{D}_{i,1} \frac{dC_1}{dx} \big|_{x_2} - \overline{D}_{i,2} \frac{dC_2}{dx} \big|_{x_2} \quad (i=1 \text{ or } 2) \]  

(26)

\[ \mathcal{J}_i \big|_{x_n} = -\overline{D}_{i,1} \frac{dC_1}{dx} \big|_{x_n} - \overline{D}_{i,2} \frac{dC_2}{dx} \big|_{x_n} \]

where \( \mathcal{J}_i \big|_{x_n} \) is the interdiffusion flux of component \( i \) at the location of \( x_n \) and \( \frac{dC_1}{dx} \big|_{x_n} \) and \( \frac{dC_2}{dx} \big|_{x_n} \) are the concentration gradients of component 1 and 2 at the location of \( x_n \). Both the Boltzmann-Matano and Sauer-Freise methods [91] can be applied to determine \( \mathcal{J}_i \big|_{x_n} \) using Eq. (2) or (9). The latter method has the advantage of avoiding the determination of the Matano plane and it is also valid in systems where the molar volume varies with composition. Eq. (26) can be expressed as matrix:

\[ B \cdot D = -J \]  

(27)

where

\[ B = \begin{bmatrix} \frac{dC_1}{dx} \big|_{x_1} & \frac{dC_2}{dx} \big|_{x_1} \\ \frac{dC_1}{dx} \big|_{x_2} & \frac{dC_2}{dx} \big|_{x_2} \\ \vdots & \vdots \\ \frac{dC_1}{dx} \big|_{x_n} & \frac{dC_2}{dx} \big|_{x_n} \end{bmatrix} \; ; \; D = \begin{bmatrix} \overline{D}_{1,1} \\ \overline{D}_{1,2} \\ \vdots \\ \overline{D}_{i,1} \\ \overline{D}_{i,2} \end{bmatrix} \; ; \; J = \begin{bmatrix} \mathcal{J}_1 \big|_{x_1} \\ \mathcal{J}_1 \big|_{x_2} \\ \vdots \\ \mathcal{J}_1 \big|_{x_n} \end{bmatrix} \]

A linear algebra transformation leads to the solution of Eq. (27) as:
This matrix transformation method determines the $\overline{D}_{ij}^{3}$ which best fits the $n$ equations in Eq. (26). The $n$ points are chosen from the selected interval $(x_1', x_2')$; therefore, the calculated $\overline{D}_{ij}^{3}$ is the best average estimate of $\overline{D}_{ij}^{3}$ for the interval. This linear algebra transformation procedure is similar to a regression process, which minimizes the sum of square difference between the predicted and experimental data. If the intervals $(x_1', x_2')$ are selected through the whole interdiffusion zone, then the composition-dependent $\overline{D}_{ij}^{3}$ can be obtained. It is also evident that Eq. (26) can provide adequate equations through selecting more points in the interval to calculate the $(n-1)^2$ interdiffusion coefficients $\overline{D}_{ij}^{n}$ for any multi-component system.

To further improve this method, a weighted factor, $W$, can be introduced into Eq. (27) as shown in Eq. (29). The weight factor is a diagonal $n \times n$ matrix that can be specific numerical values or a function of position and concentration. This weight factor provides freedom to adjust the significance of each experimental data, which is related to uncertainties from instruments or experiments.

$$W \cdot B \cdot D = -W \cdot J$$  \hspace{1cm} (29)

The ternary diffusion coefficients can be obtained from Eq. (29):

$$D = \begin{bmatrix} \overline{D}_{i1}^{3} \\ \overline{D}_{i2}^{3} \end{bmatrix} = -W \cdot J / (W \cdot B) = -(B^T W^2 B)^{-1} \cdot B^T \cdot W^2 \cdot J \hspace{1cm} (i=1 \text{ or } 2)$$  \hspace{1cm} (30)
5.1.2. Evaluation of New Method

In order to assess the accuracy and suitability, the new method has been applied to determine interdiffusion coefficients in the systems where the exact $\bar{D}_{ij}^3$ values are known. The calculated results by this method were also compared to those determined by the DASO and BOME methods. For simplification, the weight factor, $W$, was chosen as unity (i.e. “1”) in this study. The concentration profiles with constant $\bar{D}_{ij}^3$ were generated using the error function given by Fujita and Gosting [90] with the same $\bar{D}_{ij}^3$ and diffusion time $t$ employed by Bouchet utilized [32] for comparison. The compositions of the hypothetical terminal alloys and the details of generating the concentration profiles are listed in Table 3 and Table 4, respectively. Three case studies were carried out to evaluate this new method: (1) basic asymptotic concentration profiles; (2) concentration profiles with uphill diffusion and extrema; and (3) concentration profiles with noise.

Table 3 Composition of terminal alloys used for constituting the concentration profiles.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Element 1 (at. frac.)</th>
<th>Element 2 (at. frac.)</th>
<th>Element 3 (at. frac.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>B</td>
<td>0.35</td>
<td>0.15</td>
<td>0.50</td>
</tr>
<tr>
<td>C</td>
<td>0.60</td>
<td>0.05</td>
<td>0.35</td>
</tr>
<tr>
<td>D</td>
<td>0.25</td>
<td>0.35</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 4 Values of the interdiffusion coefficients and other inputs for constituting the concentration profiles.

<table>
<thead>
<tr>
<th>$\bar{D}_{11}^3$ ($10^{-12}$ m$^2$/s)</th>
<th>$\bar{D}_{12}^3$ ($10^{-12}$ m$^2$/s)</th>
<th>$\bar{D}_{21}^3$ ($10^{-12}$ m$^2$/s)</th>
<th>$\bar{D}_{22}^3$ ($10^{-12}$ m$^2$/s)</th>
<th>$t$ (hours)</th>
<th>$x_0$ (µm)</th>
<th>$x^{-\infty}$ (µm)</th>
<th>$x^{+\infty}$ (µm)</th>
<th>$\Delta x$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.009</td>
<td>0.0005</td>
<td>0.003</td>
<td>25</td>
<td>0</td>
<td>-400</td>
<td>400</td>
<td>1</td>
</tr>
</tbody>
</table>
(1) Basic Asymptotic Concentration Profiles

The basic concentration profile was applied to evaluate this new analysis in detail including effects of the number of points selected in an interval and position and extent of selected intervals. The concentration profile was generated between alloy A and B with the inputs listed in Table 4.

The concentration profile is presented in Figure 10 (a). The interdiffusion flux calculated by Eq. (9) and concentration gradients of component 1 and 2 are presented in Figure 10 (b) and (c). The relation between diffusion flux $\bar{J}_i$ and concentration gradient of component 1 and 2 based on Onsager’s formalism in Eq. (26) are presented in Figure 11. The goal of the calculation process was to find the parameters, $D_{ij}^\bar{3}$, which best describe the curve in Figure 11.
Figure 10 Concentration profile (a), interdiffusion flux (b) and concentration gradients (c) in diffusion couple A-B.
Figure 11 Plots of $\tilde{J}_1$ (a) and $\tilde{J}_2$ (b) with $dC_1/dx$ and $dC_2/dx$ in diffusion couple A-B.

The four diffusion coefficients in the selected intervals were determined by this new analysis using Eq. (28). The DASO method was also used to determine the coefficients using Eqs. (5) and (6). The computation step was 1 µm for both methods. The estimated coefficients from the various methods are reported in Table 5. Because the concentration profiles were symmetric about the Matano plane, only values on the left side of the Matano plane are reported. On either the right or left side of the Matano plane, the three methods work very well with largest relative error of less than 0.5%. However, in the middle region of the symmetric diffusion zone, the interdiffusion coefficients calculated by the DASO method show a large error of over 100%.
Table 5 Interdiffusion coefficients calculated from diffusion couple A-B using the various methods.

<table>
<thead>
<tr>
<th></th>
<th>$\tilde{D}_{11}^3$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{12}^3$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{21}^3$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{22}^3$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Value</td>
<td>0.01</td>
<td>-</td>
<td>0.009</td>
<td>-</td>
<td>0.0005</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>(-400, 0) Left Side of the Matano Plane*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>0.0100</td>
<td>0.0281</td>
<td>0.0090</td>
<td>-0.0401</td>
<td>0.0005</td>
<td>0.2176</td>
<td>0.0300</td>
<td>-0.0033</td>
</tr>
<tr>
<td>DASO</td>
<td>0.0100</td>
<td>0.0267</td>
<td>0.0090</td>
<td>-0.0371</td>
<td>0.0005</td>
<td>0.4576</td>
<td>0.0300</td>
<td>-0.0101</td>
</tr>
<tr>
<td>BOME [32]</td>
<td>0.0100</td>
<td>&lt;10^{-4}</td>
<td>0.0090</td>
<td>&lt;10^{-4}</td>
<td>0.0005</td>
<td>&lt;10^{-4}</td>
<td>0.0300</td>
<td>&lt;10^{-4}</td>
</tr>
<tr>
<td>(-100, 100) Middle Region of the Interdiffusion Zone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>0.0100</td>
<td>0.0305</td>
<td>0.0090</td>
<td>-0.0454</td>
<td>0.0005</td>
<td>0.1617</td>
<td>0.0300</td>
<td>-0.0014</td>
</tr>
<tr>
<td>DASO</td>
<td>-0.0067</td>
<td>-167.229</td>
<td>0.0376</td>
<td>317.4343</td>
<td>0.0007</td>
<td>41.9467</td>
<td>0.0296</td>
<td>-1.1937</td>
</tr>
<tr>
<td>BOME</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Because the profiles are symmetric about the Matano plane, only values on the left side of the Matano plane are reported
The influence of the number of points selected in an interval and the position and extent of the selected interval on the accuracy of the new analysis is studied systematically using the above basic concentration profiles. In a fixed interval (-100, 100), a number of points, ranging from 3 to 201, were selected to calculate the interdiffusion coefficient by varying the step length from 1 to 100 µm. As indicated in Table 6 and Figure 12, the influence of the number of points is small. The largest variation in the relative error of the interdiffusion coefficients is less than 0.05%.

Figure 12 Relative error of the interdiffusion coefficient (a) $\tilde{D}_{11}^3$, (b) $\tilde{D}_{12}^3$, (c) $\tilde{D}_{21}^3$, (d) $\tilde{D}_{22}^3$ calculated in a fixed interval (-100, 100) depends on the number of points selected from diffusion couple A-B.
Table 6 Effect of number of points selected in a fixed interval (-100, 100) on the interdiffusion coefficients from diffusion couple A-B.

<table>
<thead>
<tr>
<th>Step (µm) / Number of Selected Points</th>
<th>( \tilde{D}_{11}^3 ) (10^{-12} m²/s)</th>
<th>Relative Error (%)</th>
<th>( \tilde{D}_{12}^3 ) (10^{-12} m²/s)</th>
<th>Relative Error (%)</th>
<th>( \tilde{D}_{21}^3 ) (10^{-12} m²/s)</th>
<th>Relative Error (%)</th>
<th>( \tilde{D}_{22}^3 ) (10^{-12} m²/s)</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Value</td>
<td>0.01</td>
<td>-</td>
<td>0.009</td>
<td>-</td>
<td>0.0005</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>100/3</td>
<td>0.0100</td>
<td>0.0272</td>
<td>0.0090</td>
<td>-0.0351</td>
<td>0.0005</td>
<td>0.2092</td>
<td>0.0300</td>
<td>-0.0041</td>
</tr>
<tr>
<td>50/5</td>
<td>0.0100</td>
<td>0.0291</td>
<td>0.0090</td>
<td>-0.0422</td>
<td>0.0005</td>
<td>0.1873</td>
<td>0.0300</td>
<td>-0.0021</td>
</tr>
<tr>
<td>25/9</td>
<td>0.0100</td>
<td>0.0302</td>
<td>0.0090</td>
<td>-0.0431</td>
<td>0.0005</td>
<td>0.1761</td>
<td>0.0300</td>
<td>-0.0022</td>
</tr>
<tr>
<td>10/21</td>
<td>0.0100</td>
<td>0.0303</td>
<td>0.0090</td>
<td>-0.0453</td>
<td>0.0005</td>
<td>0.1674</td>
<td>0.0300</td>
<td>-0.0023</td>
</tr>
<tr>
<td>5/41</td>
<td>0.0100</td>
<td>0.0302</td>
<td>0.0090</td>
<td>-0.0454</td>
<td>0.0005</td>
<td>0.1642</td>
<td>0.0300</td>
<td>-0.0024</td>
</tr>
<tr>
<td>3/67</td>
<td>0.0100</td>
<td>0.0311</td>
<td>0.0090</td>
<td>-0.0450</td>
<td>0.0005</td>
<td>0.1623</td>
<td>0.0300</td>
<td>-0.0013</td>
</tr>
<tr>
<td>1/201</td>
<td>0.0100</td>
<td>0.0314</td>
<td>0.0090</td>
<td>-0.0454</td>
<td>0.0005</td>
<td>0.1624</td>
<td>0.0300</td>
<td>-0.0012</td>
</tr>
</tbody>
</table>
The effects of position and extent of the selected interval are reported in Table 7 and Table 8 and are presented in Figure 13 and Figure 14, respectively. When the influence of position was studied the extent of the interval was held constant at 100 µm, and while the effect of extent was investigated the center of the interval was fixed at the Matano plane $x_0$. The interdiffusion coefficients determined using the new method developed in this study were accurate and stable. The relative errors were found to be smaller than 0.7% when the center position and extent of the selected intervals varied between -120 to 0 µm and between 20 to 240 µm, respectively. The relative error of $\tilde{D}_{11}^3$ and $\tilde{D}_{12}^3$ increased while $\tilde{D}_{21}^3$ and $\tilde{D}_{22}^3$ decreased when the center of the selected interval shifted from -120 to 0 µm. When the extent of the interval increased from 20 to 240 µm, the relative error of $\tilde{D}_{11}^3$ and $\tilde{D}_{12}^3$ decreased continuously. However, the relative error of $\tilde{D}_{21}^3$ increased. It should be noted that the relative error of $\tilde{D}_{22}^3$ is smaller than 0.01%.
Table 7 Effect of the position of the selected intervals on the interdiffusion coefficients in a fixed interval extent of 100µm from diffusion couple A-B.

<table>
<thead>
<tr>
<th>Center Position of Selected Intervals (µm)</th>
<th>$\tilde{D}_{11}$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{12}$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{21}$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{22}$ $(10^{-12} \text{ m}^2/\text{s})$</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Value</td>
<td>0.01</td>
<td>-</td>
<td>0.009</td>
<td>-</td>
<td>0.0005</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>-120</td>
<td>0.0100</td>
<td>0.0094</td>
<td>0.0090</td>
<td>-0.0201</td>
<td>0.0005</td>
<td>0.6594</td>
<td>0.0300</td>
<td>-0.0098</td>
</tr>
<tr>
<td>-100</td>
<td>0.0100</td>
<td>0.0167</td>
<td>0.0090</td>
<td>-0.0266</td>
<td>0.0005</td>
<td>0.3833</td>
<td>0.0300</td>
<td>-0.0060</td>
</tr>
<tr>
<td>-80</td>
<td>0.0100</td>
<td>0.0235</td>
<td>0.0090</td>
<td>-0.0344</td>
<td>0.0005</td>
<td>0.2506</td>
<td>0.0300</td>
<td>-0.0036</td>
</tr>
<tr>
<td>-60</td>
<td>0.0100</td>
<td>0.0286</td>
<td>0.0090</td>
<td>-0.0420</td>
<td>0.0005</td>
<td>0.1825</td>
<td>0.0300</td>
<td>-0.0020</td>
</tr>
<tr>
<td>-40</td>
<td>0.0100</td>
<td>0.0321</td>
<td>0.0090</td>
<td>-0.0486</td>
<td>0.0005</td>
<td>0.1456</td>
<td>0.0300</td>
<td>-0.0009</td>
</tr>
<tr>
<td>-20</td>
<td>0.0100</td>
<td>0.0347</td>
<td>0.0090</td>
<td>-0.0550</td>
<td>0.0005</td>
<td>0.1222</td>
<td>0.0300</td>
<td>-0.0001</td>
</tr>
<tr>
<td>0</td>
<td>0.0100</td>
<td>0.0375</td>
<td>0.0090</td>
<td>-0.0617</td>
<td>0.0005</td>
<td>0.1039</td>
<td>0.0300</td>
<td>0.0006</td>
</tr>
</tbody>
</table>
Table 8 Effect of the extent of the selected interval on the interdiffusion coefficients with the Matano plane as the interval center from diffusion couple A-B.

<table>
<thead>
<tr>
<th>Extent of Selected Intervals (µm)</th>
<th>$\tilde{D}_{11}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{12}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{21}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{22}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Value</td>
<td>0.01</td>
<td>-</td>
<td>0.009</td>
<td>-</td>
<td>0.0005</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>0.0100</td>
<td>0.0417</td>
<td>0.0090</td>
<td>-0.0722</td>
<td>0.0005</td>
<td>0.0824</td>
<td>0.0300</td>
<td>0.0014</td>
</tr>
<tr>
<td>40</td>
<td>0.0100</td>
<td>0.0411</td>
<td>0.0090</td>
<td>-0.0706</td>
<td>0.0005</td>
<td>0.0851</td>
<td>0.0300</td>
<td>0.0013</td>
</tr>
<tr>
<td>60</td>
<td>0.0100</td>
<td>0.0401</td>
<td>0.0090</td>
<td>-0.0683</td>
<td>0.0005</td>
<td>0.0897</td>
<td>0.0300</td>
<td>0.0011</td>
</tr>
<tr>
<td>80</td>
<td>0.0100</td>
<td>0.0389</td>
<td>0.0090</td>
<td>-0.0652</td>
<td>0.0005</td>
<td>0.0959</td>
<td>0.0300</td>
<td>0.0009</td>
</tr>
<tr>
<td>100</td>
<td>0.0100</td>
<td>0.0375</td>
<td>0.0090</td>
<td>-0.0617</td>
<td>0.0005</td>
<td>0.1039</td>
<td>0.0300</td>
<td>0.0006</td>
</tr>
<tr>
<td>120</td>
<td>0.0100</td>
<td>0.0360</td>
<td>0.0090</td>
<td>-0.0580</td>
<td>0.0005</td>
<td>0.1135</td>
<td>0.0300</td>
<td>0.0002</td>
</tr>
<tr>
<td>160</td>
<td>0.0100</td>
<td>0.0329</td>
<td>0.0090</td>
<td>-0.0509</td>
<td>0.0005</td>
<td>0.1365</td>
<td>0.0300</td>
<td>-0.0006</td>
</tr>
<tr>
<td>200</td>
<td>0.0100</td>
<td>0.0305</td>
<td>0.0090</td>
<td>-0.0454</td>
<td>0.0005</td>
<td>0.1617</td>
<td>0.0300</td>
<td>-0.0014</td>
</tr>
<tr>
<td>240</td>
<td>0.0100</td>
<td>0.0290</td>
<td>0.0090</td>
<td>-0.0421</td>
<td>0.0005</td>
<td>0.1845</td>
<td>0.0300</td>
<td>-0.0022</td>
</tr>
</tbody>
</table>
Figure 13 Relative error of the interdiffusion coefficient (a) $\tilde{D}_{11}^1$, (b) $\tilde{D}_{12}^3$, (c) $\tilde{D}_{21}^3$, (d) $\tilde{D}_{22}^3$ calculated in a fixed interval extent of 100 µm depends on the position of selected intervals from diffusion couple A-B.
Figure 14 Relative error of the interdiffusion coefficient (a) $\widetilde{D}_{11}$, (b) $\widetilde{D}_{12}$, (c) $\widetilde{D}_{21}$, (d) $\widetilde{D}_{22}$, calculated with the Matano plane as the interval center depends on extent of selected intervals from diffusion couple A-B.

(2) Concentration Profiles with Uphill Diffusion and Extrema

A concentration profile was generated between alloy C and D whose compositions are reported in Table 3 with the inputs listed in Table 4. This concentration profile was applied to evaluate the suitability of the new method for uphill diffusion. The concentration profile, interdiffusion flux and concentration gradient are presented in Figure 15. Component 1 and 3 show extrema in their concentration profiles. The results calculated using the new analysis method along with the DASO and BOME methods are reported in Table 9. Each of the three
methods works well on either side of the Matano plane, however, the interdiffusion coefficients calculated by the DASO method show a large error of over 100% in the middle region of the diffusion zone. The largest relative error by the new method is -0.1568% which occurs in $\tilde{D}_2^1$ in the interval (-400, 0). Therefore, it can be concluded that the new analysis works well in a system with extrema and uphill diffusion.
Figure 15 Concentration profile (a), interdiffusion flux (b) and concentration gradients (c) in diffusion couple C-D.
Table 9 Interdiffusion coefficients calculated from diffusion couple C-D with the various methods.

<table>
<thead>
<tr>
<th></th>
<th>$\tilde{D}_{11}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{12}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{21}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{22}^3$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Value</td>
<td>0.01</td>
<td>-</td>
<td>0.009</td>
<td>-</td>
<td>0.0005</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>New (-400, 0)</td>
<td>0.0100</td>
<td>0.0212</td>
<td>0.0090</td>
<td>0.0250</td>
<td>0.0005</td>
<td>-0.1568</td>
<td>0.0300</td>
<td>-0.0010</td>
</tr>
<tr>
<td>DASO (-400, 0)</td>
<td>0.0100</td>
<td>0.0104</td>
<td>0.0090</td>
<td>0.0073</td>
<td>0.0005</td>
<td>-0.3100</td>
<td>0.0300</td>
<td>-0.0047</td>
</tr>
<tr>
<td>BOME [32] (-100, 100)</td>
<td>0.0100</td>
<td>&lt;10^{-4}</td>
<td>0.0090</td>
<td>&lt;10^{-4}</td>
<td>0.0005</td>
<td>&lt;10^{-4}</td>
<td>0.0300</td>
<td>&lt;10^{-4}</td>
</tr>
</tbody>
</table>

* Because the profiles are symmetric about the Matano plane, only values on the left side of the Matano plane are reported.
(3) Concentration Profiles with Noise

In order to test the calculations on profiles which are closer to the experimental situation, Gaussian noise with a standard deviation of 0.65% (typical of electron microprobe experimental data [32]) was added to the generated profiles from diffusion couple A-B in case 1. The concentration profiles with noise were then smoothed using the Origin™ nonlinear curve fitting tool. The concentration profiles with noise and the profiles after smoothing are presented in Figure 16. It was found that the largest relative error between the smoothed and the original A-B concentration profiles was less than 0.5%. The calculation results based on the smoothed concentration profiles are reported in Table 10. For the profiles with noise, the BOME method shows the best performance. The DASO and the new methods are similar with the largest relative error less than 10%. Particular attention has to be paid to the smoothing procedure in order to get stable and accurate results. Improper smoothing techniques can cause large error of over 100% in some cases.

![Figure 16 Concentration profile with noise added (standard deviation: 0.65%) in diffusion couple A-B.](image)
Table 10 Interdiffusion coefficients calculated with the various methods from diffusion couple A-B with noise added (standard deviation: 0.65%).

<table>
<thead>
<tr>
<th></th>
<th>$\tilde{D}_{11}$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{12}$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{21}$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
<th>$\tilde{D}_{22}$ (10^{-12} m^2/s)</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Value</td>
<td>0.01</td>
<td>-</td>
<td>0.009</td>
<td>-</td>
<td>0.0005</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>New</td>
<td>0.0094</td>
<td>-5.7524</td>
<td>0.0097</td>
<td>7.4939</td>
<td>0.0005</td>
<td>-1.8519</td>
<td>0.0300</td>
<td>0.0330</td>
</tr>
<tr>
<td>DASO</td>
<td>0.0096</td>
<td>-4.0678</td>
<td>0.0097</td>
<td>8.1911</td>
<td>0.0005</td>
<td>-0.7263</td>
<td>0.0300</td>
<td>-0.0007</td>
</tr>
<tr>
<td>BOME [32]</td>
<td>0.0100</td>
<td>&lt;10^{-8}</td>
<td>0.0090</td>
<td>&lt;10^{-8}</td>
<td>0.0005</td>
<td>&lt;10^{-8}</td>
<td>0.0300</td>
<td>&lt;10^{-8}</td>
</tr>
<tr>
<td>(-400, 0) Left Side of the Matano Plane*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>0.0094</td>
<td>-6.4983</td>
<td>0.0098</td>
<td>8.7877</td>
<td>0.0005</td>
<td>-4.1966</td>
<td>0.0300</td>
<td>0.1476</td>
</tr>
<tr>
<td>DASO</td>
<td>-0.0163</td>
<td>-263.443</td>
<td>0.0543</td>
<td>503.3954</td>
<td>0.0000</td>
<td>-100.000</td>
<td>0.0309</td>
<td>2.8479</td>
</tr>
<tr>
<td>BOME</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(-100, 100) Middle Region of the Interdiffusion Zone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Because the profiles are symmetric about the Matano plane, only values on the left side of the Matano plane is reported.
5.2 Diffusion Behavior of U-Mo Alloys

To study the interdiffusion behavior in U-Mo alloys, diffusion couples were assembled between pure U and Mo and annealed at 1000, 900, 800, 700 and 650 °C for various times as shown in Table 2.

5.2.1 Interdiffusion Microstructure and Concentration Profiles

Backscattered electron (BSE) micrographs and EPMA concentration profiles from the U vs. Mo couples annealed at 1000 and 700°C are presented in Figure 17 and Figure 18, respectively. Although there were no markers intentionally placed in the diffusion couples, marker planes were clearly observed on the cross-section of the diffusion couples due to the rapid formation of native, most likely uranium oxides. In Figure 17 and Figure 18, X_K and X_I represent the position of the marker plane and the interface between U and Mo, respectively. The marker plane in all diffusion couples shifted toward the U side suggesting that U intrinsically diffuses faster than Mo. The compositions that correspond to the marker plane were very close to those reported by Adda [67].

At the lower annealing temperatures, 650 and 700°C, two allotropic phases of U (α and γ at 650°C, β and γ at 700°C) were observed in the diffusion couples. The interface between β-U and γ-U at 700°C is marked as X_β/γ in Figure 18 (a). The interface between the two U phases is not easily distinguished because the composition difference between the two phases is less than 10 at.% Mo. Because the solubility of Mo in α-U and β-U is less than 1 at.% [35], analysis of the concentration profiles in α-U or β-U could not be carried out due to experimental uncertainty. The minimum concentration of Mo in the γ-U layer (i.e., solubility limit) was measured to be 8.4
and 6.5 at.% at 650 and 700°C, respectively. This corresponds well to the Mo-U equilibrium phase diagram shown in Figure 5 [25].

Figure 17 BSE micrograph (a) and EPMA Mo concentration profile (b) from U vs. Mo diffusion couple annealed at 1000°C for 24 hours.
5.2.2 Interdiffusion Coefficients

Based on the fitted Mo concentration profiles, interdiffusion coefficients, $\tilde{D}$, were calculated in the temperature range of 650 to 1000°C and in the Mo composition range of 2 to 26 at.% using Eq. (7). The values of $\tilde{D}$ are reported in Table 11 and are presented in Figure 19. At
650 and 700°C, $\tilde{D}$ at compositions below the lowest solubility of Mo in $\gamma$-U (8.4 at.% and 6.5 at.\% Mo, respectively) are not reported. The experimentally measured values of $\tilde{D}$ for U-Mo in the temperature range from 850 to 1050°C reported by Adda [67] are also presented in Figure 19 for comparison. The $\tilde{D}$ values determined in this study are similar to Adda’s results [67]. At each temperature examined, $\tilde{D}$ decreases with increasing Mo concentration. However, there is a difference in the results; the $\tilde{D}$ reported by Adda shows a convex variation between $N_{Mo}=0.05$ and 0.1. Furthermore, the measured values of $\tilde{D}$ in this study tend to be slightly lower than those reported by Adda [67] at high Mo concentrations.

Table 11 Interdiffusion coefficients, activation energy, and pre-exponential factor for $\gamma$(bcc) U-Mo alloy as functions of composition and temperature.

<table>
<thead>
<tr>
<th>$N_{Mo}$ (at. frac.)</th>
<th>1000 °C (x 10^{-13})</th>
<th>900 °C (x 10^{-14})</th>
<th>800 °C (x 10^{-15})</th>
<th>700 °C (x 10^{-16})</th>
<th>650 °C (x 10^{-16})</th>
<th>$\tilde{D}_0$ (m^2/s) (x 10^{-6})</th>
<th>$\tilde{Q}$ (kJ)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>10.57</td>
<td>23.46</td>
<td>77.54</td>
<td>-</td>
<td>-</td>
<td>1.05</td>
<td>147</td>
</tr>
<tr>
<td>0.04</td>
<td>6.80</td>
<td>15.41</td>
<td>41.90</td>
<td>-</td>
<td>-</td>
<td>1.84</td>
<td>157</td>
</tr>
<tr>
<td>0.06</td>
<td>4.16</td>
<td>9.41</td>
<td>22.78</td>
<td>-</td>
<td>-</td>
<td>2.18</td>
<td>164</td>
</tr>
<tr>
<td>0.08</td>
<td>2.61</td>
<td>5.87</td>
<td>13.28</td>
<td>19.28</td>
<td>-</td>
<td>2.08</td>
<td>168</td>
</tr>
<tr>
<td>0.10</td>
<td>1.73</td>
<td>3.83</td>
<td>8.15</td>
<td>12.96</td>
<td>6.64</td>
<td>2.08</td>
<td>173</td>
</tr>
<tr>
<td>0.12</td>
<td>1.18</td>
<td>2.57</td>
<td>5.34</td>
<td>8.54</td>
<td>4.60</td>
<td>1.74</td>
<td>175</td>
</tr>
<tr>
<td>0.14</td>
<td>0.82</td>
<td>1.82</td>
<td>3.64</td>
<td>5.48</td>
<td>3.13</td>
<td>1.37</td>
<td>176</td>
</tr>
<tr>
<td>0.16</td>
<td>0.60</td>
<td>1.30</td>
<td>2.55</td>
<td>3.57</td>
<td>2.09</td>
<td>1.32</td>
<td>179</td>
</tr>
<tr>
<td>0.18</td>
<td>0.45</td>
<td>0.96</td>
<td>1.84</td>
<td>2.30</td>
<td>1.43</td>
<td>1.16</td>
<td>181</td>
</tr>
<tr>
<td>0.20</td>
<td>0.34</td>
<td>0.71</td>
<td>1.39</td>
<td>1.48</td>
<td>1.01</td>
<td>0.85</td>
<td>181</td>
</tr>
<tr>
<td>0.22</td>
<td>0.26</td>
<td>0.54</td>
<td>1.04</td>
<td>0.98</td>
<td>0.68</td>
<td>0.77</td>
<td>182</td>
</tr>
<tr>
<td>0.24</td>
<td>0.21</td>
<td>0.41</td>
<td>0.81</td>
<td>0.71</td>
<td>0.52</td>
<td>0.65</td>
<td>183</td>
</tr>
<tr>
<td>0.26</td>
<td>0.16</td>
<td>0.33</td>
<td>0.61</td>
<td>0.50</td>
<td>0.35</td>
<td>0.57</td>
<td>184</td>
</tr>
</tbody>
</table>

* $\tilde{D}_0$ and $\tilde{Q}$ were calculated only for the $\gamma$(bcc) U-Mo solid solution phase in the temperature range of 800 to 1000°C.
Figure 19 Interdiffusion coefficients in $\gamma$(bcc) U-Mo alloy measured in this study (lines) and determined by Adda [67] (spots).

Figure 20 shows the temperature dependence of $\tilde{D}$ at $N_{Mo} = 0.12$, $0.18$ and $0.24$. The $\tilde{D}$ at a given composition obeys the Arrhenius relation in the temperature range of 700 to 1000°C. However, there is a small positive deviation from the Arrhenius relation at 650°C. This deviation could be caused by the fact that grain boundary diffusion plays a more significant role at lower temperatures. Another explanation could be uncertainty in the concentration profiles due to a relatively short diffusion zone (about 30µm in total).

The pre-exponential factor, $\tilde{D}_0$, and activation energy, $\tilde{Q}$, of the interdiffusion coefficient in the temperature range of 800 to 1000°C at selected Mo compositions were determined according to the Arrhenius relation. These values are reported in Table 11. The composition-dependence of $\tilde{Q}$ is presented in Figure 21, along with those reported by Adda [67]. In this study, $\tilde{D}$ monotonically decreased and, correspondingly, $\tilde{Q}$ increased with an
increase in Mo concentration. Adda [67] has previously reported that as $N_{Mo}$ increases, $\tilde{D}$ increases initially and then decreases as shown in Figure 19, while $\tilde{Q}$ increases to a maximum at $N_{Mo} = 0.1$ and then decreases as presented in Figure 21.

![Figure 20 Temperature dependence of interdiffusion coefficients in $\gamma$(bcc) U-Mo alloy at selected Mo concentrations of $N_{Mo} = 0.12, 0.18, 0.24$.](image)

![Figure 21 Composition dependent activation energy of interdiffusion coefficients in $\gamma$(bcc) U-Mo alloy determined in this study (solid circles) and those reported by Adda [67] (hollow circles).](image)
5.2.3 Intrinsic Diffusion Coefficients

In a diffusion process, each component may diffuse intrinsically at a different rate resulting in the movement of the marker plane (also called the Kirkendall plane), which is the original interface of the diffusion couple. Based on the position of the marker planes, the intrinsic diffusion coefficients of U and Mo at the marker composition, $D_U$ and $D_{Mo}$, were calculated using Eq. (13). These values are reported in Table 12. For the diffusion couples wherein only γ-U existed (800, 900 and 1000°C), U intrinsically diffused about 5-7 times faster than Mo. The composition $N_{Mo}$ at the marker plane varied from 0.08 to 0.06 when the annealing temperature decreased from 1000 to 800°C. At the lower temperatures, when two phases of U existed in the diffusion couples (α and γ at 650 °C, β and γ at 700 °C), the ratios of $D_U/D_{Mo}$ increased to about 10 and the composition near the marker plane also changed along with the solubility range of Mo in the γ-U phase.

Table 12 Intrinsic diffusion coefficients for γ(bcc) U-Mo alloy at the marker composition.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$N_{Mo}$ (at. frac.)</th>
<th>$v_k (\times 10^{11} \text{ m/s})$</th>
<th>$\bar{D} (\text{m}^2/\text{s})$</th>
<th>$D_{Mo} (\text{m}^2/\text{s})$</th>
<th>$D_U (\text{m}^2/\text{s})$</th>
<th>$D_U/D_{Mo}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C</td>
<td>0.08</td>
<td>-40.51</td>
<td>2.61 x 10^{-13}</td>
<td>1.97 x 10^{-13}</td>
<td>9.93 x 10^{-13}</td>
<td>5.04</td>
</tr>
<tr>
<td>900°C</td>
<td>0.07</td>
<td>-13.02</td>
<td>7.68 x 10^{-14}</td>
<td>5.46 x 10^{-14}</td>
<td>3.79 x 10^{-15}</td>
<td>6.94</td>
</tr>
<tr>
<td>800°C</td>
<td>0.06</td>
<td>-3.51</td>
<td>2.28 x 10^{-14}</td>
<td>1.67 x 10^{-14}</td>
<td>1.18 x 10^{-15}</td>
<td>7.07</td>
</tr>
<tr>
<td>700°C</td>
<td>0.09</td>
<td>-1.00</td>
<td>1.48 x 10^{-15}</td>
<td>7.60 x 10^{-16}</td>
<td>8.42 x 10^{-15}</td>
<td>11.08</td>
</tr>
<tr>
<td>650°C</td>
<td>0.11</td>
<td>-0.58</td>
<td>5.23 x 10^{-16}</td>
<td>2.59 x 10^{-16}</td>
<td>2.60 x 10^{-15}</td>
<td>10.04</td>
</tr>
</tbody>
</table>

5.2.4 Activity and Thermodynamic Factor of U-Mo Alloys

In this work, the activity of U and Mo, $a_U$ and $a_{Mo}$, and the thermodynamic factor, $\phi$, were calculated for the relevant composition range using the regular, subregular, and ideal
solution models. Although the thermodynamics of U-Mo alloys have been studied extensively by other authors [35-39], there are discrepancies in some of the previously reported results. In Berche’s work [35], the $a_U$ calculated using the CALPHAD method was compared to the values obtained from the equations of Vamberskii [38], which were derived from emf measurements. There was an inexplicable disparity between the values determined by the two methods as shown in Figure 22. The molar excess Gibbs free energy for the formation of the U-Mo alloy, $\Delta G^E$, which relates to $a_U$ or $a_{Mo}$, was given by Parida [39] in polynomial form of U composition for the $\alpha$, $\beta$, $\gamma$ and liquid phases based on the data reported by Brewer [36]. Based on these $\Delta G^E$ expressions, $a_U$ was calculated using the regular solution and subregular solution models [102] and the values were compared to those obtained from the ideal solution model, the CALPHAD method [35] and Vamberskii’s work [38]. Details of the thermodynamic formulation are presented in Appendix A.

The $a_U$ values calculated by the above methods show variation as observed in Figure 22. The values from both the regular and subregular solution models show positive deviation from the ideal solution. However, the deviation of the subregular solution model is much smaller than that of the regular solution model. Typically the subregular solution model, having a greater number of parameters, is more accurate than the regular solution model. The $a_U$ calculated by CALPHAD [35] exhibits only a slight negative deviation from the ideal solution. The $a_U$ deduced by Vamberskii [38] shows a large negative deviation from the ideal solution and a concave shape as presented in Figure 22 (a) and (b).
Figure 22 Thermodynamic activities of U determined using various thermodynamic models at 800°C (a), 900°C (b), and 1000°C (c).
The deviation from the ideal solution is negligible in the subregular solution model and CALPHAD method when $N_{Mo}$ is less than 0.1. Therefore, the dilute U-Mo alloy can be considered an ideal solution. This may be true because there was no strong interaction between U and Mo reported in literature for the dilute solution. Since the $N_{Mo}$ values at the marker planes are below 0.1 and the $a_U$ determined by the ideal, subregular, and CALPHAD models are nearly identical below this $N_{Mo}$ value, the $\Phi$ calculated using the three approaches are also identical and estimated as unity. The $a_U$ values obtained by the regular solution model and Vamberskii’s method were also employed to calculate $\Phi$ using Eq. (15) as reported in Table 13.

Table 13 Thermodynamic factor for $\gamma$(bcc) U-Mo alloy at 800, 900, and 1000°C.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Temperature (°C) and Mo Composition (at. frac.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800 (N_{Mo} = 0.06)</td>
</tr>
<tr>
<td>Ideal solution model or CALPHAD Method or Subregular solution model</td>
<td>1.00</td>
</tr>
<tr>
<td>Regular solution model</td>
<td>0.85</td>
</tr>
<tr>
<td>Vamberskii</td>
<td>4.35</td>
</tr>
</tbody>
</table>

5.2.5 Tracer Diffusivity, Atomic Mobility and Vacancy Wind Effect of U and Mo

The thermodynamic factors determined by the ideal solution model (equal to the CALPHAD method and subregular solution model), regular solution model, and Vamberskii’s method were applied to estimate the tracer diffusion coefficients, $D_U^I$ and $D_{Mo}^I$, and vacancy wind parameters, $\Psi_U$ and $\Psi_{Mo}$, at the marker composition using Eqs. (14) and (16). The atomic mobilities, $\beta_U$ and $\beta_{Mo}$, were also determined based on the values of $D_U^I$ and $D_{Mo}^I$ using Eq. (17). All of the calculated values are listed in Table 14.
Table 14 Tracer diffusivity, atomic mobilities and vacancy wind parameters of U and Mo for $\gamma$(bcc) U-Mo alloy at 800, 900, and 1000°C.

<table>
<thead>
<tr>
<th></th>
<th>Ideal solution model or CALPHAD Method or Subregular solution model</th>
<th>Regular solution model</th>
<th>Vamberskii</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800°C ($N_{Mo} = 0.06$)</td>
<td>900°C ($N_{Mo} = 0.07$)</td>
<td>1000°C ($N_{Mo} = 0.08$)</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$D_{Mo}^{*} \times 10^{-14}$ m$^2$/s</td>
<td>1.68</td>
<td>5.53</td>
<td>20.38</td>
</tr>
<tr>
<td>$\beta_{Mo} \times 10^6$ m/N*s</td>
<td>1.13</td>
<td>3.42</td>
<td>11.60</td>
</tr>
<tr>
<td>$\Psi_{Mo}$</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>$D_{U}^{*} \times 10^{-14}$ m$^2$/s</td>
<td>8.95</td>
<td>28.91</td>
<td>78.85</td>
</tr>
<tr>
<td>$\beta_{U} \times 10^6$ m/N*s</td>
<td>6.05</td>
<td>17.86</td>
<td>44.88</td>
</tr>
<tr>
<td>$\Psi_{U}$</td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>0.845</td>
<td>0.840</td>
<td>0.835</td>
</tr>
<tr>
<td>$D_{Mo}^{*} \times 10^{-14}$ m$^2$/s</td>
<td>2.01</td>
<td>6.65</td>
<td>24.20</td>
</tr>
<tr>
<td>$\beta_{Mo} \times 10^6$ m/N*s</td>
<td>1.36</td>
<td>4.11</td>
<td>13.78</td>
</tr>
<tr>
<td>$\Psi_{Mo}$</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>$D_{U}^{*} \times 10^{-14}$ m$^2$/s</td>
<td>10.72</td>
<td>34.72</td>
<td>93.50</td>
</tr>
<tr>
<td>$\beta_{U} \times 10^6$ m/N*s</td>
<td>7.24</td>
<td>21.45</td>
<td>53.22</td>
</tr>
<tr>
<td>$\Psi_{U}$</td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>4.35</td>
<td>3.62</td>
<td>-</td>
</tr>
<tr>
<td>$D_{Mo}^{*} \times 10^{-14}$ m$^2$/s</td>
<td>0.39</td>
<td>1.54</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_{Mo} \times 10^6$ m/N*s</td>
<td>0.26</td>
<td>0.95</td>
<td>-</td>
</tr>
<tr>
<td>$\Psi_{Mo}$</td>
<td>0.98</td>
<td>0.98</td>
<td>-</td>
</tr>
<tr>
<td>$D_{U}^{*} \times 10^{-14}$ m$^2$/s</td>
<td>2.08</td>
<td>8.06</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_{U} \times 10^6$ m/N*s</td>
<td>1.41</td>
<td>4.98</td>
<td>-</td>
</tr>
<tr>
<td>$\Psi_{U}$</td>
<td>1.30</td>
<td>1.30</td>
<td>-</td>
</tr>
</tbody>
</table>
The calculated tracer diffusion coefficients, atomic mobilities and vacancy wind parameters using the ideal solution model are close to those using the regular solution model. In the temperature range of 800 to 1000°C, both $D_U^*$ and $\beta_U$ were about 5 times higher than $D_{Mo}^*$ and $\beta_{Mo}$. When the temperature was increased from 800 to 1000°C, $D_U^*$ and $D_{Mo}^*$ increased by about 9 and 12 times, respectively. The estimated tracer diffusion coefficients and atomic mobilities of U and Mo from Vamberskii’s thermodynamics report are smaller than those determined by the ideal and regular solution models. The vacancy wind parameters of U and Mo remained almost constant regardless of which models or methods were applied to derive the thermodynamic factor in the temperature range of 800 to 1000°C. The $\Psi_U$ and $\Psi_{Mo}$ values reported in Table 14 indicate that the vacancy flux enhances the intrinsic diffusion of U by about 30% and suppresses the intrinsic diffusion of Mo by about 2%.

The $D_U^*$ values estimated by the various methods in this study, along with the experimentally measured values by Adda [68, 71], are presented in Figure 23. Figure 23 clearly illustrates that the $D_U^*$ values calculated based on the ideal (equal to CALPHAD method and subregular solution model) and regular solution models agree with Adda’s experimental results better than those computed using Vamberskii’s thermodynamic data. The magnitude of $D_U^*$ calculated using the regular solution model was approximately 15% higher than that using the ideal solution.
Figure 23 Temperature dependence of U tracer diffusivity in γ(bcc) U-Mo alloy calculated in this study at the marker compositions using the various thermodynamic models (hollow spots) and experimentally determined in pure U [68] and U-10at.%Mo alloy [71] by Adda (solid spots).

5.3 Diffusion Behavior Between U-Mo Alloys and Barrier/Non-Reacting Matrix Materials

5.3.1 U-10wt.%Mo vs. Mo Diffusion Couples

Solid-to-solid U-10wt.%Mo vs. Mo diffusion couples were assembled and annealed at 600, 700, 800, 900 and 1000°C for various times. The composition of the U-Mo alloy was measured by EPMA at 10 random locations. The average value and standard deviation were calculated and are reported in Table 15. The average composition (20.91 at.% Mo) was measured to be very close to the theoretical composition of U-10wt.%Mo fuel, which is 21.61 at.% Mo. The standard deviation of the 10 measured points was 0.15 at%.
Table 15 Composition of as-fabricated U-10wt.%Mo alloy.

<table>
<thead>
<tr>
<th>Point Number</th>
<th>Composition of Mo (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.82</td>
</tr>
<tr>
<td>2</td>
<td>21.22</td>
</tr>
<tr>
<td>3</td>
<td>20.89</td>
</tr>
<tr>
<td>4</td>
<td>20.71</td>
</tr>
<tr>
<td>5</td>
<td>20.74</td>
</tr>
<tr>
<td>6</td>
<td>20.85</td>
</tr>
<tr>
<td>7</td>
<td>21.01</td>
</tr>
<tr>
<td>8</td>
<td>20.85</td>
</tr>
<tr>
<td>9</td>
<td>20.96</td>
</tr>
<tr>
<td>10</td>
<td>21.03</td>
</tr>
<tr>
<td>Average Composition</td>
<td>20.91</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.15</td>
</tr>
</tbody>
</table>

A typical backscattered electron (BSE) micrograph obtained from one of the diffusion couples is presented in Figure 24 and the EPMA concentration profiles from the U-Mo vs. Mo couples annealed at 1000, 900 and 800°C are presented in Figure 25. Since the interdiffusion zone at 700°C was relatively small (~20µm) and negligible interdiffusion was observed at 600°C, their concentration profiles are not presented here and quantitative analyses for interdiffusion were not carried out. However, in each diffusion couple, good bonding between the U-Mo alloy and Mo was observed. In Figure 24 and Figure 25, $X_0$ and $X_I$ represent the position of the Matano plane and the interface between $\gamma$(bcc) U-Mo solid solution and Mo, respectively. The thickness of the interdiffusion zone (IZ) in this study is defined as the distance between pure Mo and the point where the Mo composition reaches 22 at.%, which is 1 at.% higher than the initial composition of the U-Mo alloy at the terminal end. The value of 22 at.% Mo was selected to define the interdiffusion zone based on the following reasons. First, the concentration profiles scatter near the U-Mo terminal end due to uncertainties of EPMA, therefore, it is not possible to
find the exact position where the interdiffusion process terminates. Second, less than 1 at.% Mo variation in the U-Mo composition has a small influence on the U-Mo fuel performance. Therefore, the effect of interdiffusion on the fuel performance below 22 at.% Mo could be ignored and it is reasonable to set 22 at.% Mo as the critical point to define the interdiffusion zone. Unfortunately there was no marker plane observed in any of the couples, and therefore, intrinsic diffusion behavior of U and Mo was not explored in this study. The maximum solubility of Mo in $\gamma$(bcc) U-Mo solid solution was observed to be approximately 37 at.%, which agrees well with the Mo-U equilibrium phase diagram shown in Figure 5 [25].

Figure 24 BSE micrograph from U-10wt.%Mo vs. Mo diffusion couple annealed at 900°C for 240 hours.
Figure 25 EPMA Mo concentration profiles from U-10wt.%Mo vs. Mo diffusion couples annealed at 1000°C for 96 hours (a), at 900°C for 240 hours (b) and at 800°C for 480 hours (c).
In this study, the Mo composition within the U-Mo solid solution varied between 21 and 37 at.%, which corresponds to less than a 5% variation in molar volume based on Vegard’s law. Hence, a simple Boltzmann-Matano analysis [91] was applied to determine the composition-dependent interdiffusion coefficients using Eq. (7). Interdiffusion coefficients, \( \tilde{D} \)'s, were calculated for the temperature range of 800 to 1000°C and the Mo concentration range of 22 to 32 at.%. The values of \( \tilde{D} \) are reported in Table 16 and are presented in Figure 26. As previously mentioned, the interdiffusion coefficients at 700 and 600°C were not calculated since the interdiffusion zone was too small to determine accurate concentration gradients. The \( \tilde{D} \) values determined in this study agreed with the previous study presented in section 5.2.2 (i.e., diffusion couples of U vs. Mo) very well as shown in Figure 26.

Table 16 Interdiffusion coefficients, activation energy, and pre-exponential factor for \( \gamma \)(bcc) U-Mo alloy as functions of composition and temperature.

<table>
<thead>
<tr>
<th>( N_{Mo} ) (at. frac.)</th>
<th>( \tilde{D} ) (m²/s)</th>
<th>( \tilde{D}_0 ) (m²/s) (x 10⁻⁶)</th>
<th>( \tilde{Q} ) (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C (x10⁻¹⁴)</td>
<td>900°C (x10⁻¹⁵)</td>
<td>800°C (x10⁻¹⁶)</td>
</tr>
<tr>
<td>0.22</td>
<td>2.87</td>
<td>5.35</td>
<td>9.28</td>
</tr>
<tr>
<td>0.24</td>
<td>2.25</td>
<td>3.71</td>
<td>6.93</td>
</tr>
<tr>
<td>0.26</td>
<td>1.70</td>
<td>2.90</td>
<td>5.36</td>
</tr>
<tr>
<td>0.28</td>
<td>1.40</td>
<td>2.21</td>
<td>4.01</td>
</tr>
<tr>
<td>0.30</td>
<td>1.15</td>
<td>1.83</td>
<td>3.31</td>
</tr>
<tr>
<td>0.32</td>
<td>0.96</td>
<td>1.51</td>
<td>2.78</td>
</tr>
</tbody>
</table>
Figure 26 Interdiffusion coefficients in $\gamma$(bcc) U-Mo alloy as a function of Mo concentration at various temperatures measured from the diffusion couples of U-10wt.%Mo vs. Mo (solid spots) and U vs. Mo (hollow spots).

Because the annealing time in this study was much longer than the previous study and the terminal end composition was a U-Mo alloy instead of pure U, the concentration profiles at high Mo compositions (near the interface) were obtained accurately. Thus, $\tilde{D}$ values in U-Mo alloys at higher Mo concentrations were determined with confidence. The Mo composition range where $\tilde{D}$ has been experimentally determined now extends from 2 to 32 at.%. At each temperature, the value of $\tilde{D}$ decreased with increasing Mo concentration. Typically, in a binary solid solution, if the alloying addition increases the melting point, $\tilde{D}$ tends to decrease with increasing alloy content [103]. Since the addition of Mo increases the solidus and liquidus of $\gamma$-U according to the phase diagram shown in Figure 5, $\tilde{D}$ should decrease with increasing Mo content.
Figure 27 shows the temperature dependence of $\widetilde{D}$ at $N_{\text{Mo}} = 0.22$, 0.26 and 0.30. The $\widetilde{D}$’s at the given composition obey the Arrhenius relation in the temperature range examined in this study. The pre-exponential factor, $\widetilde{D}_0$, and activation energy, $\widetilde{Q}$, of the interdiffusion coefficient at selected Mo compositions were also determined according to the Arrhenius relation and are reported in Table 16. The composition-dependence of $\widetilde{Q}$ is presented in Figure 28 along with those reported from the U vs. Mo diffusion couples. The estimated activation energy of interdiffusion in both studies agrees with each other with the largest difference being less than 7% at a given composition. It is found that $\widetilde{Q}$ increases with increasing Mo concentration, and therefore, the $\widetilde{D}$ values should monotonically decrease with Mo concentration as presented in Figure 26.

![Figure 27 Temperature dependence of interdiffusion coefficients in $\gamma$(bcc) U-Mo alloy at selected Mo concentrations of $N_{\text{Mo}} = 0.22$, 0.26, 0.30.](image-url)
Figure 28 Composition dependence of activation energy of interdiffusion in $\gamma$(bcc) U-Mo alloy for the temperature range of 800 to 1000°C measured from the diffusion couples of U-10wt.%Mo vs. Mo (solid spots) and U vs. Mo (hollow spots).

To compare the interdiffusion behavior of U-Mo vs. Mo and U-Mo vs. Al or Al-Si quantitatively (the growth rates for these two systems are presented in Table 31 in section 6.3), the growth rate of the IZ in U-Mo and Mo system was calculated. The thickness of the IZ is marked in Figure 25. The growth rate, $K$, of the interdiffusion zone is calculated under the assumption of parabolic growth using Eq. (21). The calculated $K$ values for the couples annealed at 800, 900 and 1000°C are reported in Table 17. Figure 29 shows the Arrhenius temperature dependence of the calculated $K$ values. The pre-exponential factor, $K_0$, and activation energy, $Q_K$, of the growth rate were also determined as reported in Table 17. Based on the Arrhenius relation, the growth rates at 700, 600, 500°C were predicted and are listed in Table 17 and are presented in Figure 29.
Table 17 Growth rates of the interdiffusion zone in U-10wt.%Mo vs. Mo diffusion couples.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thickness of IZ (µm)</th>
<th>Annealing Time (hours)</th>
<th>Growth Rate (m²/s)</th>
<th>$\tilde{D}_0$ (m²/s)</th>
<th>$Q_k$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>218</td>
<td>96</td>
<td>6.88x10⁻¹⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>144</td>
<td>240</td>
<td>1.20x10⁻¹⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>81</td>
<td>480</td>
<td>1.90x10⁻¹⁵</td>
<td>1.48x10⁻⁰⁵</td>
<td>203.39</td>
</tr>
<tr>
<td></td>
<td>Predicted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>-</td>
<td>-</td>
<td>1.76x10⁻¹⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>-</td>
<td>9.89x10⁻¹⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>-</td>
<td>-</td>
<td>2.63x10⁻¹⁹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 29 Temperature dependence of the growth rate of the interdiffusion zone measured from 800 to 1000°C (solid circles) and predicted in the temperature range of 500 to 700°C (hollow circles) from diffusion couples of U-10wt.%Mo vs. Mo.
5.3.2 U-10wt.%Mo vs. Zr Diffusion Couples

Backscattered electron (BSE) micrographs and concentration profiles from the U-Mo vs. Zr diffusion couples annealed at 1000, 900, 800, 700°C are presented in Figure 30 through Figure 33. Figure 34 shows the interfacial microstructure developed at 600°C where the couple had a negligible interaction. The large dark precipitates near the interface in Figure 30 through Figure 33 were identified as Mo$_2$Zr using semi-quantitative composition analysis by XEDS and the Mo-Zr equilibrium binary phase diagram presented in Figure 35 [25]. When the diffusion anneal temperature decreased from 1000 to 700°C, the volume fraction of the Mo$_2$Zr precipitates increased. The U-Mo vs. Zr ternary diffusion couples examined in this study have the extra degree of freedom based on Gibbs phase rule that allow the development of a two-phase layer that includes Mo$_2$Zr precipitates. Small dark precipitates present throughout the U-Mo alloy were identified as a Zr-rich phase, which is composed of greater than 95 at.% Zr and a few at.% of U and Mo. These tiny Zr-rich precipitates should be α-Zr which most likely formed during quenching. The U-Zr solid solution present at high temperature during the anneal could yield α-Zr with limited solubility for U and Mo upon cooling according to the U-Zr phase diagram shown in Figure 7 [25].
Figure 30 BSE micrograph and EPMA concentration profile from U-10wt.%Mo vs. Zr diffusion couple annealed at 1000°C for 96 hours.

Figure 31 BSE micrograph and EPMA concentration profile from U-10wt.%Mo vs. Zr diffusion couple annealed at 900°C for 240 hours.
Figure 32 BSE micrograph and EPMA concentration profile from U-10wt.%Mo vs. Zr diffusion couple annealed at 800°C for 480 hours.

Figure 33 BSE micrograph and EPMA concentration profile from U-10wt.%Mo vs. Zr diffusion couple annealed at 700°C for 720 hours.
The concentration profiles determined by EPMA show uphill diffusion of U on the U-Mo side. Scatter in the concentration profiles is observed near the interface because of the Mo$_2$Zr precipitates. When the diffusion anneal temperature decreased to 600°C, the U-Mo and Zr
diffusion couple exhibited a negligible interaction despite the 960 hours of diffusion anneal. Small precipitates with a size of about 1-2 μm were observed discretely at the interface as seen in Figure 34. The composition of these precipitates was not determined accurately since the size was too small.

There is an allotropic transformation between α-Zr and β-Zr at 863°C according to the U-Zr phase diagram shown in Figure 7 [25]. Therefore, both α-Zr and β-Zr exist on the Zr side of the diffusion couples annealed at 800 and 700°C as shown in Figure 32 and Figure 33, while only β-Zr exists at 1000 and 900°C as shown in Figure 30 and Figure 31. A marker plane was clearly observed in the diffusion couple annealed at 1000°C as marked in Figure 30. However, unfortunately, markers could not be identified in the other diffusion couples.

Mo-U-Zr ternary isotherms have been determined by Ivanov and Bagrov for temperatures of 500, 575, 600, 625, 650, 675, 700, 750 and 1000 °C [104, 105]. The concentration profiles of the diffusion couples were plotted as diffusion paths on the Mo-U-Zr ternary phase diagrams as shown in Figure 36. Since there is no available ternary phase diagram at 900 and 800°C, the diffusion paths are presented on the isotherms at 1000 and 750 °C, respectively. The solid circles fitted with solid lines in Figure 36 represent the composition measured by EPMA in single-phase regions. The experimental data within the two-phase region with Mo$_2$Zr precipitates had scatter in composition. Therefore, the diffusion path in the two-phase region was estimated based on the average composition by considering the composition and volume fraction of the U-Zr solid solution and precipitates, which is shown as a dotted line in Figure 36. In general, the diffusion paths constructed based on EMPA measurement were consistent with the ternary phase diagrams determined by Ivanov and Bagrov [104, 105].
Based on the shape of the diffusion paths and concentration profiles, it is clear that Zr diffuses slowly on the U-Mo alloy side and Mo is the slow moving species on the Zr side. On the U-Mo alloy side, gradients of concentration for Mo and U develop even without a significant diffusional penetration of Zr as shown in Figure 30 through Figure 33. This is also reflected on the diffusion paths in Figure 36 wherein the diffusion paths take off towards the pure U corner. While Mo moved down the concentration gradient, uphill diffusion of U was observed. This result suggests that Zr is an excellent diffusion barrier to retain the high U-density in the U-Mo
With an increase in Zr concentration, the diffusion path enters the two-phase (Mo$_2$Zr and $\gamma$-U) region. This is consistent with the observation that Mo$_2$Zr precipitates in the $\gamma$-matrix exist at the interface. The Mo-U-Zr isotherms in Figure 36 clearly show that a decrease in the temperature from 1000 to 700°C reduces the U-Zr solid solution phase field and expands the two-phase (Mo$_2$Zr and $\gamma$-U) field. Correspondingly, the volume fraction of Mo$_2$Zr increased as shown in Figure 30 through Figure 33.

Towards the Zr end, the diffusion path passes through the U-Zr solid solution and ends at pure $\beta$-Zr at the higher temperatures of 1000 and 900°C as presented in Figure 36 (a) and (b). At 800 and 700°C, the diffusion path goes through U-Zr solid solution and jumps into $\alpha$-Zr with negligible solubility for either U or Mo as presented in Figure 36 (c) and (d). The diffusion paths within the $\beta$-Zr, for example at 1000 and 900°C, take off from pure Zr towards the U-corner of the isotherm and suggest that Mo is the slow moving species in the $\beta$-Zr solid solution. The presence of Mo plays a significant role on the diffusion path and solubility of Zr in U-Zr solid solution, especially at 700°C. Based on the U-Zr binary phase diagram shown in Figure 7, the solubility range of Zr in U-Zr solid solution at 700°C should be 50-to-87 at.%. However, the addition of Mo changes the shape of the diffusion paths dramatically and alters the diffusion paths to pass just a small U-Zr solid solution region as shown in Figure 36 (d). This causes the solubility range of Zr in the U-Zr solid solution to be much smaller at 85-to-90 at.%.

For Zr to be an effective diffusion barrier between the U-Mo fuel and Al matrix, the overall magnitude of the diffusional interaction must be small. Figure 34 shows that negligible interdiffusion was observed even after 960 hours of isothermal anneal at 600°C. To compare and contrast the interdiffusion behavior of the U-Mo vs. Zr diffusion couples to U-Mo vs. Al (or Al-
Si alloy), the parabolic growth rate, $K$, of the interdiffusion zone was calculated at 1000, 900 and 800°C. The thickness of the interdiffusion zone (IZ) was simply defined as the distance between U-10wt%Mo and pure Zr where the concentration gradient becomes negligible (terminal ends where $\frac{\partial C}{\partial x} = 0$). The growth rate, $K$, of the interdiffusion zone was calculated using Eq. (21), and the values are reported in Table 18 for 1000, 900, and 800°C. Figure 37 shows that the temperature dependence of the IZ growth rate, $K$, obeys the Arrhenius relation in the temperature range from 800 to 1000°C very well. The pre-exponential factor, $K_o$, and activation energy, $Q_K$, of the growth rate were determined and are also reported in Table 18. The growth rates at 700, 600, 500°C were then calculated following the Arrhenius extrapolation as reported in Table 18 and presented in Figure 37.

Table 18 Growth rates of the interdiffusion zone in U-10wt.%Mo vs. Zr diffusion couples.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thickness of IZ (µm)</th>
<th>Annealing Time (hours)</th>
<th>Growth Rate (m²/s)</th>
<th>$\tilde{D}_o$ (m²/s)</th>
<th>$Q_K$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>1130</td>
<td>96</td>
<td>1.85 x 10⁻¹²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>990</td>
<td>240</td>
<td>5.67 x 10⁻¹³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>650</td>
<td>480</td>
<td>1.22 x 10⁻¹³</td>
<td></td>
<td>7.95 x 10⁻⁰⁵</td>
</tr>
<tr>
<td>Calculated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>183.83</td>
</tr>
<tr>
<td>700</td>
<td>-</td>
<td>-</td>
<td>2.10 x 10⁻¹⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>-</td>
<td>2.36 x 10⁻¹⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>-</td>
<td>-</td>
<td>1.51 x 10⁻¹⁶</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 37 Temperature dependence of the growth rate of the interdiffusion zone measured from 800 to 1000°C (solid circles) and predicted in the temperature range of 500 to 700°C (hollow circles) from diffusion couples of U-10wt.%Mo vs. Zr.

5.3.3 U-10wt.%Mo vs. Nb Diffusion Couples

Backscattered electron (BSE) micrographs from the U-Mo vs. Nb diffusion couples annealed at 1000, 900, 800, 700 and 600°C are presented in Figure 38 through Figure 42. The EPMA concentration profile from the couple annealed at 1000°C is also presented at Figure 43. At the three higher temperatures, 1000, 900 and 800°C, uniform interdiffusion zones formed and are marked as IZ in Figure 38 though Figure 40. In the diffusion zones, the two phases were identified as pure U (white precipitates) and Mo-Nb-U solid solution (gray matrix). There is no Mo-Nb-U ternary phase diagram available to the author’s best knowledge. This solid solution could be the Nb-U solid solution according to Nb-U phase diagram shown in Figure 44 [25]. The small dark regions are polishing defects. The concentration profile in Figure 43 shows that the diffusion zone is Nb-rich and has a low Mo content. The concentration of U shows scattering because of the existence of pure U precipitates. Thermal cracks were observed consistently between the U-Mo alloy terminal end and interdiffusion zone in the temperature range of 800 to
1000°C, which may have resulted from thermal stress during quenching due to different thermal expansion coefficients. This was not observed in the U-Mo vs. Zr or U-Mo vs. Mo systems.

At the two lower temperatures, 700 and 600°C, only a discontinuous intermediate phase formed at the interface as shown in Figure 41 and Figure 42. This phase is U rich with 3~4 at.% Nb and negligible Mo based on XEDS composition analysis. O and C peaks were also found in these phases. This U rich phase could be α-U or β-U decomposed from γ-U.

Figure 38 BSE micrograph from U-10wt.%Mo vs. Nb diffusion couple annealed at 1000°C for 96 hours.
Figure 39 BSE micrograph from U-10wt.%Mo vs. Nb diffusion couple annealed at 900°C for 240 hours.

Figure 40 BSE micrograph from U-10wt.%Mo vs. Nb diffusion couple annealed at 800°C for 480 hours.
Figure 41 BSE micrograph from U-10wt.%Mo vs. Nb diffusion couple annealed at 700°C for 720 hours.

Figure 42 BSE micrograph from U-10wt.%Mo vs. Nb diffusion couple annealed at 600°C for 960 hours.
Figure 43 EPMA concentration profile from U-10wt.%Mo vs. Nb diffusion couple annealed at 1000°C for 96 hours.

Figure 44 Equilibrium binary phase diagram of the Nb-U system [25].
The parabolic growth rate, $K$, of the interdiffusion zone was calculated at 1000, 900 and 800°C using Eq. (21). The thickness of the interdiffusion zone (IZ) was simply defined as the distance between U-10wt%Mo and pure Nb as shown in Figure 38 though Figure 40. The growth rate along with pre-exponential factor and activation energy are presented in Table 19. The growth rate at the lower temperatures, 700, 600 and 500°C, were predicted based on Arrhenius relation and are also reported in Table 19. Figure 45 shows that the temperature dependence of the IZ growth rate, $K$, obeys the Arrhenius relation in the temperature range from 800 to 1000°C well.

Table 19 Growth rates of the interdiffusion zone in U-10wt.%Mo vs. Nb diffusion couples.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thickness of IZ (µm)</th>
<th>Annealing Time (hours)</th>
<th>Growth Rate $\bar{D}^2$ (m²/s)</th>
<th>$\tilde{\bar{D}}_0$ (m²/s)</th>
<th>$Q_K$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>27.5</td>
<td>96</td>
<td>1.10 $\times 10^{-15}$</td>
<td>9.76 $\times 10^{-10}$</td>
<td>146.33</td>
</tr>
<tr>
<td>900</td>
<td>20.1</td>
<td>240</td>
<td>2.33 $\times 10^{-16}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>16.7</td>
<td>480</td>
<td>8.11 $\times 10^{-17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Predicted</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>-</td>
<td>-</td>
<td>1.35 $\times 10^{-17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>-</td>
<td>1.70 $\times 10^{-18}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>-</td>
<td>-</td>
<td>1.25 $\times 10^{-19}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 45 Temperature dependence of the growth rate of the interdiffusion zone measured from 800 to 1000°C (solid circles) and predicted in the temperature range of 500 to 700°C (hollow circles) from diffusion couples of U-10wt.%Mo vs. Nb.

5.3.4 U-7wt.%Mo vs. Mg Diffusion Couple

A diffusion couple of U-7wt.%Mo vs. Mg was assembled and annealed at 550°C for 96 hours. A backscattered electron (BSE) micrograph and XEDS element map are presented in Figure 46 and Figure 47, respectively. The U-7wt.%Mo was observed to be bonded well to Mg as presented in Figure 46. There were no reaction products observed at the interface, which agrees with the Mg-U and Mg-Mo phase diagrams shown in Figure 48 and Figure 49 [25], respectively. The element map in Figure 47 shows that there is no discernable concentration of U or Mo on the Mg side. Semi-quantitive chemical composition analysis based on XEDS yielded the composition of the U-Mo side to be 85.65 at.% U and 14.35 at.% Mo with a negligible Mg concentration. On the Mg side the composition was identified as 100 at.% Mg. This suggests that the interdiffusion between U-Mo and Mg is indeed negligible after 96 hours annealing at 550°C.
Figure 46 BSE micrograph from U-7wt.%Mo vs. Mg diffusion couple annealed at 550°C for 96 hours.

Figure 47 XEDS element map of Mg, Mo and U from U-7wt.%Mo vs. Mg diffusion couple annealed at 550°C for 96 hours.
Figure 48 Equilibrium binary phase diagram of the Mg-U system [25].

Figure 49 Equilibrium binary phase diagram of the Mg-Mo system [25].
To examine the nature of bonding and composition distribution at the interface in detail, TEM equipped with XEDS was employed. Bright-field and HAADF micrographs taken at the interface of the diffusion couple are presented in Figure 50 and Figure 51, respectively. The circles and line in Figure 51 are the spots and line-scan, respectively, where XEDS was performed. Figure 50 and Figure 51 both clearly demonstrate that the U-Mo fuel bonded very well to the Mg. Extensive analyses of composition and diffraction did not reveal any other contaminant-related phases (e.g., oxides) at the interface.

![U-7Mo](image)

Figure 50 Bright-field TEM micrograph of the interface from the U-7wt.%Mo vs. Mg diffusion couple annealed at 550°C for 96 hours.
Figure 51 HAADF micrograph of the interface from the U-7wt.%Mo vs. Mg diffusion couple annealed at 550°C for 96 hours.

Both a semi-quantitative chemical composition analysis on either side of the interface and a line-scan across the interface were performed by XEDS equipped in TEM. No Mg was detected on the U-Mo side (circle labeled 1 in Figure 51), while only a Mg peak was detected on the Mg side (circle labeled 2 in Figure 51). Semi-quantitative analysis from the line-scan across the interface is presented in Figure 52. There is evidence of interdiffusion, particularly on the U-Mo alloy side where there is penetration of Mg to a depth of about 200 nm. However, the concentration gradients observed may be a result of a few artifacts including (1) interaction volume between the electron beam and sample is estimated at about 50 nm for the TEM
operating condition employed in this study and (2) the interface between the U-Mo alloy and Mg may not be perfectly normal to the beam and the potential overlap (e.g., smearing) of U-Mo and Mg near the interface, especially due to the softness of Mg, may cause the “false” concentration profiles. Still, the development of the concentration profile could result from the slow interdiffusion between U, Mo and Mg, since the U-Mo-Mg ternary system, rather than the Mg-U or Mg-Mo binary systems, may have some extended solubility. Regardless of the origin of the concentration gradients, the interdiffusion zone is less than 250 nm after 96 hours annealing at 550°C, which is several orders of magnitude smaller than U-Mo vs. Al or Al alloys, in which complex ternary aluminides grew rapidly [9, 42]. The oxygen concentration profile in Figure 52 is quantitatively inaccurate due to the detection limit, but it can be understood relatively to demonstrate that (1) the oxygen content is higher in the U-Mo alloy than in pure Mg and (b) the slow interaction between the U-Mo alloy and Mg observed is not due to preferential contamination and/or oxidation at the interface.

Figure 52 XEDS concentration profile obtained from semi-quantitative XEDS via scanning TEM from the interface of the U-7wt.%Mo vs. Mg diffusion couple annealed at 550°C for 96 hours.
5.4 Diffusion Behavior Between Uranium and Stainless Steel

5.4.1 U vs. Fe Diffusion Couples

To study the effects of the allotropic transformation between α-U and β-U on the reactions between U and Fe, three annealing temperatures (580, 615 and 650°C) were selected in the α-U temperature range below the allotropic transformation point at 668°C based on the Fe-U equilibrium phase diagram as shown in Figure 53 [25]. Only two annealing temperatures (680 and 700°C) were selected in the β-U temperature range below the Fe-U eutectic temperature around 720°C.

Figure 53 Equilibrium binary phase diagram of the Fe-U system [25].
A typical backscattered electron micrograph and concentration profile obtained from the U vs. Fe diffusion couple annealed at 650°C for 96 hours are presented in Figure 54. The four phases shown in Figure 54 (a) are pure U, U₆Fe, UFe₂ and pure Fe in accordance with the U-Fe equilibrium phase diagram in Figure 53 [25].

Figure 54 BSE micrograph (a) and EPMA concentration profile (b) obtained from the U vs. Fe diffusion couple annealed at 650°C for 96 hours.
The thickness and interface between each phase are uniform and planar, respectively. Because the compositional ranges in all four phases are negligible, the concentration profile does not exhibit any discernable gradient. False gradients appearing at the interfaces are a result of the interaction volume of the electron beam at the sample interfaces that comprise the two neighboring phases. The average thickness, \( \Delta x^{(v)} \), and its standard deviation (as the indicated uncertainty) for the \( \text{U}_6\text{Fe} \) and \( \text{UFe}_2 \) layers at each temperature are reported in Table 20. The \( \text{U}_6\text{Fe} \) phase is thicker than \( \text{UFe}_2 \) in all of the diffusion couples investigated in this study, although the difference, evaluated by the thickness ratio, gets smaller with increasing temperature.

Table 20 Thickness of \( \text{U}_6\text{Fe} \) and \( \text{UFe}_2 \) from U vs. Fe diffusion couples.

<table>
<thead>
<tr>
<th>Allotropic Phase of U</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>( \Delta x^{(\text{U}_6\text{Fe})} ) (µm)</th>
<th>( \Delta x^{(\text{UFe}_2)} ) (µm)</th>
<th>Ratio ( \Delta x^{(\text{U}_6\text{Fe})} / \Delta x^{(\text{UFe}_2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-U (orthorhombic)</td>
<td>580</td>
<td>240</td>
<td>46.4±0.9</td>
<td>2.5±0.1</td>
<td>18.56</td>
</tr>
<tr>
<td></td>
<td>615</td>
<td>240</td>
<td>70.1±0.8</td>
<td>6.0±0.4</td>
<td>11.68</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>96</td>
<td>64.1±2.5</td>
<td>7.8±0.6</td>
<td>8.22</td>
</tr>
<tr>
<td>( \beta )-U (tetragonal)</td>
<td>680</td>
<td>96</td>
<td>78.4±2.0</td>
<td>8.4±0.3</td>
<td>9.33</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>96</td>
<td>90.3±2.1</td>
<td>12.1±0.5</td>
<td>7.46</td>
</tr>
</tbody>
</table>

Since there are negligible concentration gradients in both \( \text{U}_6\text{Fe} \) and \( \text{UFe}_2 \), the interdiffusion flux remains constant within each phase. A modified Fe concentration profile for the U vs. Fe diffusion couple annealed at 650°C for 96 hours can be calculated from the average measured thickness and the stoichiometry of \( \text{U}_6\text{Fe} \) and \( \text{UFe}_2 \) as presented in Figure 55. The corresponding interdiffusion flux of Fe calculated by Eq. (2) is presented in Figure 56 and is reported in Table 21. The interdiffusion flux in \( \text{U}_6\text{Fe} \) is higher than that in \( \text{UFe}_2 \) and the ratio between them decreases from 2.1 to 1.67 with an increase in temperature from 580 to 700°C.
Figure 55 Modified concentration profile of Fe from U vs. Fe diffusion couple annealed at 650°C for 96 hours.

Figure 56 Interdiffusion flux profile of Fe from U vs. Fe diffusion couple annealed at 650°C for 96 hours.
Table 21 Interdiffusion flux of Fe in U₆Fe and UFe₂ from U vs. Fe diffusion couples.

<table>
<thead>
<tr>
<th>Allotropic Phase of U</th>
<th>T (°C)</th>
<th>( \mathcal{J}^{U_{6}Fe} ) (x10⁻¹² at. frac. m/s)</th>
<th>( \mathcal{J}^{UFe_2} ) (x10⁻¹² at. frac. m/s)</th>
<th>Ratio ( \frac{\mathcal{J}^{U_{6}Fe}}{\mathcal{J}^{UFe_2}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-U (orthorhombic)</td>
<td>580</td>
<td>3.36</td>
<td>1.60</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>615</td>
<td>5.14</td>
<td>2.70</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>11.90</td>
<td>6.92</td>
<td>1.72</td>
</tr>
<tr>
<td>( \beta )-U (tetragonal)</td>
<td>680</td>
<td>14.48</td>
<td>8.10</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>16.84</td>
<td>10.11</td>
<td>1.67</td>
</tr>
</tbody>
</table>

The integrated interdiffusion coefficients in \( U_{6}Fe \) and \( UFe_2 \) at each temperature were calculated based on the Fe concentration profile using Eq. (19) or (20). The molar volume variation with composition was ignored for this calculation. The calculated \( \mathcal{D}^{int,(v)} \) using the two methods were exactly the same since both methods are based on Fick’s first law. The calculated magnitude of \( \mathcal{D}^{int,U_{6}Fe} \), \( \mathcal{D}^{int,UFe_2} \) and their activation energies are reported in Table 22. Figure 57 shows the temperature dependence of \( \mathcal{D}^{int,U_{6}Fe} \) and \( \mathcal{D}^{int,UFe_2} \), distinguishing the case of \( \alpha \)-U and \( \beta \)-U as the terminal phase of the diffusion couple. Linear relationships between \( Ln(\mathcal{D}^{int,(v)}) \) and the reciprocal absolute temperature were obtained. \( \mathcal{D}^{int,U_{6}Fe} \) is much larger than \( \mathcal{D}^{int,UFe_2} \) at each temperature and the activation energy of \( \mathcal{D}^{int,U_{6}Fe} \) is correspondingly smaller than that of \( \mathcal{D}^{int,UFe_2} \) in both the \( \alpha \)-U and \( \beta \)-U temperature ranges.
Table 22 Integrated interdiffusion coefficients of Fe in U₆Fe and UFe₂ from U vs. Fe diffusion couples.

<table>
<thead>
<tr>
<th>Allotropic Phase of U</th>
<th>T (°C)</th>
<th>( \tilde{D}^{\text{Int},U_{6}Fe} ) (x10⁻¹⁶ at. frac. m²/s)</th>
<th>( Q^{\tilde{D}^{\text{Int},U_{6}Fe}} ) (kJ/mol)</th>
<th>( \tilde{D}^{\text{Int},UFe_{2}} ) (x10⁻¹⁶ at. frac. m²/s)</th>
<th>( Q^{\tilde{D}^{\text{Int},UFe_{2}}} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha-U ) (orthorhombic)</td>
<td>580</td>
<td>1.56</td>
<td>148</td>
<td>0.040</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>615</td>
<td>3.60</td>
<td></td>
<td>0.162</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>7.63</td>
<td></td>
<td>0.534</td>
<td></td>
</tr>
<tr>
<td>( \beta-U ) (tetragonal)</td>
<td>680</td>
<td>11.35</td>
<td>113</td>
<td>0.680</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>15.21</td>
<td></td>
<td>1.22</td>
<td></td>
</tr>
</tbody>
</table>

Figure 57 Temperature dependence of the integrated interdiffusion coefficients of U₆Fe and UFe₂ from U vs. Fe diffusion couples.

In this study, diffusion couples with pure U and pure Fe as the terminal ends were examined, so the extrinsic growth constants, \( K^{U_{6}Fe}_{f} \) and \( K^{UFe_{2}}_{f} \), were calculated simply using Eq. (21). The values are reported in Table 23. The integrated interdiffusion coefficient \( \tilde{D}^{\text{Int},(v)} \) and intrinsic growth constant \( K^{(v)}_{d} \) are material constants for the U₆Fe and UFe₂ phases. Utilizing the
correlation given by Eq. (24), the intrinsic growth constants, $K_{II}^{U,Fe}$ and $K_{II}^{UF_2}$, were calculated and are reported in Table 24.

Table 23 Extrinsic growth constants of U6Fe and UFe2 from U vs. Fe diffusion couples.

<table>
<thead>
<tr>
<th>Allotropic Phase of U</th>
<th>$T$ (°C)</th>
<th>$K_{II}^{U,Fe}$ (x10^{-16} m^2/s)</th>
<th>$Q_{K_{II},U,Fe}$ (kJ/mol)</th>
<th>$K_{II}^{UF_2}$ (x10^{-16} m^2/s)</th>
<th>$Q_{K_{II},UF_2}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-U (orthorhombic)</td>
<td>580</td>
<td>12.46</td>
<td>146</td>
<td>0.036</td>
<td>299</td>
</tr>
<tr>
<td></td>
<td>615</td>
<td>28.44</td>
<td></td>
<td>0.208</td>
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</tr>
<tr>
<td></td>
<td>650</td>
<td>59.44</td>
<td></td>
<td>0.880</td>
<td></td>
</tr>
<tr>
<td>$\beta$-U (tetragonal)</td>
<td>680</td>
<td>88.93</td>
<td>109</td>
<td>1.021</td>
<td>281</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>117.97</td>
<td></td>
<td>2.118</td>
<td></td>
</tr>
</tbody>
</table>

Table 24 Intrinsic growth constant of U6Fe and UFe2 from U vs. Fe diffusion couples.

<table>
<thead>
<tr>
<th>Allotropic Phase of U</th>
<th>$T$ (°C)</th>
<th>$K_{II}^{U,Fe}$ (x10^{-16} m^2/s)</th>
<th>$Q_{K_{II},U,Fe}$ (kJ/mol)</th>
<th>$K_{II}^{UF_2}$ (x10^{-16} m^2/s)</th>
<th>$Q_{K_{II},UF_2}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-U (orthorhombic)</td>
<td>580</td>
<td>13.88</td>
<td>148</td>
<td>0.196</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>615</td>
<td>32.05</td>
<td></td>
<td>0.797</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>67.91</td>
<td></td>
<td>2.652</td>
<td></td>
</tr>
<tr>
<td>$\beta$-U (tetragonal)</td>
<td>680</td>
<td>101.05</td>
<td>113</td>
<td>3.342</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>135.40</td>
<td></td>
<td>6.008</td>
<td></td>
</tr>
</tbody>
</table>

The temperature dependence of $K_I^{(v)}$ and $K_n^{(v)}$ is presented in Figure 58. Again, linear relations between $Ln(K_I^{(v)})$, $Ln(K_n^{(v)})$ and the reciprocal absolute temperature were observed within both the $\alpha$-U and $\beta$-U temperature ranges. The values of $K_{II}^{U,Fe}$ are close to $K_{II}^{U,Fe}$ independent of the allotropic phase of U (i.e., $\alpha$ or $\beta$) at the terminal end. Accordingly, the activation energy of $K_{II}^{U,Fe}$ is almost the same as that of $K_{II}^{U,Fe}$ as reported in Table 23 and Table
24. However, $K^{UFe_2}_{I}$ was smaller than $K^{UFe_2}_{II}$, and correspondingly, $Q^{K^{UFe_2}_{I}}$ was higher than $Q^{K^{UFe_2}_{II}}$.

![Figure 58](image)

Figure 58 Temperature dependence of extrinsic ($K_{I}$) and intrinsic ($K_{II}$) growth constants of $U_6Fe$ and $UFe_2$ from U vs. Fe diffusion couples.

### 5.4.2 U vs. Fe-15wt.%Cr Diffusion Couple

U vs. Fe-Cr diffusion couples were assembled and annealed at 600, 650 and 700°C. Figure 59 presents a typical BSE micrograph and XEDS concentration profile from the U vs. Fe-Cr diffusion couple annealed at 650°C for 96 hours. The element map of U, Fe and Cr is also shown in Figure 60. The microstructures in the U vs. Fe-Cr diffusion couples are similar to the U vs. Fe system. The concentration profiles show that the solubility of Cr is ranges from about 12 to 20 at.% in $UFe_2$ and is negligible in $U_6Fe$, which agrees with Nakamura’s observation [17]. In
the UFe\textsubscript{2} phase, the Fe and Cr content decrease and increase, respectively, from the Fe-Cr side while the ratio of (Fe + Cr) to U remains constant at about 2. The compositions of U\textsubscript{6}Fe and UFe\textsubscript{2} are reported in Table 25.

Figure 59 BSE micrograph (a) and XEDS concentration profile (b) obtained from U vs. Fe-15wt.%Cr diffusion couple annealed at 650°C for 96 hours.
Figure 60 XEDS element map obtained from U vs. Fe-15wt.%Cr diffusion couple annealed at 650°C for 96 hours.

Table 25 Compositions of U₆Fe and UFe₂ in U vs. Fe-15wt.%Cr diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>U₆Fe</th>
<th>UFe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U (at.%)</td>
<td>Fe (at.%)</td>
</tr>
<tr>
<td>U vs. Fe-Cr</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>Sum (Fe, Cr)=15</td>
</tr>
</tbody>
</table>

Cr rich layers were found at the interface of Fe-Cr/UFe₂ and UFe₂/U₆Fe based on the Cr concentration profile and element map shown in Figure 59 (b) and Figure 60, respectively. At the interface between Fe-Cr and UFe₂, the Cr rich layer (i.e., Fe depletion) resulted from faster diffusion of Fe into U, which was also observed in U-Zr vs. Fe-Cr [17] and U-Zr vs. Fe-Cr-Ni
[29] diffusion couples. The Cr rich layer at the interface of UFe₂/U₀Fe could have resulted from negligible solubility of Cr in U₀Fe, while Fe can diffuse further into U to form U₀Fe. The thicknesses and parabolic growth rates of U₀Fe and UFe₂ were also calculated and are reported in Table 26 and Table 27, respectively, and are presented in Figure 61. The ratio of the thickness of U₀Fe to UFe₂ in this system shows a similar trend to the U vs. Fe diffusion couples in that the ratio decreases with increasing anneal temperature. The activation energy of the growth rates were also determined based on the Arrhenius relation and it was found that these activation energies were greater than the system of U vs. Fe.

Table 26 Thicknesses of U₀Fe and UFe₂ in U vs. Fe-15wt.%Cr diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>Δx(U₀Fe) (µm)</th>
<th>Δx(^2)UFe (µm)</th>
<th>Ratio Δx(U₀Fe)/Δx(UFe₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U vs. Fe-15wt.%Cr</td>
<td>600</td>
<td>240</td>
<td>40.2±0.7</td>
<td>3.6±0.2</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>96</td>
<td>51.7±1.1</td>
<td>6.1±0.4</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>96</td>
<td>120.5±1.4</td>
<td>22.2±1.5</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Table 27 Parabolic growth rates of U₀Fe and UFe₂ in U vs. Fe-15wt.%Cr diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>T (°C)</th>
<th>K^U₀Fe (x10⁻¹⁶ m²/s)</th>
<th>Q^K,U₀Fe (kJ/mol)</th>
<th>K^UFe₂ (x10⁻¹⁶ m²/s)</th>
<th>Q^K,UFe₂ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U vs. Fe-15wt.%Cr</td>
<td>600</td>
<td>9.36</td>
<td>219.7</td>
<td>0.074</td>
<td>322.3</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>38.66</td>
<td></td>
<td>0.534</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>210.18</td>
<td></td>
<td>7.115</td>
<td></td>
</tr>
</tbody>
</table>
Figure 61 Temperature dependence of growth rates of $U_6Fe$ and $UFe_2$ in U vs. Fe-15wt.%Cr diffusion couples.

5.4.3 U vs. Fe-15wt.%Cr-15wt.%Ni Diffusion Couples

U vs. Fe-Cr-Ni diffusion couples were also investigated and annealed at 600, 650 and 700°C. A typical BSE micrograph and concentration profile obtained from the U vs. Fe-Cr-Ni diffusion couple annealed at 700°C for 96 hours are presented in Figure 62. The element map from this couple is also shown in Figure 63.
Figure 62 BSE micrograph of interaction microstructure (a), detailed BSE micrograph of dendritic morphology (b), and XEDS concentration profile (c) obtained from U vs. Fe-15wt.%Cr-15wt.%Ni diffusion couple annealed at 700°C for 96 hours.
The most different feature of the U vs. Fe-Cr-Ni diffusion couples is the two-phase region (i.e., UFe$_2$ and Fe-Cr-Ni solid solution) with dendritic morphology existing between Fe-Cr-Ni solid solution and UFe$_2$. This two-phase layer suggests that interdiffusion of Fe, Cr, Ni and U occurs along grain boundaries and these atoms spread parallel between UFe$_2$ and the Fe-Cr-Ni alloy. The reaction between Fe, Cr, Ni and U formed UFe$_2$ with this dendritic feature in the Fe-Cr-Ni alloy. Finally, the dendritic UFe$_2$ grows into a uniform UFe$_2$ layer. Some dark gray precipitates were randomly found on the pure U side and they were identified as uranium with carbon enrichment (e.g. contaminant) based on XEDS semi-quantitative composition analysis.

The concentration profile in Figure 62 and element map in Figure 63 clearly show that the dendritic two-phase region is rich in Cr due to the fast diffusion of Fe and Ni, while UFe$_2$ is rich in Ni and the dendritic two-phase region is depleted of Ni. In the UFe$_2$ phase, the content of...
U and Ni remain almost unchanged while Fe decreases continuously and Cr increases slightly. The solubilities of Fe, Cr, Ni and U in UFe₂ are 42~48, 3~7, 14, and 35 at.%, respectively. The ratio of (Fe + Cr + Ni) to U remains approximately 2. In the U₆Fe phase, all concentrations remain constant at about 85 at.% for U, 12.5 at.% for Fe, 2.5 at.% for Ni and negligible for Cr. These compositions of the U₆Fe and UFe₂ layers are presented in Table 28. The thicknesses, growth rates and activation energies of U₆Fe and UFe₂ are reported in Table 29 and Table 30, respectively. The growth rates of U₆Fe and UFe₂ as a function of temperature are shown in Figure 64. The slope of the Arrhenius trend line for the growth of U₆Fe and UFe₂ in this system is less steep than that of the U vs. Fe-Cr diffusion couples.

Table 28 Compositions of U₆Fe and UFe₂ in U vs. Fe-15wt.%Cr-15wt.%Ni diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>U₆Fe</th>
<th>UFe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U (at.%)</td>
<td>Fe (at.%)</td>
</tr>
<tr>
<td>U vs. Fe-Cr-Ni</td>
<td>85</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>Sum (Fe, Cr, Ni)=15</td>
</tr>
</tbody>
</table>

Table 29 Thicknesses of U₆Fe and UFe₂ in U vs. Fe-15wt.%Cr-15wt.%Ni diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>Δx(U₆Fe) (µm)</th>
<th>Δx(UFe₂) (µm)</th>
<th>Ratio Δx(U₆Fe) / Δx(UFe₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U vs. Fe-15wt.%Cr-15wt.%Ni</td>
<td>600</td>
<td>240</td>
<td>54.2±0.8</td>
<td>3.8±0.3</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>96</td>
<td>56.5±1.3</td>
<td>5.6±0.6</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>96</td>
<td>84.4±1.4</td>
<td>11.1±0.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>
Table 30 Parabolic growth rates of $U_6Fe$ and $UFe_2$ in $U$ vs. Fe-15wt.%Cr-15wt.%Ni diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>$T$ (°C)</th>
<th>$K^{U,Fe}$ ($x10^{-16}$ m$^2$/s)</th>
<th>$Q^{K, U_6Fe}$ (kJ/mol)</th>
<th>$K^{UFe_2}$ ($x10^{-16}$ m$^2$/s)</th>
<th>$Q^{K, UFe_2}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U vs. Fe-15wt.%Cr-15wt.%Ni</td>
<td>600</td>
<td>17.00</td>
<td>127.3</td>
<td>0.083</td>
<td>216.5</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>46.10</td>
<td></td>
<td>0.449</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>103.13</td>
<td></td>
<td>1.773</td>
<td></td>
</tr>
</tbody>
</table>

Figure 64 Temperature dependence of growth rates of $U_6Fe$ and $UFe_2$ in $U$ vs. Fe-15wt.%Cr-15wt.%Ni diffusion couples.
CHAPTER SIX: DISCUSSION

6.1 New Method for Determining Ternary Diffusion Coefficients

The case studies presented in section 5.1.2 demonstrate that this new method works well for asymptotic concentration profiles and concentration profiles with uphill diffusion with extrema. The case of a concentration profile with noise suggests that this method can be applied to analyze real experimental concentration profiles after properly smoothing the scatter in the experimental data. On both sides of the Matano plane, this method works well similar to the DASO method [31]. However, in the middle region of the diffusion zone, this method presents accurate results while the coefficients calculated by the DASO method exhibit large error.

The influence of the number of points selected in an interval and the effect of position and extent of the selected interval on the determination of ternary diffusion coefficients is not significant based on the analysis of the generated asymptotic concentration profile A-B. Since the generated concentration profiles perfectly obey an error function [90] and each data point contains equally the same information of interdiffusion coefficients mathematically, the calculation process is not sensitive to the points selected. However, this may not be true for experimental data with noise because this noise presents diffusion information that deviates far from the true diffusion process. Therefore, a proper smoothing method is very important to obtain accurate and reliable diffusion coefficients. Improper smoothing techniques can cause over 100% relative error [32].

The weight factor, W, in Eq. (29) can be used to adjust the significance of each point, which provides a possibility of combining the smoothing of experimental concentration profiles
and the determination of ternary diffusion coefficients into one step. This weight factor, W, can be obtained from the instruments, smoothing function, or experience. It is also evident that Eq. (26) can provide adequate equations through selecting more points in the interval to calculate the 

\[(n-1)^2 \overline{D}_{ij}^{n} \] for any n-component system.

### 6.2 Diffusion Behavior of U-Mo Alloy

In this study, \( \tilde{D} \) monotonically decreased and, correspondingly, \( \tilde{Q} \) increased with an increase in Mo concentration. Adda [67] has previously reported that as \( N_{Mo} \) increases \( \tilde{D} \) increases initially and then decreases as shown in Figure 19, while \( \tilde{Q} \) increases to a maximum at \( N_{Mo} = 0.1 \) and then decreases as presented in Figure 21. Typically, in a binary solid solution, if the addition of an alloying element increases the melting point, \( \tilde{D} \) will decrease with increasing alloying addition [103]. Because the addition of Mo increases the solidus and liquidus of \( \gamma \)-U according to the phase diagram shown in Figure 5, \( \tilde{D} \) would decrease with an increasing Mo content.

There are exceptions to the above rule due to variations in the thermodynamic factor. For example, in U-Zr alloys the interdiffusion coefficient shows a concave variation near \( N_{Zr} = 0.3 \) in the temperature range of 700 to 950°C because the thermodynamic factor decreases [74]. However, there is no convex variation in the thermodynamic factor near \( N_{Mo} = 0.1 \) based on the activity of U, \( a_U \), as shown in Figure 22 in section 5.2.4. Furthermore, a reduction of the tracer diffusivity of U with the addition of 10 at.% Mo has been observed [71]. Therefore, the unusual
composition-dependence of \( \tilde{D} \) and \( \tilde{Q} \) observed by Adda [67] may not exist according to the results of this study wherein consistent and repeated EPMA measurements were employed. Though the composition-dependent activation energy of interdiffusion varies between the two studies, the averaged activation energies within the studied composition range of 2 to 26 at.% Mo are close to each other. The value is 196 kJ/mole in Adda's work and 173 kJ/mole in this study with a relative error of about 11%.

Adda measured \( D_U^* \) in pure U [68] and a U-10 at.% Mo alloy [71] and found that it was reduced by the addition of Mo. The \( D_U^* \) values experimentally measured by Adda and estimated by various methods in this study are presented in Figure 23. Since the \( N_{Mo} \) values at the marker planes were less than 0.1, the magnitude of the calculated \( D_U^* \) should be located between the measured \( D_U^* \) of pure U and the U-10 at.% Mo alloy [68, 71]. Figure 23 clearly illustrates that the \( D_U^* \) values calculated based on the ideal (equal to CALPHAD method and subregular solution model) and regular solution models agree with Adda’s experimental results of \( D_U^* \) better than those computed using Vamberskii’s thermodynamic data. The magnitude of \( D_U^* \) calculated using the regular solution model was approximately 15% higher than that using the ideal solution.

Both intrinsic and tracer diffusion coefficients (shown in Table 12 and Table 14) indicate that U diffused intrinsically faster than Mo. This is reasonable because Mo, with a high melting point of 2623 °C, is more stable than U, which has a melting point of 1132°C [23].

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6.3 Diffusion Behavior of U-Mo Alloys and Barrier/Non-Reacting Matrix Materials

The ideal barrier materials/non-reacting matrix materials for metallic fuel systems require the following properties: (1) interdiffusion or reactions between barriers and metallic fuels should be slow; (2) no or an insignificant amount of intermetallic phases should form for better structural integrity. Thermal expansion coefficients and other thermo-mechanical properties of intermetallic phases may vary significantly. Solid solution phases are therefore preferred because the relevant properties would vary gradually with composition; (3) intermetallic phases, if formed due to interdiffusion and reaction, should be stable under irradiation; (4) the melting point should be high; (5) the neutron adsorption rate should be low; (6) the thermal conductivity should be high; and (7) the corrosion resistance should be good.

The diffusion couple investigation of the U-Mo vs. Mo, Zr, Nb or Mg systems presented in section 5.2 suggests that the interdiffusion reaction rates between these barrier materials and the U-Mo fuel are slow. It was found that the interdiffusion reaction of U-Mo with Mo, Zr, and Nb at 600°C and Mg at 550°C were negligible. The growth rates of the diffusion zones in the U-Mo vs. Mo, Zr and Nb couples are presented in Figure 65 for comparison. Generally, the growth rates obey an Arrhenius relation well in the three systems studied. The diffusion couples of U-Mo vs. Zr and U-Mo vs. Nb show the highest and lowest growth rates, respectively. However, the U-Mo vs. Mo system presents the steepest temperature dependence.

The growth rate of intermetallic phases between U-Mo vs. Al and U-Mo vs. Al-Si have been experimentally measured by Perez [9, 42] as reported in Table 31. It is noted from examination of Table 31 and Figure 65 that the growth rate of the interdiffusion zone between U-10wt.%Mo and Zr, Mo, and Nb is about $10^3$, $10^5$ and $10^6$ times slower, respectively, than those
determined from the diffusion couples of U-10wt.%Mo vs. Al or Al-Si. In the U-7wt.%Mo vs. Mg diffusion couple, negligible interdiffusion reaction was observed after 96 hours of annealing at 550°C. Therefore, Mo, Zr, Nb and Mg can be considered as effective barrier layers for U-Mo fuels.

![Graph](image.png)

Figure 65 Temperature dependence of the growth rates of the interdiffusion zones measured from 800 to 1000°C (solid circles) and predicted in the temperature range of 500 to 700°C (hollow circles) from U-10wt.%Mo vs. Zr, Mo and Nb diffusion couples.

Table 31 Growth rates of the interdiffusion zones in U-Mo vs. Al and U-Mo vs. Al-Si diffusion couples [9, 42].

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
<th>Annealing Temperature (°C)</th>
<th>Growth Rate (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-7wt.%Mo vs. Al</td>
<td>600</td>
<td>4.05x10⁻¹⁵</td>
</tr>
<tr>
<td>U-10wt.%Mo vs. Al</td>
<td>600</td>
<td>1.69x10⁻¹²</td>
</tr>
<tr>
<td>U-12wt.%Mo vs. Al</td>
<td>600</td>
<td>7.20x10⁻¹³</td>
</tr>
<tr>
<td>U-10wt.%Mo vs. Al-2wt.%Si</td>
<td>550</td>
<td>1.45x10⁻¹⁴</td>
</tr>
<tr>
<td>U-10wt.%Mo vs. Al-5wt.%Si</td>
<td>550</td>
<td>1.62x10⁻¹⁴</td>
</tr>
</tbody>
</table>
Other relevant physical properties of Mo, Zr, Nb and Mg are listed in Table 32. If Mo is applied as a barrier layer, only $\gamma$-(U-Mo) solid solution exists between the U-Mo fuel and Mo above 600°C. Gradual variation in the composition of the U-Mo solid solution should result in a smooth variation of the thermal expansion coefficient and would help avoid thermal stress accumulation and/or cracks. When the temperature is below 600°C, only the $\gamma'$-UMo$_2$ intermetallic phase can form according to the Mo-U phase diagram in Figure 5 [25]. However, the growth of this intermetallic phase should be very slow at low temperatures.

Table 32 Physical properties of Zr, Mo, Nb and Mg as barrier materials [23, 24].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Zr</th>
<th>Mo</th>
<th>Nb</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction rate (compared to Al or Al-Si alloy)</td>
<td>About $10^3$ times lower</td>
<td>About $10^5$ times lower</td>
<td>About $10^6$ times lower</td>
<td>N/A*</td>
</tr>
<tr>
<td>Reaction products</td>
<td>Mo$_2$Zr, Zr rich, U-Zr, UZr$_2$</td>
<td>Solid solution</td>
<td>Pure U, solid solution</td>
<td>None</td>
</tr>
<tr>
<td>Melting point</td>
<td>1855 °C</td>
<td>2623 °C</td>
<td>2477 °C</td>
<td>650 °C</td>
</tr>
<tr>
<td>Neutron adsorption rate</td>
<td>0.18 barn</td>
<td>2.48 barn</td>
<td>1.15 barn</td>
<td>0.059 barn</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>22.6 W·m$^{-1}$·K$^{-1}$</td>
<td>138 W·m$^{-1}$·K$^{-1}$</td>
<td>53.7 W·m$^{-1}$·K$^{-1}$</td>
<td>156 W·m$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>Corrosion resistant</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Bad</td>
</tr>
</tbody>
</table>

* Negligible interaction was found between U-Mo alloy and Mg.

Using a Mo barrier would also maintain a simple binary system since Mo is already the alloying addition used in U for $\gamma$-phase stabilization. In addition, the Mo composition of either $\gamma$-(U-Mo) solid solution or $\gamma'$-U$_2$Mo is below 37 at.%, which means interdiffusion would make the fuel Mo rich and the composition variation in U-10wt.%Mo fuel would be less than 15 at.% Mo.
Therefore, the effect of the interdiffusion on the fuel composition could be minimized. As a refractory element, molybdenum has the highest melting temperature of 2623°C among the above metals and its thermal conductivity is high compared to that of magnesium. The corrosion resistance of Mo is comparable to that of Zr and Nb. The cross section for 2200 m/s neutrons of Mo is 2.48 barn. Though the neutron absorption rate of Mo is the highest among the four candidates, it is still low and acceptable for natural metals [106].

Zirconium could also be a promising barrier candidate. For the temperature range investigated in this study, only the Mo2Zr intermetallic and Zr rich phases exist as precipitates near the interface. However, at lower temperatures, other intermetallic or solid solution phases may form according to the Mo-U-Zr ternary phase diagram [105], such as UZr2, U6Zr3Mo, U6Zr3Mo and U2Mo. In Perez’s study [24], multiple phases including α-U, Mo2Zr, U-Zr solid solution, UZr2, and Zr rich phases were observed at the interface between the U-Mo and Zr in the hot-rolled and annealed U-Mo fuel plate with Al matrix and Zr barrier. However, Robinson [107] has reported that the interaction products containing Zr appear to be stable during irradiation. The neutron absorption rate of Zr is fairly low. The cross section for 2200 m/s neutrons of Zr is 0.185 barn, which is one of the lowest among naturally occurring metals [106]. Moreover, Zr is highly resistant to corrosion by alkalis, acids, salt water, and other agents [23]. The diffusional interaction between Zr and Al has been studied by Kidson [108] and Laik [109]. However, there are discrepancies regarding the development and growth rates of intermetallic phases between the two studies. Further investigation into these discrepancies needs to be conducted.
Niobium has good corrosion resistance, a high melting temperature and a low neutron adsorption rate. Only Mo-Nb-U solid solution and U precipitates formed between the U-Mo fuel and Nb. The reaction rate between U-Mo and Nb is lower than Mo or Zr and Nb forms less intermetallic phases with Al compared to Zr and Mo [26]. However, thermal cracks were consistently observed at the interface in the couples annealed at 800, 900 and 1000°C where uniform reaction layers formed. At the lower temperatures of 600 and 700°C, the interaction phase was not continuous and the diffusion couples were found to be bonded well. Therefore, the thermal mismatch between the U-Mo alloy and the interaction layer could be the reason that caused the crack at the interface. Because the processing and operating temperature of the U-Mo alloy is below 600°C, the crack should not be an issue.

According to the Mg-U and Mg-Mo phase diagrams shown in Figure 48 and Figure 49, there is negligible solubility in each other and no intermetallic phase that can form. This study showed that no significant interdiffusion occurred between U-7wt.%Mo and Mg annealed at 550°C for 96 hours. Mg would be an excellent matrix or barrier since it has a high thermal conductivity of 156 W·m⁻¹·K⁻¹ [23]. The neutron absorption rate of Mg is fairly low. The cross section for 2200 m/s neutrons of Mg is 0.059 barn, which is one of the lowest among naturally occurring metals [106]. Moreover, Mg is soft and easy to machine with a Brinell hardness of 260 MPa and a Young’s modulus of 45 GPa [23]. However, environmental interaction of Mg would be of concern [23]. Mg easily reacts with water or air at room temperature. Also, the eutectic point between Mg and Al at 437°C should be considered for fuel processing and application in systems with Al alloy cladding. Significant interdiffusion and reaction was observed between the Mg matrix and Al-alloy cladding after hot rolling at 415°C [27]. However, the interaction
between the Mg-matrix and Al-alloy cladding has been reduced effectively by optimizing the hot rolling technique to be conducted at a lower temperature of 275°C [27]. Therefore, Mg could be a good candidate for a barrier or non-reacting matrix for the RERTR program if environmental interaction issues can be solved.

6.4 Diffusion Behavior Between U and Stainless Steel

6.4.1 U vs. Fe Diffusion couples

The intrinsic growth constant \( K^{(v)}_{II} \) is a characteristic value for a phase \( v \), while the values of extrinsic growth constant \( K^{(v)}_I \) may be influenced by other phases that exist in the diffusion zone. The fact that \( K^{UFe_2}_I \) is smaller than \( K^{UFe_2}_{II} \) for the UFe_2 phase indicates that the growth of UFe_2 was impeded by the rapid growth of the adjacent \( U_6Fe \) phase layer. The magnitudes of \( K^{UFe}_I \) and \( K^{UFe}_II \) were found to be almost the same, which indicates that the growth of \( U_6Fe \) was not influenced by the presence of UFe_2. Both \( \tilde{D}^{int,(v)} \) and \( K^{(v)}_{II} \) are characteristic constants inherent to diffusion within a phase \( v \) and show the same temperature dependence with the same activation energy as reported in Table 22 and Table 24.

The allotropic transformation of U had an influence on the growth of both \( U_6Fe \) and UFe_2. The activation energies of \( \tilde{D}^{int,U_6Fe} \) and \( \tilde{D}^{int,UFe_2} \) when U existed as the \( \alpha \)-phase were larger than those when U existed as the \( \beta \)-phase and the difference in the activation energy was more significant for the \( U_6Fe \) phase than the UFe_2 phase. This is also true for both the extrinsic and intrinsic growth constants. Both \( \tilde{D}^{int} \) and \( K_{II} \) are material constants for a specific phase [99, 101], and should obey the Arrhenius relation. However, there is a discontinuity of \( \tilde{D}^{int} \) and \( K_{II} \) at the
allotropic transformation temperature and corresponding changes in the activation energy for the α-U and β-U temperature ranges. This indicates that the allotropic transformation of U plays a role on the growth of the intermetallic phases, specifically the U₆Fe phase. The growth of U₆Fe requires: (a) diffusion reactions at the U/U₆Fe interface; (b) diffusion of U and Fe in U₆Fe; and (c) diffusion reactions at the U₆Fe/UFe₂ interface. In this study, factors (b) and (c) remained unchanged and only factor (a) may have changed due to the allotropic transformation of U.

In the phenomenological description via irreversible thermodynamics, the specific heat of U changes at the allotropic transformation temperature and hence a change in the temperature dependence of the thermodynamic driving force for the reaction may be expected when U transforms between α and β. This would only cause the driving force of diffusion/reaction to change. From the mechanism perspective, the allotropic transformation of U causes the crystal structure and binding energy to change, which would affect the rate and distance of atomic motion at the interface. This variation in the growth of U₆Fe caused by interfacial changes implies that the growth of U₆Fe may not be completely lattice diffusion controlled and the interfacial reaction process may be significant. The effect of the allotropic transformation on the growth mechanism of U₆Fe needs to be further examined based on the growth as a function of time.

The variation in the growth of U₆Fe, of course, would indirectly affect the growth of UFe₂. Therefore, the influence of the U allotropic transformation on the growth of U₆Fe through changes in the U/U₆Fe interface would also affect the growth of UFe₂. Wagner [99] defined the intrinsic growth constant $K_{II}$ without the consideration of the allotropic transformation of the
neighboring phases. This study indicates that the allotropic transformation of the neighboring phases can result in a variation of $K_{II}$, which would no longer be a material constant.

Both experimental observation and quantitative analysis demonstrated that $U_6Fe$ grew faster than $UFe_2$. Funamizu [110] reviewed several potential factors and summarized that an intermediate phase layer will grow more rapidly if: (1) the diffusion coefficient in the layer is larger; (2) the diffusion coefficient in the adjoining phases is smaller; (3) the homogeneity range of the phase in the phase diagram is wider; (4) the concentration range of the adjoining two-phase areas in the phase diagram is narrower (meaning the miscibility gap between the phase and the adjoining phases is smaller); (5) the heat of formation of the phase is higher (meaning the thermodynamic stability of a phase is higher and has a greater driving force for formation); and (6) the crystal structures between the adjoining phases are similar.

Results of this study show that the magnitude of $\tilde{D}_{\text{fr}, U_6Fe}$ is larger than that of $\tilde{D}_{\text{fr}, UFe_2}$ to satisfy criteria (1) and (2). According to the U-Fe phase diagram presented in Figure 53 [25], both $U_6Fe$ and $UFe_2$ are line compounds, but the miscibility gap in concentration of Fe is 14.3% between pure U and $U_6Fe$ and 33.3% between $UFe_2$ and pure Fe in regards to criterion (4). Also, $U_6Fe$ has a lower melting point (about 800°C) than $UFe_2$ (about 1230°C) consistent with faster interdiffusion, which is contradictory to criterion (5). $U_6Fe$ has a body-centered tetragonal crystal structure [111] which is similar to the $\alpha$-U (orthorhombic) or $\beta$-U (tetragonal) structure. However, $UFe_2$ has a complex Laves phase structure (C15 fcc crystal structure, symmetry Fd3m) [112], which is very different from $\alpha$-Fe (body center cubic structure). As the $UFe_2$ crystal structure is dissimilar from both of its neighbors, it would be expected to grow more slowly as per criterion (6). Therefore it is reasonable that the $U_6Fe$ phase layer was observed to grow faster than $UFe_2$. 

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6.4.2 U vs. Fe-15wt.%Cr and U vs. Fe-15wt.%Cr-15wt.%Ni Diffusion Couples

In the diffusional reactions between U and Fe, Fe-Cr or Fe-Cr-Ni alloy, U and Fe play dominant roles though the addition of alloying elements Cr and Ni affect these reactions. Only $U_6Fe$ and $UFe_2$ with some solubilities of Cr and Ni formed according to the U-Fe equilibrium phase diagram [25]. Negligible solubility of Cr was found in $U_6Fe$, while some solubility of Cr was detected in $UFe_2$. Cr rich layers observed in the diffusion couples of U vs. Fe-Cr and U vs. Fe-Cr-Ni suggest that Cr diffused slower than Fe or Ni. This agrees with previous studies regarding reactions between U-Zr and Fe-Cr-Ni alloys [17, 29].

For alloying element Ni, constant solubilities of 2.5 and 14 at.% were observed in $U_6Fe$ and $UFe_2$, respectively. According to the equilibrium phase diagram between U and Ni [25], $U_6Ni$ and $UNi_2$ can form. This may explain the constant ratio between U and Ni in both the $U_6Fe$ and $UFe_2$ phases. The depletion of Ni between Fe-Cr-Ni and the $UFe_2$ phase shown in Figure 62 and Figure 63 indicates that Ni diffused fast into U and formed $U(Fe,Ni)_2$. Therefore, Cr variably substituted for Fe in $UFe_2$, while Ni replaced Fe at constant ratios in both the $U_6Fe$ and $UFe_2$ phases.

To investigate the effects of alloying elements Cr and Ni on the growth of $U_6Fe$, $UFe_2$ and the total reaction zone, the growth rates of each phase are reported in Table 33 and are presented as a function of temperature in Figure 66. For simplification, the allotropic transformation of U at 668°C will not be considered. Since the thicknesses of the $UFe_2$ phase are small, the growth rates show relatively large scatter, while the growth rates of $U_6Fe$ and the total interdiffusion zone obey the Arrhenius relation very well. The growth of $U_6Fe$, $UFe_2$ and the total
reaction zone in the three systems present a similar trend. The largest temperature dependence of the growth rates (i.e., activation energy of growth) was found in the diffusion couples of U vs. Fe-Cr in which the growth rates of U$_6$Fe, UFe$_2$ and the total reaction zone were the highest at 700°C while they were the lowest at 600°C. The system of U vs. Fe and U vs. Fe-Cr-Ni show similar temperature dependence, however, the growth rates in the U vs. Fe diffusion couples were slightly higher than in the U vs. Fe-Cr-Ni couples.
Table 33 Parabolic growth rates of U₆Fe, UFe₂, and the diffusion zone in U vs. Fe, U vs. Fe-15wt.%Cr and U vs. Fe-15wt.%Cr-15wt.%Ni diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion couples</th>
<th>T (°C)</th>
<th>( K_{U₆Fe} ) (x10⁻¹⁶ m²/s)</th>
<th>( Q_{K,U₆Fe} ) (kJ/mol)</th>
<th>( K_{UFe₂} ) (x10⁻¹⁶ m²/s)</th>
<th>( Q_{K,UFe₂} ) (kJ/mol)</th>
<th>( K^{Total} ) (x10⁻¹⁶ m²/s)</th>
<th>( Q^{K,Total} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U vs. Fe</td>
<td>580</td>
<td>12.46</td>
<td>129.2</td>
<td>0.036</td>
<td>224.9</td>
<td>13.84</td>
<td>136.9</td>
</tr>
<tr>
<td></td>
<td>615</td>
<td>28.44</td>
<td></td>
<td>0.208</td>
<td></td>
<td>33.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>59.45</td>
<td></td>
<td>0.880</td>
<td></td>
<td>74.79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>680</td>
<td>88.93</td>
<td></td>
<td>1.021</td>
<td></td>
<td>109.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>117.97</td>
<td></td>
<td>2.118</td>
<td></td>
<td>151.70</td>
<td></td>
</tr>
<tr>
<td>U vs. Fe-15wt.%Cr</td>
<td>600</td>
<td>9.36</td>
<td>219.7</td>
<td>0.074</td>
<td>322.3</td>
<td>11.11</td>
<td>230.8</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>38.66</td>
<td></td>
<td>0.534</td>
<td></td>
<td>48.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>210.18</td>
<td></td>
<td>7.115</td>
<td></td>
<td>294.64</td>
<td></td>
</tr>
<tr>
<td>U vs. Fe-15wt.%Cr-15wt.%Ni</td>
<td>600</td>
<td>17.00</td>
<td>127.3</td>
<td>0.083</td>
<td>216.5</td>
<td>19.45</td>
<td>135.2</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>46.10</td>
<td></td>
<td>0.449</td>
<td></td>
<td>55.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>103.13</td>
<td></td>
<td>1.773</td>
<td></td>
<td>131.95</td>
<td></td>
</tr>
</tbody>
</table>
Figure 66 Temperature dependence of growth rates of $U_6Fe$ (a), $UFe_2$ (b), and the total interaction zone (c) in the diffusion couples of U vs. Fe, U vs. Fe-15wt.%Cr and U vs. Fe-15wt.%Cr-15wt.%Ni.
CHAPTER SEVEN: CONCLUSIONS

In this study, a new method was proposed to determine ternary interdiffusion coefficients using a single diffusion couple by a matrix transformation approach. This method is clear in physical meaning and simple in mathematical calculation. The uncertainties from instruments and experiments can be considered by introducing a weight factor, W. The reliability and accuracy of this method were evaluated by three case studies including a basic asymptotic concentration profile, a concentration profile with extrema and a smoothed concentration profile with noise. It was found that this new method worked well in all three cases. The largest relative error of the calculated interdiffusion coefficients was less than 0.5% of the originally inputted values in the first two cases, and less than 10% in the case with noise. A comparison to the DASO and BOME methods suggests that this new method has a competitive performance over the range of either side of the Matano plane, and shows a better performance than the DASO method when dealing with the middle of the diffusion zone. For experimental concentration profiles with noise, a proper smoothing technique must be applied to improve the stability and accuracy of the interdiffusion coefficients.

In the diffusion couples between pure U and Mo, interdiffusion coefficients of $\gamma$ (bcc) U-Mo alloys were determined in the temperature range of 650 to 1000°C and in the composition range of 2 to 26 at.% Mo. It was observed that $D$ decreases with an increase in Mo concentration. The pre-exponential factor and activation energy as a function of composition were determined. A Kirkendall marker plane was clearly identified in each diffusion couple and utilized to determine intrinsic diffusion coefficients. The intrinsic diffusion coefficients
calculated at the marker compositions indicated that U intrinsically diffused 5-10 times faster than Mo. The activity of U and the thermodynamic factor of U-Mo alloys were determined using the ideal solution, regular solution, and subregular solution models based on the molar excess Gibbs free energy of U-Mo alloys. The tracer diffusion coefficients and vacancy wind effects of U and Mo at the marker compositions were also estimated by Manning’s formalism. In the temperature range of 800 to 1000°C, both tracer diffusivities and atomic mobilities of U were about 5 times higher than Mo, and the vacancy flux enhanced the intrinsic diffusion of U by about 30% and suppressed the intrinsic diffusion of Mo by about 2%. The tracer diffusion coefficient of U calculated using the ideal solution, regular solution, and subregular solution models and the CALPHAD method agreed with Adda’s experimental determination.

Solid-to-solid U-10wt.%Mo vs. Mo diffusion couples were assembled and annealed at 600, 700, 800, 900 and 1000°C for various times. The interdiffusion microstructures and concentration profiles were examined via scanning electron microscopy and electron probe microanalysis, respectively. As the Mo concentration increased from 22 to 32 at.%, the interdiffusion coefficient decreased while the activation energy increased, which agrees well with the results obtained from diffusion couples of U vs. Mo. The interdiffusion coefficients in the composition range of 2 to 32 at.% Mo were determined by combining the results from the U vs. Mo and U-10wt.%Mo vs. Mo diffusion couples. The growth rates of the interdiffusion zone between U-10wt.%Mo vs. Mo were also calculated. Compared to the U-10wt.%Mo vs. Al and U-10wt.%Mo vs. Al-Si systems, the growth rates in the U-10wt.%Mo vs. Mo system are about 10^5 times lower. Mo could be a promising barrier candidate due to its high melting point, high
thermal conductivity, and good corrosion resistance. Moreover, using a Mo barrier forms only one interaction product and maintains a simple binary system with the U-Mo fuel.

Diffusion couples of U-10wt.%Mo vs. Zr were assembled and annealed at 600, 700, 800, 900 and 1000°C for various times. The intermetallic phase, Mo$_2$Zr, was found at the interface and its volume fraction increased as annealing temperature decreased. Diffusion paths were also plotted on the Mo-U-Zr ternary phase isotherms with consistency. The growth rates of the interdiffusion zone between U-10wt.%Mo and Zr were also calculated under the assumption of parabolic diffusion, and were determined to be about $10^3$ times lower than the growth rates of the diffusional interaction layer found in the U-10wt.%Mo vs. Al or Al-Si diffusion couples. Other desirable physical properties of Zr, such as a low neutron absorption rate, high melting point and good corrosion resistance are presented as supplementary information to demonstrate its great potential as a diffusion barrier for U-Mo fuel systems.

Solid-to-solid U-10wt.%Mo vs. Nb diffusion couples were examined at 600, 700, 800, 900 and 1000°C for various times. Only Mo-Nb-U solid solution and U precipitates formed between the U-Mo fuel and Nb. The reaction rate between U-Mo and Nb was found to be lower than that of Mo or Zr. Niobium has good corrosion resistance, a high melting temperature and a low neutron absorption rate. Nb forms less intermetallic phases with Al compared to Zr and Mo [26]. However, thermal cracks were consistently observed at the interface in this study.

A solid-to-solid U-7wt.%Mo vs. Mg diffusion couple was assembled and annealed at 550°C for 96 hours. The microstructure in the interdiffusion zone and the development of concentration profiles were examined via scanning electron microscopy, transmission electron microscopy and X-ray energy dispersive spectroscopy. The U-7wt.%Mo alloy was bonded well
to the Mg at the atomic scale, without any evidence of oxidation, cracks or pores. Despite the good bonding, very little or negligible interdiffusion was observed. This is consistent with expectations based on the equilibrium phase diagrams. Along with other desirable properties, Mg is a potential inert matrix or barrier material for low-enriched U-Mo fuel systems being developed in the RERTR program.

Solid-to-solid diffusion couples were assembled between pure U and Fe, and annealed at 580, 615 and 650°C where U exists as orthorhombic α, and at 680 and 700°C where U exists as tetragonal β. The U₆Fe and UFe₂ intermetallics developed in all of the diffusion couples, and U₆Fe was observed to grow faster than UFe₂. The interdiffusion fluxes of U and Fe were calculated to determine the integrated interdiffusion coefficients of U₆Fe and UFe₂. The extrinsic (K_I) and intrinsic (K_II) growth constants of U₆Fe and UFe₂ were also calculated according to Wagner’s formalism. The difference between K_I and K_II of UFe₂ indicated that its growth was impeded by the fast-growing U₆Fe phase. However, because the K_I and K_II values calculated for U₆Fe are similar, it appears that the thin UFe₂ layer played only a small role in its growth. The allotropic transformation of uranium from α to β was observed to influence the growth of U₆Fe directly because its activation energy changed upon the transformation. The change in the chemical potential and crystal structure of U due to the allotropic transformation affected the interdiffusion between U and U₆Fe. The reason for the more rapid growth of U₆Fe was also examined with respect to various factors including crystal structure, phase diagram, and diffusion.

Diffusion couples of U vs. Fe-15wt.%Cr and U vs. Fe-15wt.%Cr-15wt.%Ni were examined at 600, 650 and 700°C to study the effects of the alloying elements Cr and Ni on the growth of U₆Fe and UFe₂. The diffusion of Cr into U was slower than that of Fe or Ni.
Negligible solubility of Cr was found in U$_6$Fe, while some solubility of Cr with a discernable concentration gradient of 3 to 20 at.% was detected in UFe$_2$ depending on the concentration of Ni. The solubility of Ni in U$_6$Fe and UFe$_2$ was found to be constant at 2.5 and 14 at.% in U$_6$Fe and UFe$_2$, respectively. Therefore, Cr variably substituted for Fe in UFe$_2$, while Ni replaced Fe at constant ratios in both the U$_6$Fe and UFe$_2$ phases.

The growth of U$_6$Fe, UFe$_2$ and the total reaction zone in the three systems (i.e., U vs. Fe, Fe-Cr and Fe-Cr-Ni) follow a similar trend. The largest temperature dependence of the growth rates (i.e., activation energy of growth) were found in the U vs. Fe-Cr diffusion couples, in which the growth rates of U$_6$Fe, UFe$_2$ and the total reaction zone were highest at 700°C and lowest at 600°C. The U vs. Fe and U vs. Fe-Cr-Ni systems show a similar temperature dependence; however, the growth rates of U$_6$Fe, UFe$_2$ and the total reaction zone in the U vs. Fe diffusion couples were slightly higher than in the U vs. Fe-Cr-Ni system.
APPENDIX A: THERMODYNAMIC ASSESSMENT OF U-Mo ALLOY
The thermodynamic activity of U, $a_U$, as a function of $N_U$ at a given temperature, was evaluated by the ideal solution, regular solution, and subregular solution models. The $a_U$ is related to $N_U$ by the activity coefficient $\gamma_U$ as [102]:

$$a_U = \gamma_U \cdot N_U \quad (A1)$$

In the ideal solution model, the interaction between U and Mo is ignored [102], and $\gamma_U$ is unity. Therefore, $a_U$ is equal to $N_U$. In both the regular solution and subregular solution models, $\gamma_U$ is not unity and can be derived from the molar excess Gibbs free energy, $\Delta G^E$. This is expressed as [102]:

$$\Delta G^E = N_{Mo} \Delta \overline{G}_{Mo} + N_U \Delta \overline{G}_U = \Omega N_{Mo} N_U \quad (A2)$$

where $\Omega$ is a parameter in the regular solution model and is a function of $N_{Mo}$ or $N_U$ in the subregular solution model. $\Delta \overline{G}_{i=Mo}^E$ is the partial molar excess Gibbs free energy of U or Mo and is related to its respective $\gamma_i$ as [102]:

$$\Delta \overline{G}_i^E = RT \ln(\gamma_i) = \Omega N_j^2 \quad (i \neq j) \quad (A3)$$

where $R$ is the molar gas constant with a value of 8.31 J/mol-K and $T$ is the temperature in Kelvin.

The molar excess Gibbs free energy, $\Delta G^E$, of the U-Mo alloy ($\gamma$ phase) in the temperature range of 838 to 1557 K is given by Parida [39] as:

$$\Delta G^E = N_U (1 - N_U) \{(21.533 - \frac{33.680 T}{1000}) N_U + (\frac{25.698 T}{1000} - 2.120)\} \quad (A4)$$
In the regular solution model, $\Delta G^E$ at a specific composition and temperature is calculated using Eq. (A4). Then the value of $\Delta G^E$ is applied to determine $\Omega$ through Eq. (A2). Finally, $\gamma^U$ is obtained by substituting the value of $\Omega$ into Eq. (A3).

The subregular solution model can be more flexible than the regular solution model because it arbitrarily allows $\Omega$ to vary with composition as $\Omega = a + bN_U$ [102]. Thus, Eq. (A2) can be expressed as:

$$\Delta G^E = (a + bN_U)N_U N_{Mo} = N_U (1 - N_U)(bN_U + a) \quad (A5)$$

where $a$ and $b$ can be determined through equating the corresponding terms in Eqs. (A4) and (A5) and can then be utilized to calculate the value of $\Omega$ to obtain $\gamma^U$. The value of $a_U$ in either the regular or subregular solution models is then simply determined by substituting $\gamma^U$ into Eq. (A1).
APPENDIX B: LIST OF PUBLICATIONS AND PRESENTATIONS
Peer-Reviewed Journal Publications


**Conference Presentations**


LIST OF REFERENCES


[94] Garimella N, Sohn Y, Brady M. Interdiffusion in γ (face-centered cubic) Ni-Cr-X (X=Al, Si, Ge, or Pd) alloys at 900 °C. J Phase Equil Diff 2006;27:665.


