

INTERDIFFUSION BEHAVIOR OF URANIUM SILICIDE AND FERRAL VIA DIFFUSION
COUPLE STUDIES

by

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ABSTRACT

Tri-uranium di-silicide (U_3Si_2) is a candidate for use in accident tolerant fuel systems because of its higher thermal conductivity at elevated temperatures and higher fissile density - relative to the current standard light water reactor (LWR) fuel, UO_2 . Advanced steels, including FeCrAl, for its superior mechanical and thermal properties and oxidation resistance, are being considered as an alternative to the standard LWR cladding, Zircalloy. The interaction between U_3Si_2 and FeCrAl was investigated in this study. U_3Si_2 pellets were fabricated and placed in diffusion couples with FeCrAl. Individual tests were ran at temperatures ranging from 500 °C to 1000 °C for 30 hours (h) and 100 h. The interdiffusion was analyzed with an optical microscope, scanning electron microscope (SEM), and transmission electron microscope (TEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. Distinct $\text{U}_2\text{Fe}_3\text{Si}$ / UFe_2 and UFeSi layers were observed at the material interface. U diffused far into the FeCrAl and Fe diffused far into the U_3Si_2 in the higher temperature tests.

1.0 Introduction

1.1 Background

Safe, reliable, and economic operation of the current nuclear power reactor fleet is a top priority for the nuclear industry. After the events at Fukushima in 2011, resulting from the Great East Japan Earthquake, emphasis has been placed on enhancing the accident tolerance of light water reactors (LWR)s. In addition to the Nuclear Regulatory Commission requiring compliance to a mitigation strategy order (EA-12-049) (Leeds, 2012)¹, the Department of Energy initiated an Accident Tolerant Fuel (ATF) Development program. Nuclear fuel development prior to this was focused on increased power density and fuel reliability. An ATF would tolerate loss of cooling in the reactor core or other beyond design basis events while maintaining or improving the fuel performance, relative to the current fuel, during normal operation (Bragg-Sitton, 2014).

The current nuclear industry standard fuel system is uranium dioxide with a zirconium alloy cladding (UO₂-Zry). Any candidate for ATF must perform as good as or better than UO₂-Zry in all three areas to be considered as a viable replacement. The UO₂-Zry system has performed adequately for many years, however it can be improved upon, not only for safety reasons, but for economic reasons as well. Uranium silicide (U₃Si₂) is in use as a dispersion plate fuel in test reactors, but has not been fully tested in LWR conditions. U₃Si₂ pellets have been fabricated for use in commercial LWRs as part of an ATF system. (Harp, 2015) U₃Si₂ has higher uranium loading density as well as a higher thermal conductivity relative to UO₂, listed in Table 2.1 and Fig. 2.1 respectively. FeCrAl alloy is a candidate cladding material to replace Zry. FeCrAl has outstanding high-temperature mechanical strength and oxidation resistance under accident conditions. (Pint, 2013) The U₃Si₂-FeCrAl system is expected to provide more than double the amount of time from control rod insertion (SCRAM) until failure criteria for the reactor is met, as well as producing roughly half the amount of hydrogen gas (H₂) in the event of a loss of coolant accident (LOCA). (Wu, 2015)

1.2 Objective and Methods

This study aims to elucidate some of the behavior of the U_3Si_2 -FeCrAl nuclear fuel system and provide greater opportunity for predicting, to a reasonable degree, performance under LWR conditions. Because the U_3Si_2 -FeCrAl fuel system is a new concept, very little data exists for it. This work investigates the extent of chemical interaction between U_3Si_2 and FeCrAl by means of diffusion couple annealing at a range of temperatures and times. Multiple examination techniques including optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM), were applied to the diffusion couple cross section to characterize the interface of the materials tested. Concentration plots, derived from data acquired with energy-dispersive X-ray spectroscopy (EDS), were used to calculate diffusion parameters/the diffusivity of selected elements using both Boltzman-Matano (B-M) and Sauer-Freise (S-F) analysis based on Fick's Laws. TEM crystal diffraction was also used to verify phases within the system.

1.3 Characterization Methods

1.3.1 Optical Microscope

The optical microscope can be used as a tool to inform the quality of sample preparation step. The optical microscope is used to verify an adequate finish on the sample before a sample is coated and loaded into the SEM. The optical images also provide a large scale picture of the diffusion couple. These images provide perspective on what the electron microscopes can show in greater detail. The optical microscope provides the “big picture” that the electron microscopes are not able to do.

1.3.2 Scanning Electron Microscope

A JOEL 7600F field emission scanning electron microscope was used for the bulk of this work

with a Phenom XL bench top SEM used as a supplement. Two different types of electron detectors were used on the Joel 7600. The first is a low angle backscatter electron detector (LBE) exclusive to the JOEL 7600F, which provides a top-down perspective on the sample that is sensitive to compositional differences with differences in atomic number represented as contrast in the resultant micrograph. The second type is the LEI, a conventional Evert-Thornley detector sensitive to both high energy secondary and backscatter electrons that is more sensitive to topographic variations on the surface.

The Oxford Aztec software was used for all SEM EDS analytical analysis. SEM LBE and EDS were used to identify interaction layers, determine the width of interaction, identify secondary phases, and homogeneity.

All samples examined in the SEM were coated with either carbon or gold to overcome the charging due to the presence of epoxy around the mounted sample. The layer was typically 5 nm or less, preferably no thicker than necessary to eliminate charging.

1.3.3 Transmission Electron Microscope

TEM was used to investigate interdiffusion layers and their interfaces with higher resolution than can be achieved with SEM characterization. The TEM has a resolution of 0.24 nm and the scanning TEM (STEM) has a point resolution of 0.16 nm. The EDS on the TEM can provide elemental mapping resolution at the atomic scale.

A diffraction pattern is the result of parallel rays scattering off the same surface and brought to focus at a back focal plane resulting in a series of spots distributed in two dimensions. From this pattern unknown materials can be determined by measuring the distance between the transmitted spot and diffracted spot. Materials have unique atom positions that are some known distance apart unique to the

material's crystal structure. Polycrystalline material superimposes multiple diffraction patterns. TEM provides a spatial distribution of diffraction information. (Fultz, 2013)

Because electrons pass through the material to form the diffraction patterns the sample must be thin enough for electron passage. This is achieved through dual-beam focused ion beam (FIB) sample preparation techniques that are able to remove a thin section of the material, called a lamella, for TEM examination.

2.0 Literature Review

Relevant physical properties of U_3Si_2 and FeCrAl are summarized in Table 2.1. Greater than 16% increase of U mass can theoretically be achieved by substituting U_3Si_2 for UO_2 in LWR fuel systems. This increase in U loading represents a substantial economic benefit allowing for greater flexibility in enrichment and time between reloading the reactor, while the melting point for both U_3Si_2 and FeCrAl is less than their traditional counterparts UO_2 and Zry. Fig. 2.1 illustrates the comparison of thermal conductivity for each material from room temperature up to 1200 °C for FeCrAl and greater for the other materials, as shown. The dramatic improvement in thermal conductivity of U_3Si_2 over UO_2 allows for cooler reactor operating temperatures and faster cooling in the event of a LOCA, increasing the coping time of the reactor as mentioned in section 1.1. Fig. 1.1 also shows that FeCrAl has a similar thermal conductivity to Zry.

Table 2.1

Thermal properties of U_3Si_2 and FeCrAl

Property	U_3Si_2	UO_2	FeCrAl	Zry
U-Density (g-U/cm ³)	11.3 (Hoffman, 1996)	9.7	Not applicable	Not applicable
Melting Point (°C)	1665 (Chatain, 2006)	2847	1500 ²	1850

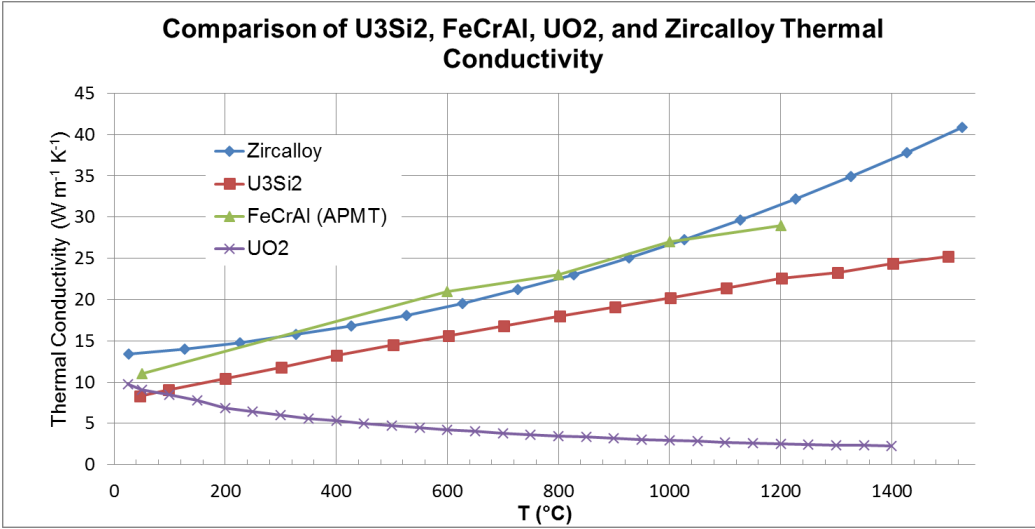


Fig. 2.1

Thermal conductivity comparison for selected LWR fuel system materials and candidate materials.

U and Fe have well known eutectics shown in the binary phase diagram, Fig. 2.2, that enhance diffusion of the U_3Si_2 -FeCrAl fuel system. The interaction of Fe with molten U has been investigated by Walter. In the U-Fe system, UFe_2 , which melts congruently at 1236 °C, forms a eutectic with iron that melts at 1078 °C and has a composition of U-77at% Fe. UFe_2 also forms a eutectic with U_6Fe that melts at 719 °C and has a composition of U-33at% Fe. (Walter, 1996) U_6Fe is formed at 831 °C with a composition of U-86 at% Fe. Normal LWR operating temperatures for U_3Si_2 fuel is expected to be around 300 - 400°C.

The eutectic reactions of an Fe-U system would nominally only be of concern in an accident scenario. Careful and detailed analysis of diffusion interaction between pure Fe and U was carried out by Huang. (Huang, 2012) It was shown that pure Fe and U will readily interact. The current study replicated Huang in some aspects, but added other elements (specifically Si, Cr, Al, and Mo) to the system that, based upon experimental observation, drastically stagnate the interdiffusion process. Parallel to the current study, an investigation of the interdiffusion behavior of U_3Si_2 and Zry-4 showed a primary

interaction layer of ZrSi_2 and secondary phases containing Fe, Cr, U, and Si. The low melting point eutectic phase U_6Fe was also identified in the test at 1000 °C. (He, 2017)

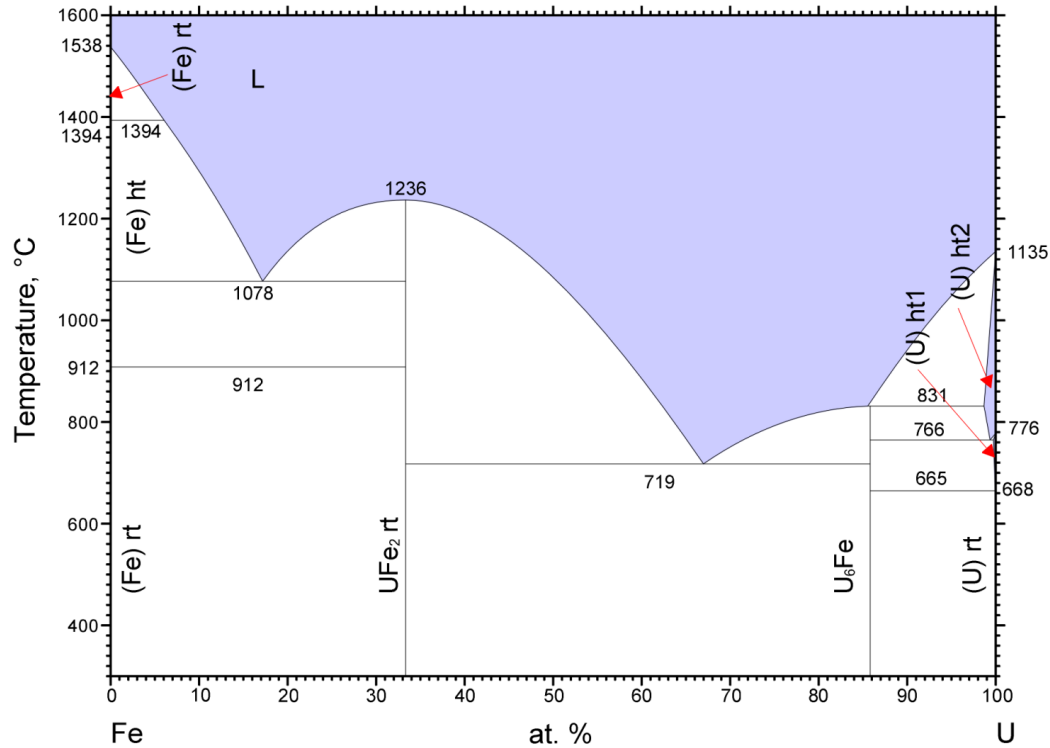


Fig. 2.2 Binary phase diagram of U-Fe system labeled with the corresponding intermetallic phases (UFe_2 and U_6Fe) and individual phases of Fe and U respectively.

2.1 U_3Si_2

The interaction of U_3Si_2 and aluminum (Al) in research reactor fuel plates, where the U_3Si_2 in irregular powder form is dispersed among an Al matrix, has been studied by multiple groups with both pre and post irradiated samples. Kim et al. (1999) observed very little fuel matrix interaction (FMI) after annealing at 400 °C for 888 h and significant FMI layers at 530 °C for 10 h for comminuted U_3Si_2 powder. A. Leenaers et al. (2004) reported the FMI composition as, close to, $\text{U}_3\text{Al}_7\text{Si}_2$. Formation of pores observed in the Al matrix is thought to be an example of the Kirkendall effect, and resulting from a more rapid diffusivity of Al into the U_3Si_2 than that of U into Al.

It is well known that U_3Si_2 is likely to become amorphous upon irradiation at low temperatures. This will have an effect on its interaction with surrounding material. Microstructural characterization of U_3Si_2/Al silicide dispersion fuel has been done at INL. (Gan, 2011) During fabrication of the fuel no discernable interaction layer was found after exposure to 500 °C for less than 2 hours. Upon irradiation at research reactor temperatures, around 100 °C, the thermal diffusion mechanism of migrating vacancies was not present, causing the fuel to become amorphous. U_3Si_2 is expected to remain crystalline in LWR conditions because LWR temperatures are higher than the glass transition temp of U_3Si_2 . (Kim, 2012) The greater heat allows vacancies to migrate to grain boundaries and other sinks more effectively.

Irradiation damage is caused by the interaction of fission fragments with the material via direct hard sphere Rutherford collisions as well as electron excitation. While the hard sphere collisions will create the same amount of vacancies and interstitials, the rate of damage from electron excitation should be greater in materials of poor electrical and thermal conductivity. At low temperatures irradiation enhancement of diffusivities is linked to electron excitation, and U_3Si_2 may be less susceptible than UO_2 to this mechanism because of its higher electrical conductivity. (Turnbull, 1982)

2.2 FeCrAl

Three basic fuel cladding options: zirconium alloys, silicon carbide, and FeCrAl alloys, each with their own optimized variants, are being pursued as part of the ATF system described in section 1.0. The current FeCrAl alloy candidate is Kanthal APMT, but optimization alloy composition and fabrication studies continue. (Rebak, 2016) Other U alloys are also included as options in the ATF systems. Each system has advantages and disadvantages based on thermal, chemical, and mechanical properties, economics, ease of fabrication, etc. Each of these aspects is not trivial and much has been published on the comparison of many combinations of the ATF fuel-cladding system.

One of the main advantages of FeCrAl over Zry is the avoidance of rapid oxidation in steam that creates hydrogen and the associated exothermic reaction. Brookhaven National Laboratory (BNL) showed that there is little or no impact on the thermal-hydraulic properties of the system by using a fuel rod clad with a FeCrAl alloy. It is expected that a FeCrAl alloy clad fuel rod can be designed with minimal thermal-hydraulic design changes. (Rebak, 2015) FeCrAl has a resistance to steam corrosion above 1200 °C and up to its melting point. (Rebak, 2016) Extensive immersion studies with chemistries typically observed in both BWR and PWR reactors showed excellent corrosion resistance of the FeCrAl alloys. (Ellis, 2016) Zry absorbs and becomes embrittled by H, lowering its mechanical strength. FeCrAl does not absorb H, but this also turns out to be one of its challenges. FeCrAl is expected allow tritium (radioactive H), created as a process of ternary fission in the fuel, to pass through from the fuel to the reactor coolant, and potentially into the environment. This expectation is based on a UO_2 -FeCrAl fuel system, and U_3Si_2 may release less tritium than UO_2 does. Zry avoids tritium permeation by forming an impermeable ZrO_2 layer. An impermeable coating on the FeCrAl cladding to mitigate the tritium permeation has been proposed. (Hu, 2015)

An economic assessment by George et al (2015) reported an increase in fuel cost per cladding design of about twenty percent for FeCrAl relative to Zry based on the use of UO_2 fuel and its higher enrichment requirement due to the neutronic penalty associated with FeCrAl. The thermal neutron absorption cross section of FeCrAl is 2.43 barns, while that of Zry is 0.20 barns. George et al (George, 2013) also found the yield stress of APMT to be approximately four times higher than for Zircaloy-2. Because FeCrAl is mechanically stronger than Zry, its cladding wall thickness can be made thinner than Zry, reducing the material area for neutron absorption as well as increasing the area available for fuel. The higher U density of the U_3Si_2 fuel may also offset the neutronic penalty of the FeCrAl cladding, and counter the economic disadvantage reported by George et al.

An analysis of the benefits during a BWR station black out event showed that the substitution of Zry with FeCrAl delayed accident progression and decreased the amount of gases generated. These analyses were done ignoring possible eutectics between FeCrAl and other core components because there was not enough data available. (Robb, 2015) The present study will help to inform future analysis.

Fuel clad chemical interaction (FCCI), and the chemical compatibility between the fuel and clad material is of prime importance because of the formation of low melting eutectics which may often limit the life of the fuel pin in a reactor. The temperature of the eutectic reaction between the fuel and the cladding is considered as a critical parameter for the design of the metallic fuel pin. The integrity of the cladding is of fundamental concern for designers since it provides the primary barrier to the release of radionuclides. (Mishra, 2015)

UO₂-Zry fuel systems have a fuel - clad gap engineered into the fuel rod design to accommodate for fuel swelling (from fission gas) and cladding creep (from radiation exposure). (Martin, 2004) U₃Si₂-FeCrAl fuel systems would potentially suffer from these known traits: swelling and creep. One to three years after irradiation starts (depending on the materials), the fuel-clad gap will close and the compressive stress experienced by the cladding and due to the primary fluid pressure is reversed to a tensile stress induced by continued fuel swelling.

Formation of contact materials or bonding layers occurs at the interface of the fuel and the cladding. The formation of eutectics greatly influences the core degradation process in the existing reactors utilizing Zry. (Ott, 1989) In UO₂-Zry fuel, the interface layers are made up of zirconia/urate and fission products. Complex triplex layers were found to exist in UO₂-Zry fuel, especially – and somewhat randomly – within fuel pellet cracks and at pellet-pellet interfaces. The (UO₂-Zry) fuel examined was un-ramped fuel of modest burn-ups. It was concluded that fuel oxygen potential appears to be an important variable in dictating the nature and composition of bonding layer compounds. (Martin,

2004) This may also be the case with $\text{U}_3\text{Si}_2\text{-FeCrAl}$ fuel systems. The formation of a pellet-cladding bonding layer in high burnup boiling water reactor (BWR) fuels was investigated by Nogita et al. They found that during an early stage of irradiation, small amounts of U are transported to the cladding inner surface from the UO_2 pellet. (Nogita, 1997)

2.3 Diffusion Theory

Intermixing of two species is governed by the diffusion equation, where the diffusivity is a measure of how fast the intermixing proceeds (Greer, 2016). Diffusion in solid materials can be described by Fick's first law, given steady state. Non - steady state diffusion is modeled by Fick's second law, and with Boltzmann's transformation can be written to describe a concentration profile, $C(x,t)$, as a function of time and position given the appropriate initial and boundary conditions. (Matano, 1933)

$$\tilde{D}(C) = \frac{-1}{2t} \left(\frac{\partial x}{\partial C} \right) \int_{C_0}^C x dC$$

Equation 1

$\tilde{D}$ is the interdiffusion coefficient or diffusivity with units of m^2/s . The diffusivity is treated as a composition-dependent parameter. The equation is applied to a concentration profile taken at a fixed diffusion time, so t is a constant. X is the position perpendicular to the material interface. The integral is the area between the concentration profile and the Matano plane, as shown in Fig. 2.3.

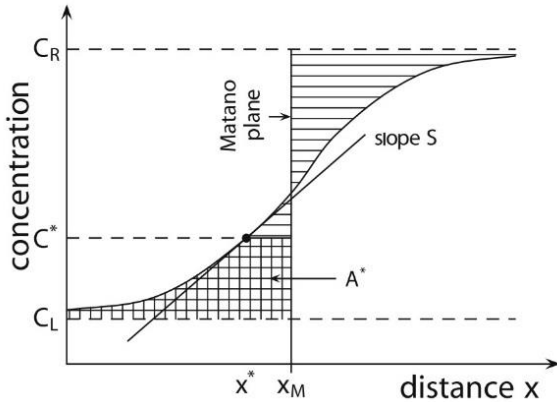


Fig. 2.3 Schematic illustration of the B-M method describing the integral in equation 1. A given composition C^* at a distance x^* an area A^* is calculated with starting compositions C_L and C_R .

(Mehrer,2007)

The concentration profile of an isothermal diffusion couple in a multicomponent system can provide the integrated interdiffusion coefficient (diffusivity) for any component in the system for any selected concentration range. These coefficients help to compare the interdiffusion behavior of the individual components and assess their effective penetration depth in the terminal alloys of the diffusion couple. (Dayananda, 1996) The terminal alloys are assumed to stretch to infinity, which means in practice that they are large enough that the concentration at their other ends is unaffected by the transient for the entire duration of the experiment. (Mehrer, 2007) The boundary conditions of the equation assume that the initial and final concentrations are that of the two different alloys respectively.

Analytical methods for analysis of concentration profiles based on the classical B-M method described above are assumed for the simple case of binary alloys. FCCIs involve multi-component diffusion. A set of $(n-1)^2$ interdiffusion coefficients are required to describe the diffusion process in an n-component system. To extract more information from a single diffusion couple, methods based on the integration of diffusion fluxes and the improved S-F analysis (Dayananda, 2006) determine the multiple coefficients using one diffusion couple are employed.

The interdiffusion flux of each component in the diffusion couple is solved for using the following equation:

$$\tilde{J}_i(C) = \frac{1}{2t} \int_{C_0}^{C_i^*} x - x_M dC_i$$

Equation 2

where C_0 is the composition of the i th component of the system at the terminal end, C^* is the concentration of the i th component at the point at which the interdiffusion flux is being determined, and t is the annealing time. Because the diffusion couple compositions are restricted to the solid solution regime, molar volume effects are ignored. This may introduce error into the calculation, as the volume of the

species may change slightly during the process. X_M , known as the Matano interface, is defined below, Equation 3.

Fundamental to the B-M method is the ability to precisely determine the position of the Matano plane, X_M . The Matano interface is defined as being the plane across which an equal number of atoms have crossed in both directions. Based on the boundary conditions mentioned for equation 1, the position of the Matano plane is calculated from the following equation

$$x_M = \frac{1}{C_L - C_R} \int_{C_R}^{C_L} x dC$$

Equation 3.

Here X_M is the Matano interface; the average position weighted on concentration. C_L and C_R are the left and right terminal ends of the diffusion couple, respectively. The integral term is the area under the concentration curve with respect to concentration, shown in Fig. 2.3. Numerical integration allows the position of the Matano plane to be determined. Since the concentration profile is a set of discrete values rather than a function, pairs of adjacent values were used to form right angled trapezoids for approximation of the integral. This method also calculates any noise in the data, so care must be taken to smooth the data as to not calculate a meaningless negative area in some spots. The error introduced through this method leads to a loss of precision in the position of the Matano plane. A drawback of the B-M method is that near the ends of the concentration plots the integral in equation 1 becomes very small, and the inverse of the concentration gradient, $\frac{\partial x}{\partial C}$, becomes unbounded. Because the numerical evaluation of the integral and the inverse of the slope toward the ends of the penetration profile are difficult to perform accurately, large uncontrolled errors are introduced in the determination of the diffusivity. In binary alloys a common assumption is that the Matano interface would be identical for all components. (Kailasam, 1999) For the FeCrAl-U₃Si₂ case each component must be evaluated separately to determine its unique Matano interface.

An alternative to the B-M method makes use of relative concentrations. The concentration plot can be represented in terms of relative concentration variables, Y_i , first introduced by Sauer and Freise (Sauer, 1962), defined as:

$$Y_i = \frac{C_i - C_i^+}{C_i^- - C_i^+} \quad (i=1,2, \dots, n).$$

Equation 4

C_i^- and C_i^+ represent the concentrations of the component i in the terminal alloys of the couple. An advantage of Y_i versus x plot lies in the fact that the concentration profiles of all components are displayed over the diffusion zone L^- to L^+ such that Y_i is 1 at L^- and is 0 at L^+ for all components regardless of their flux directions within the diffusion zone. (Dayananda, 2006) Den Broeder (denBroeder, 1969) showed that equation 1 can be rewritten as

$$D(C) = \frac{1}{2t} \left(\frac{dx}{dc} \right) \left\{ (1 - Y^*) \int_{-\infty}^{x^*} (C(x) - C^-) dx + Y^* \int_{x^*}^{+\infty} (C^+ - C(x)) dx \right\}$$

Equation 5

where the first integral is everything below the concentration curve and the second integral is everything above the concentration curve. The superscript “*” indicates values at the location where the interdiffusion flux is being determined. The use of equation 5, referred to as the S-F method in the current study, allows us to solve for the diffusivity without locating the Matano plane. (Dayananda, 2006)

A higher value of diffusivity means faster mixing. A negative value for the diffusivity would mean concentration, or depending on the frame of reference it could indicate direction of diffusion. In the current study some of the negative values for diffusivity were ignored as they are a result of the negative concentration gradient at $C(x)$ which is an artifact of the way the data was collected as point sources along one line in the interface. In the case of diffusion in binary systems, the diffusing species will generally diffuse in the direction that reduces the composition gradient of the system. This leads to reduction of the chemical potential and maximizes entropy. For the case of multi-component systems the diffusing species

may interact with each other so that reduction of the chemical potential does not necessarily imply that diffusion takes place in the direction that reduces the concentration gradient in the system. (Perez, 2005)

Darken defined a diffusivity term to explain the case of a diffusion couple of a binary system. The chemical interdiffusion coefficient, $\tilde{D}$, is a weighted average of the diffusion coefficients of the individual components, with respect to alloy composition and describes the whole system, i.e.:

$$\tilde{D} = x_A D_B + x_B D_A$$

Equation 6

where A and B represent the two components of the system, x is the atom fraction and, D is the intrinsic diffusion. Measured diffusion rates give an average value of the measurement over several grains, thus simulating a macroscopic isotropy of diffusion, even though diffusion in each grain (single crystal) in essence is highly anisotropic. Generally, oversized (compared to the host atom) substitutional impurities have higher migration energy than of undersized substitutional impurities. Vacancy mechanism of diffusion explains how the diffusion rate of U_3Si_2 into FeCrAl is different from the diffusion rate of FeCrAl into U_3Si_2 . FeCrAl, with a lower melting point than U_3Si_2 , is expected to diffuse faster.

2.3.1 Kirkendall Effect

In a solid state diffusion process, each component may diffuse intrinsically at a different rate. (Mehrer, 2007) This results in the movement of the marker plane (also called the Kirkendall plane), which is the original interface of the diffusion couple. (Huang, 2012) If each component in a diffusion couple diffused at the same rate the Matano plane would be the same as the initial contact interface. Factors producing this marker shift are a general feature of the mechanism of diffusion. (Sietz, 1953) Porosity observed along the diffusion interface, known as Kirkendall porosity, was previously observed, and is likely a general phenomenon, and should be considered an essential part of the diffusion process. When diffusion is controlled by vacancy mechanism, the net flow of matter in one direction will be balanced by

a net flow of vacancies in the opposite direction. (Paul, 2004) Pores form as a result of the difference in diffusion rate of the two species in a diffusion couple. The pores attempt to restore equilibrium in the system by acting as a sink for vacancies. Darken (Darken, 1948) assumed that the lattice will swell or shrink in such a way as to maintain the equilibrium density, therefore doesn't account for porosity. Pitting observed during diffusion may arise as the result of a large deviation from the equilibrium density of imperfections, a super concentration of vacancies, or a subnormal concentration of interstitial atoms. Small voids, cracks, or inclusions may act as sinks for vacancies or sources for interstitial atoms, and produce large voids when an appropriate supersaturation of the former or subnormal concentration of the latter is present. (Sietz, 1953)

Lattice or grain boundary diffusion may play a dominant role in diffusion. Lattice diffusion is likely to occur under high temperatures with a high vacancy concentration, and large grains whereas, grain boundary diffusion is likely to occur at low temperatures when there are a lack a vacancies. As annealing continues in a diffusion couple the grains grow, and the diffusion mechanism may switch from grains to lattice. (Paul, 2017)

3.0 Material and methods

3.1 U₃Si₂ Characterization

Polycrystalline depleted U₃Si₂ sample pellets used in the present work were sintered at Idaho National Laboratory following the procedure provided by Harp (2015), with the exception that some of the pellets had not been centerless ground prior to sectioning, as seen in Fig. 3.1. This was a traditional powder metallurgy route where elemental uranium powder was mixed with elemental silicon powder in a stoichiometric ratio, pressed into a compact, agglomerated, and arc melted to form the U₃Si₂ compound. Great care was taken in the fabrication process to achieve an optimal density. The density of sintered U₃Si₂ pellets was 11.8 g/cm³, which was 96.9% of the theoretical density. This density was achieved by maintaining the proper grain size distribution of the U₃Si₂ powder prior to pressing the green pellet.



Fig. 3.1. Uranium silicide pellets. The one on the left is a green pressed pellet, while the two on the right have been sintered.

Fig. 3.2 shows a STEM images of a typical as-sintered U₃Si₂ pellet. Small UO₂ grains (marked by arrows) and medium size USi grains (relatively darker than U₃Si₂ matrix) coexist with large U₃Si₂ grains in the FIB lamella. This is very consistent with early SEM observation, which showed roughly 84-88 wt.% U₃Si₂, 8-13 wt.% USi and 2-4 wt.% UO₂ determined by XRD. (Harp, 2015) The oxygen was from the surface oxides of powders as well as the O₂ impurity in Ar gas fabrication and sintering environment. The oxidation of U causes the formation of Si-rich USi phases when using U and Si powers in a stoichiometric ratio of U₃Si₂. UO₂ and U₃Si₂ grains are nearly free of defects (Fig. 3.2b) and 3.2d)), while the USi grains show several stacking faults, Fig. 3.2c). (He, 2017) More characterization was done on the U₃Si₂ because of its novel/lab scale fabrication approach compared to the FeCrAl that is a commercially

fabricated product.

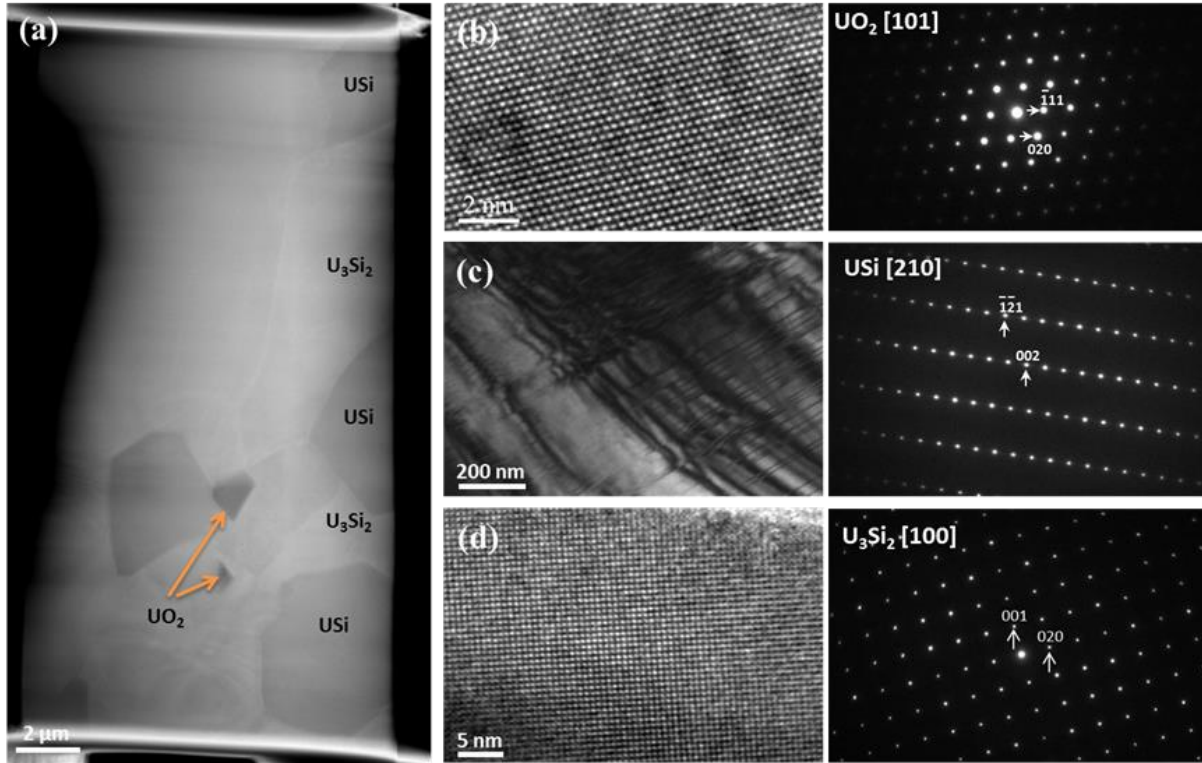


Fig. 3.2 Microstructure of as-sintered U_3Si_2 pellets. **a)** STEM image of a TEM lamella prepared by FIB showing the USi and UO_2 impurity phases in U_3Si_2 matrix. **b)** HRTEM image of a UO_2 grain with the electron beam parallel to the zone axis of $[101]$. **c)** TEM image of stacking faults in USi with the electron beam parallel to the zone axis of $[210]$. HRTEM image of a U_3Si_2 grain with the electron beam parallel to the zone axis of $[100]$. The selected area diffraction patterns of each phase are shown on the right side. (He, 2017)

3.2 FeCrAl Characterization

A rod of FeCrAl, commercially available, was obtained. The specific FeCrAl alloy used was Kanthal APMT, a trademark specific to Kanthal, a Part of Sandvick Group. The APMT is an advanced powder metallurgical dispersion strengthened alloy used for structural parts in high-temperature applications. (Kanthal, 2017) The FeCrAl rod was machined down to the approximate diameter of the

U₃Si₂ pellets, about 8 mm. The approximate composition of the FeCrAl is 70 wt% Fe (66.4 at.%), 22.2 wt% Cr (22.6 at.%), 4.75 wt% Al (9.3 at.%), 3.09 wt% Mo (1.7 at.%), and 0.3 wt% Si (0.6 at.%)

The FeCrAl was sectioned and polished in a similar manner to the U₃Si₂ (Section 3.3) in preparation for placement in diffusion couples. Fig. 3.3 shows preparation steps for the FeCrAl rod. Fig. 3.3a) is the rod after sectioning, while Fig. 3.3b) shows the FeCrAl disks once polished. Fig. 3.3c) is a backscattered electron (BSE) micrograph of a representative area on the FeCrAl disk. EDS revealed the white spots were a Si rich phase while the darker/black regions are an Al rich phase.

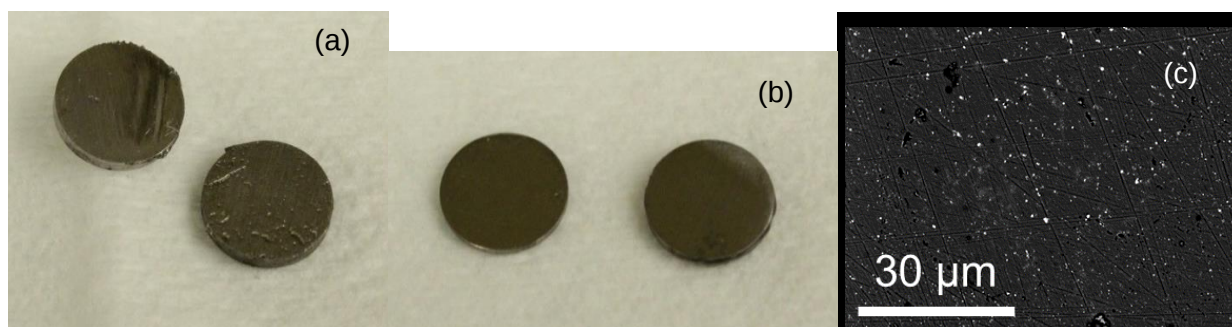


Fig. 3.3 Sectioned FeCrAl disks **a)** after sectioning, **b)** after polishing, and **c)** BSE micrograph.

3.3 Methods

The U₃Si₂ pellets were sectioned into ~2 mm thick disks with a Struers high speed precision saw, Accutom-50, using a cylindrical jig and SiC cut-off wheel, 10S15. The SiC blade was preferable to a diamond blade to get thin sections. The diamond blade tended to bend/flex upon rotation making it hard to determine where it would cut. 3000 rpm with a very slow feed rate (0.003 mm/sec) was used to reduce chipping of the brittle U₃Si₂ material.

Both sides of the disks were polished to mirror finish with a Beuhler EcoMet 250 grinder/polisher prior to diffusion tests. The sectioned disks were mounted using Crystalbond mounting wax onto a metal

cylinder that had raised edges to help keep the samples on the cylinder, and keep all the samples flat as shown in Fig.3.4.

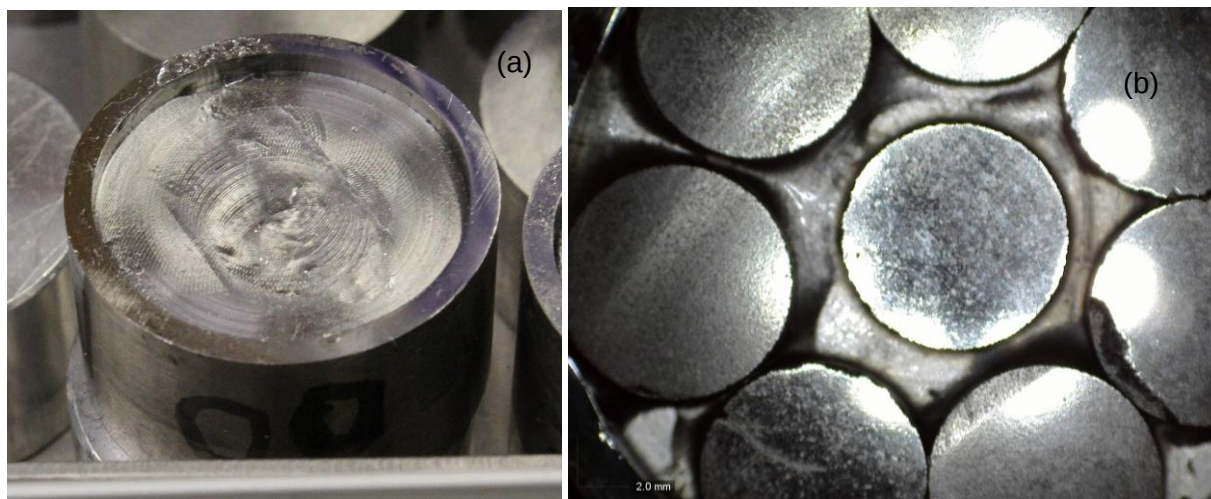


Fig. 3.4 a) Metal cylinder with raised edges used to polish sectioned disks flat. b) U₃Si₂ disks mounted on polishing jig.

Diamond grinding disks were used initially to get a good flatness in successively smaller grits. Then, the disks were polished using diamond paste suspension and polishing cloths recommended for ceramics. The disks were polished down to 1 μm . Polishing was done to maximize the surface area of the material interface, and ensure a good contact between the materials in the diffusion couple.



Fig. 3.5 Diffusion couple, composed of a U₃Si₂ disk surrounded by two FeCrAl disks surrounded by tantalum foil, in first generation Invar alloy jig.

The diffusion couple, composed of a U_3Si_2 disk surrounded by two FeCrAl disks, was fixed in an Invar alloy jig, shown in Fig. 3.5. The material composing the diffusion couple was forced together (hand tightened) in the jig, to replicate the mechanical interaction that would be experienced after time in a reactor do to swelling and creep. Tantalum foils were used to eliminate interaction between the diffusion couple and jig, and to absorb any excess O_2 in the heating process.

The diffusion tests were conducted in a RD Webb “Red Devil” vacuum furnace for 30 h and 100 h at several different temperatures, summarized in Table 3.1.

Table 3.1

Annealing time and temperature of the diffusion couple experiments.

No.	Temperature (°C)	Time (hours)
1.	1000	100
2.	1000	30
3.	800	100
4.	800	30
5.	600	100
6.	500	100
7.	500	30

In order to further prepare the vacuum environment, upon initial pump-down, H/Ar gas was purged into the furnace chamber 3 times. The H gas was used as an O_2 absorber. The vacuum was then allowed to pump down for several hours before heating started. The final pressure inside the furnace during annealing was around 1×10^{-6} Torr. Higher temperatures than are expected during normal operation conditions were chosen for these tests (fuel cladding temperatures of 300-400°C are nominally expected).

This was done both to accelerate any possible diffusion, and to simulate conditions that might occur during a LOCA. Neutron irradiation, and creation of fission products may also accelerate interdiffusion, as some phases of U and Si may become amorphous under irradiation. (Finlay, 2004)³ Thus, it is necessary to test the un-irradiated system at more extreme conditions than expected in operation.

Initially the diffusion couples were removed from the jig after heating, placed in a Beuhler mounting spring, mounted in Beuhler brand EpoThin 2 epoxy resin, and polished for cross section microstructure study. It was found that many of the diffusion couples had a very weak bond or possibly no bonding at all. In an effort to maintain the bond, the entire jig was mounted in epoxy resin and later sectioned for polishing, Fig. 3.6.

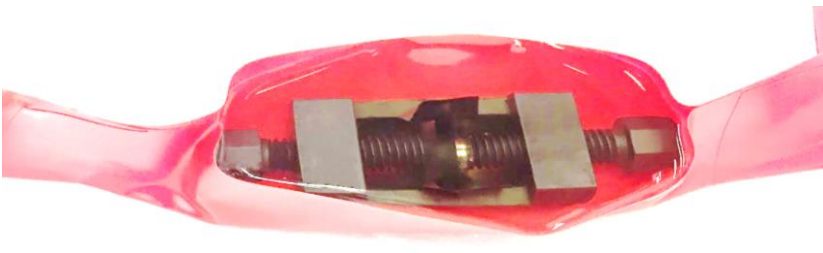


Fig. 3.6 Entire jig mounted in epoxy after annealing, before sectioning.

A third generation jig was fabricated for ease of loading and sectioning, shown in **Fig. 3.7**.

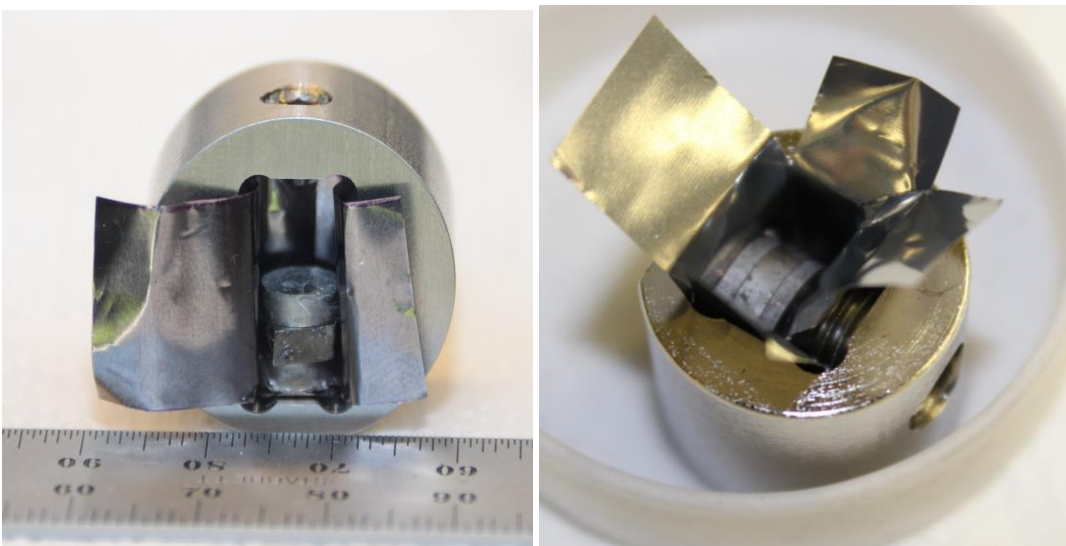
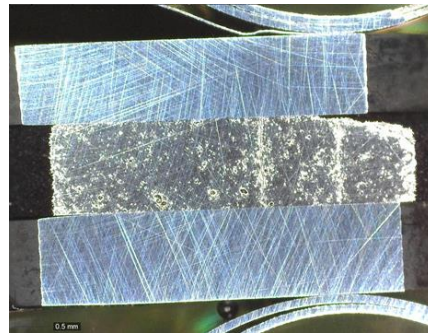


Fig. 3.7 New jig allowing diffusion couple to remain in contact for microscopy preparation, as well as making it easier to load the samples.

The annealed diffusion couple, remaining in the jig, was surrounded in epoxy for stabilization before sectioning.

Some difficulty was encountered when polishing the soft FeCrAl material next to the brittle U_3Si_2 material. The soft material responded to SiC grinding media better than the brittle U_3Si_2 material, so an iteration of both types of media (diamond and SiC) was sometimes necessary, as shown in **Fig. 3.8**.

Fig. 3.8 Example of the FeCrAl- U_3Si_2 diffusion couple system in an early polishing stage. Where the U_3Si_2 has responded favorably to the diamond grinding disks and the FeCrAl requires more iterations to remove scratches.



Diamond grinding disks were used initially to grind down to a representative cross section of the diffusion couple. Special care was taken to avoid excess polishing damage. Bits of U_3Si_2 seemed to pull out of the sample, so cleaning between polishing steps was important to reduce polishing media carry over as well as using an optimized polishing force. Diamond suspension and polishing cloths were used to polish the diffusion couple to a mirror finish, down to $1\text{ }\mu\text{m}$. Some of the diffusion couples were further polished with the use of a vibratory polisher, Beuhler, VibroMet2. Others were further polished by hand to $0.2\text{ }\mu\text{m}$ grit with colloidal silica. Generally, $1\text{ }\mu\text{m}$ finish was sufficient.

The microstructure of the samples after diffusion tests was examined by SEM, STEM, and optical

microscopy. Surface morphologies were evaluated using the JEOL 7600 SEM LEI detector, and phase composition evaluated with the SEM LABE (BSE) detector and Phenom XL with EDS detector. Standardless semi-quantitative EDS equipped on the SEM and STEM was applied to obtain a rough chemical composition of each phase, a concentration profile across the interface, and elemental mapping. Concentration profiles from selected couples were obtained utilizing an accelerating voltage of 20 kV. The material boundaries and diffusion zones, where present, were examined by TEM on selected samples prepared by a dual-beam FIB (Quanta 3D FEG, FEI Company) system. TEM lamellae were created by coarse trenching $20 \times 1 \times 15 \mu\text{m}^3$ samples using the FIB. Samples were thinned in the FIB down to a final milling step of 5 kV at 77 pA ion emission current until small perforations were observed. A 200 kV Titan scanning transmission electron microscope (STEM) equipped with EDS system, was used for structure and composition analysis of diffusion zones.

Concentration profiles across the interface from selected couples were obtained utilizing a (standardless) EDS point-to-point scan with a $\sim 3 - 10 \mu\text{m}$ step size. While a large number of points evaluated can alleviate some of the noise associated with experimental data, Huang, in similar work demonstrated that the number of points does not significantly impact the outcome. (Huang, 2012) However, noise present in the experimental data presents diffusion information that can deviate far from the true diffusion process. (Huang, 2012) Noise in the data comes from both low accuracy EDS measurements on low concentration elements in the system as well as EDS line point analysis on points that land on a precipitate or secondary phase in the system that producing an non representative composition at that point..

4.0 Results

The average width for the total interdiffusion layer thickness of each diffusion test are listed in Table 4.1. The measured thickness may have been slightly skewed by the fact that when the diffusion couples were sectioned and prepared for examination they may not have been sectioned at an angle perfectly perpendicular to the plane, making the diffusion zone appear slightly larger. Every effort was made to achieve a surface perfectly perpendicular to the interface, however, there may have been slight deviation from this as a result of sectioning and sample preparation. The thickness measurement was made by averaging multiple point to point distances on backscattered electron micrographs of the diffusion zone with image analysis software. Diffusivity calculations from SEM EDS composition data were carried out on the higher temperature tests.

Table 4.1

List of diffusion couple experiments with annealing time, temperature, and average total interaction zone.

Number	Temperature (°C)	Time (hours)	Width of reaction layer (μm)
1.	1000	100	110.7 ± 3.5
2.	1000	30	65.2 ± 2.9
3.	800	100	NA
4.	800	30	13.2 ± 1.7
5.	600	100	3.0 ± 1.1
6.	500	100	NA
7.	500	30	0

4.1 1000 °C 100 h

This diffusion couple was loaded into the new style jig, section 3.0. Observation with the optical microscope showed porosity develop in the fuel matrix, Fig. 4.1. Complete characterization of this U_3Si_2 fuel form is ongoing at present, and the possible development of porosity at high temperatures for long hold times was not investigated here. This optical image shows a combination of both porosity and polishing induced material pull-out. A diagonal crack across the fuel should not be seen as a result of diffusion. This is most likely a result of force from the jig upon tightening, or from sample preparation.

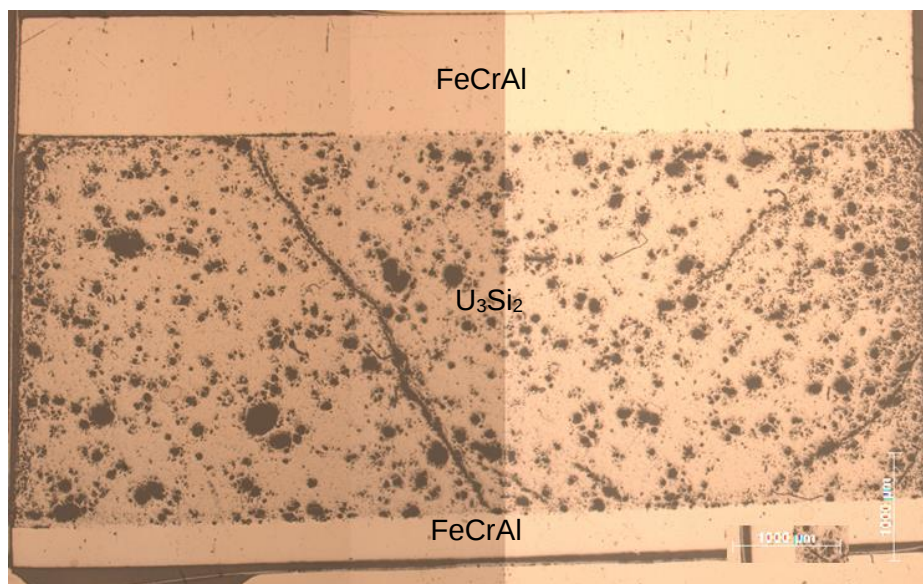
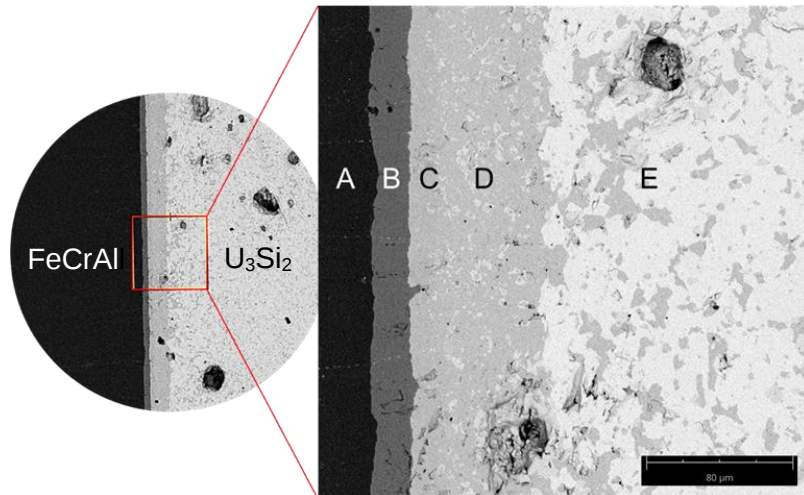


Fig. 4.1 Optical image of entire area of diffusion couple annealed at 1000 °C for 100 h at 25x magnification.

Microstructural analysis of the diffusion couple revealed an excellent bond formation at the interface after annealing. The diffusion zone was also visible with the optical microscope at 200x magnification. As seen in Fig. 4.2, the thickness and interface between two of the phases are mostly uniform and planar, respectively. This is further illustrated with EDS mapping, Fig 4.3 b-h), showing an intensity concentration of each major constituent element and a qualitative composition of each interaction layer.

Fig. 4.2

Backscatter electron micrograph of diffusion zone in couple annealed at 1000 °C for 100 h. Each layer is labeled A-D, and an average composition of each layer is given in Table 4.2.



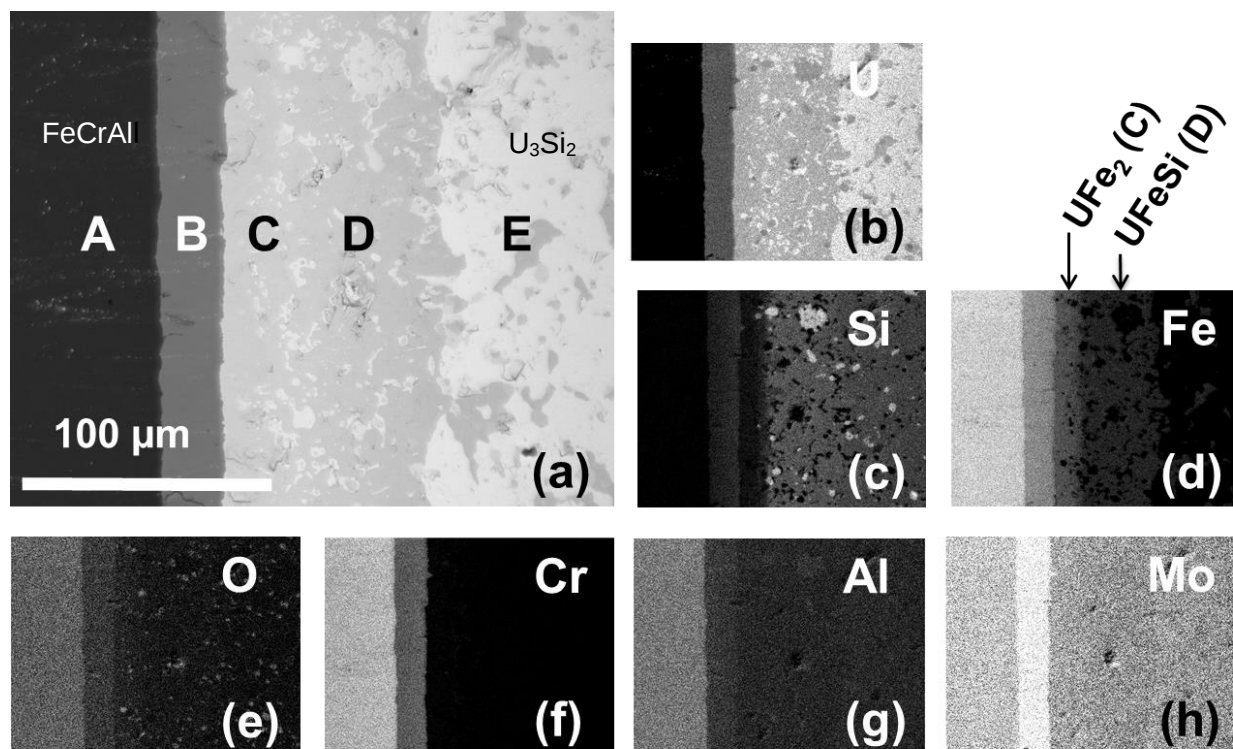


Fig. 4.3 a) SEM backscattered electron micrograph of a diffusion couple heated at 1000°C for 100 h labeled A-E with the A layer the FeCrAl side of the diffusion couple and the E layer the U_3Si_2 side of the diffusion couple. **b-h)** are the elemental composition intensity maps for each of the major constituents with whiter hue indicating higher concentration and blacker hue indicating lower concentration.

The map for Fe, Fig. 4.3d), shows the presence of the C layer most obviously, as this layer was very subtle in the rest of the maps and images. The C layer contains $\text{U}_2\text{Fe}_3\text{Si}$ and UFe_2 based on EDS. TEM analysis on similar structures in section 4.4 confirm the UFe_2 phase. The implications of this interdiffusion layer are discussed in section 5. The Fe map also shows Fe rich phases penetrating further back into the fuel matrix. EDS quantification confirms the composition of the iron rich phase to be a U-Fe-Si phase. The D layer contains a main UFeSi phase along with other U-Fe-Si phases and UO_2 and U-Si impurities from the original composition of the as-sintered U_3Si_2 . The U map, Fig. 4.3b), shows some penetration of U into the B layers as well as a few tiny white specs back into the FeCrAl. EDS

quantification, discussed below, indicates these features were U_6Fe . This U map, Fig. 4.3b), along with the Cr and Al maps, Fig. 4.3f) and 4.3g) respectively, and the BSE micrograph, Fig. 4.3a), give a good indication the original material interface was likely between the C and D layers. This assumption is strengthened by diffusion couples annealed in the original style jig at lower temperatures where the interdiffusion layers had started to form before losing contact between those layers. The Cr map and composition is similar to that seen in similar alloy systems, reported by Huang. The Cr increasing gradient between the B and C layers correlates with Fe depletion resulting from faster diffusion of Fe into U, this Cr gradient has been observed in similar systems containing those elements. (Huang, 2012) The silicon map, Fig. 4.3c), shows Si rich phases within the U_3Si_2 , as expected from the original fuel composition. The Si map shows the C layer depleted of Si, and Si migration into the B layer. This is also shown in the concentrations listed in Table 4.2. The Mo map, Fig. 4.3h), shows an elevated concentration of Mo in the B layer. This shows a higher composition in the interaction zone than for the original material, indicating Mo diffusion towards the U_3Si_2 . Both Fig. 4.3h) and 4.3g) show Mo and Al, respectively, across the entire area which is an artifact of the small signal reading making their results somewhat unreliable.

Table 4.2 below indicates the average thickness and elemental composition of each layer. Three interdiffusion layers can be discerned in Fig. 4.4a), a concentration profile that shows the atomic percent of each element with respect to an EDS line point spectra perpendicular to the material interface, the x axis. The line is composed of 58 points every 3 μm . The element profiles illustrate the concentration gradients in both the B and C layer. The concentration profile also includes slight false gradients at the layer interfaces as a result of the interaction volume of the electron beam at the neighboring phases. The inhomogeneity in each layer causing the composition profiles to not be smooth is a result of secondary phases within an otherwise homogenous matrix. Diffusion flux, calculated from the concentration profile with the B-M method, Equation 2, in Fig. 4.4b) shows U and Fe with the highest flux, proportional to the atom percent in the system. The highest flux also corresponds with the region of the C layer.

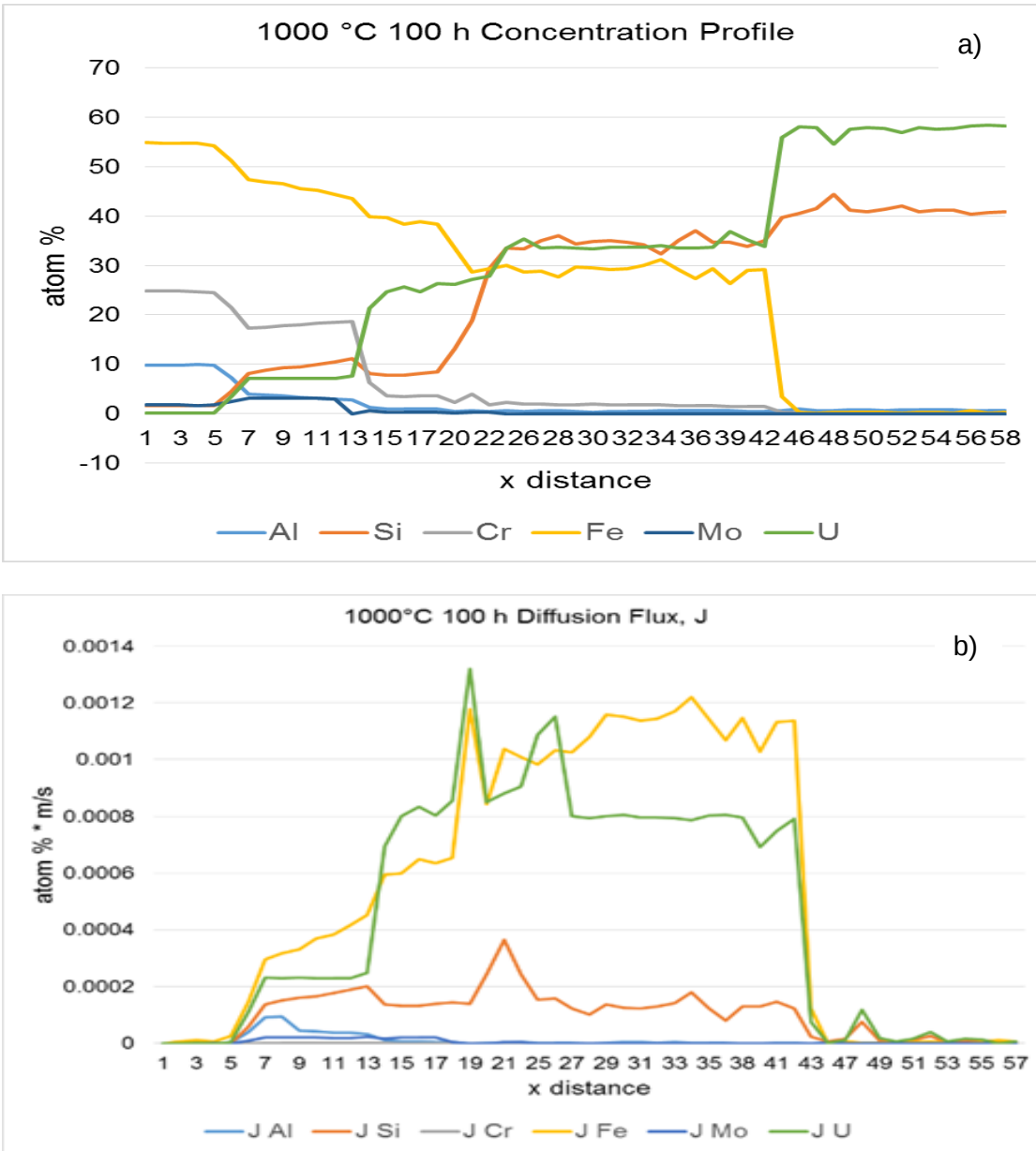


Fig. 4.4 a) 1000°C 100 h composition profile of each major element in the system from points perpendicular to the material interface given in atom percent. **b)** Corresponding diffusion flux calculated from the B-M method.

To employ the S-F method of diffusion parameter calculation the relative concentration variable, Y , must be calculated. The S-F method's relative concentration variable is plotted in Fig 4.5 for the

1000°C 100 h test. The large anomaly for Mo is a result of the increase composition in the diffusion zone, an indication of concentration in that region. As discussed in section 2.3, the advantage of the Y vs. x plot is that the composition profile of all the diffusion couple components are displayed over the diffusion zone $-L$ to $+L$ such that Y is 0 at $-L$ and 1 at $+L$ for all components regardless of their flux directions within the diffusion zone. (Dayananda, 2006)

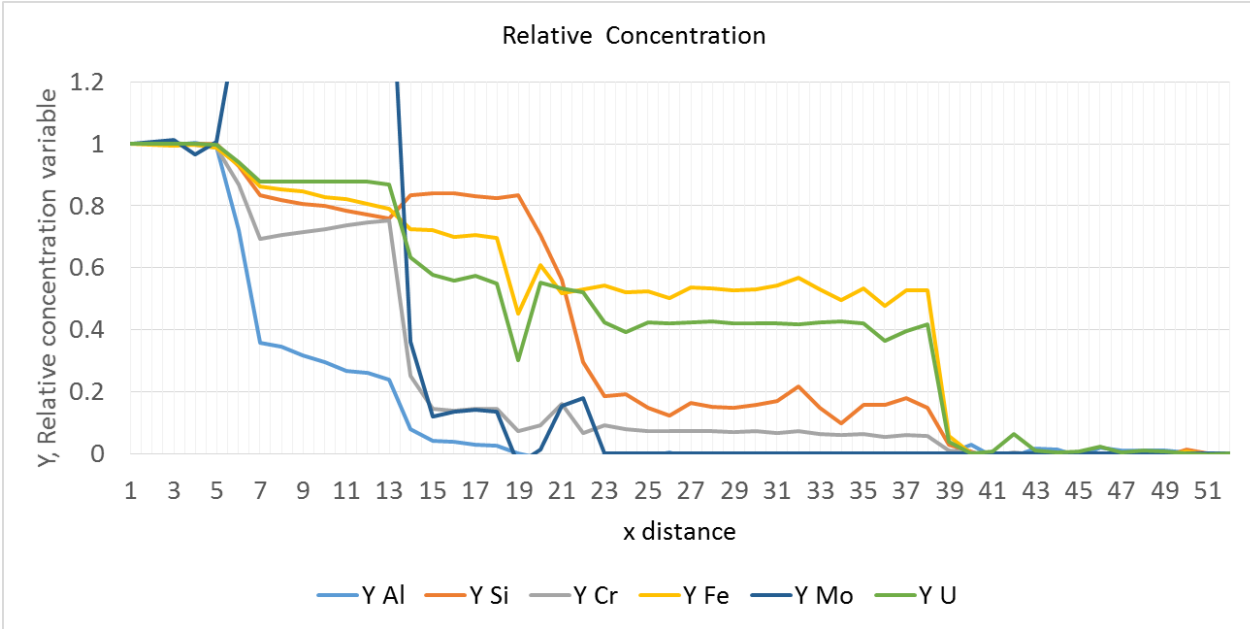


Fig. 4.5 Relative concentration variables for the interdiffusion zone of the diffusion couple heated to 1000 °C for 100 h plotted with respect to position perpendicular to the material interface across the interaction region, used to calculate chemical diffusivity with the S-F method.

The diffusivity for the major components in the system were calculated using both the S-F and B-M methods, assuming constant molar volume and disregarding the Fe and U phases present far back into the matrix of the terminal ends of the system. Diffusivity values comparing the two methods were plotted with respect to elemental composition in atomic percent in Fig 4.6.

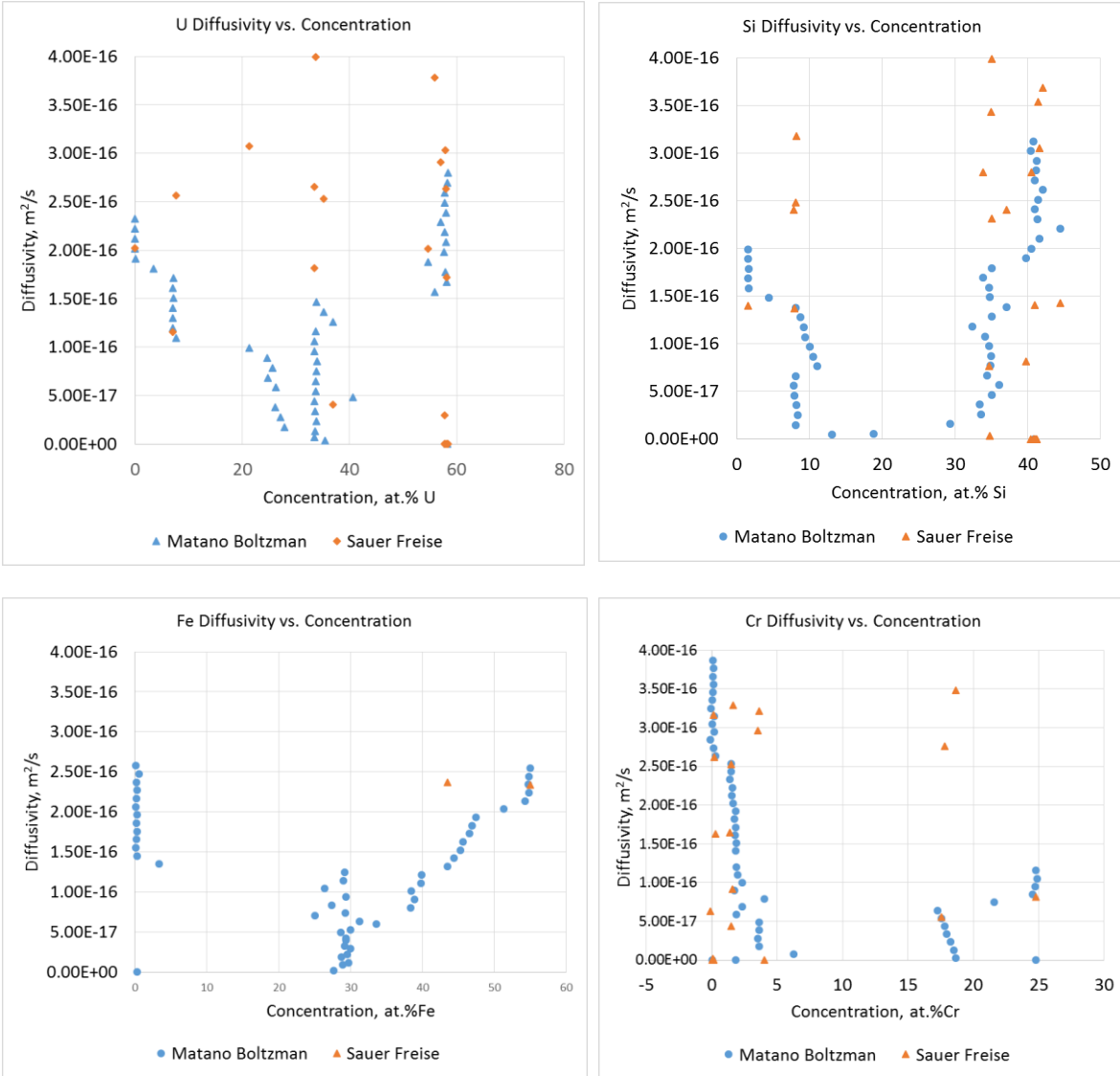


Fig 4.6 Diffusivity values for the diffusion couple heated to 1000 °C for 100 h calculated with both the B-M and S-F methods for major elements in the system plotted with respect to atomic percent.

C_L from the notation in Section 2.3 is the composition of the FeCrAl, and C_R is the composition of the U_3Si_2 . The comparison between values from each method of calculation were expected show good agreement, as both are derived from Fick's law. However, differences arose from uncertainty in determining the Matano plane from experimental data, as described in section 2.3 and taking the molar volume change as 0. The location of the Matano plane, calculated individually for each component in the

system from equation 3 are shown in Fig. 4.7. The low atomic percent of Mo in the system makes its concentration values unreliable and calculating an accurate position of its Matano plane impossible.

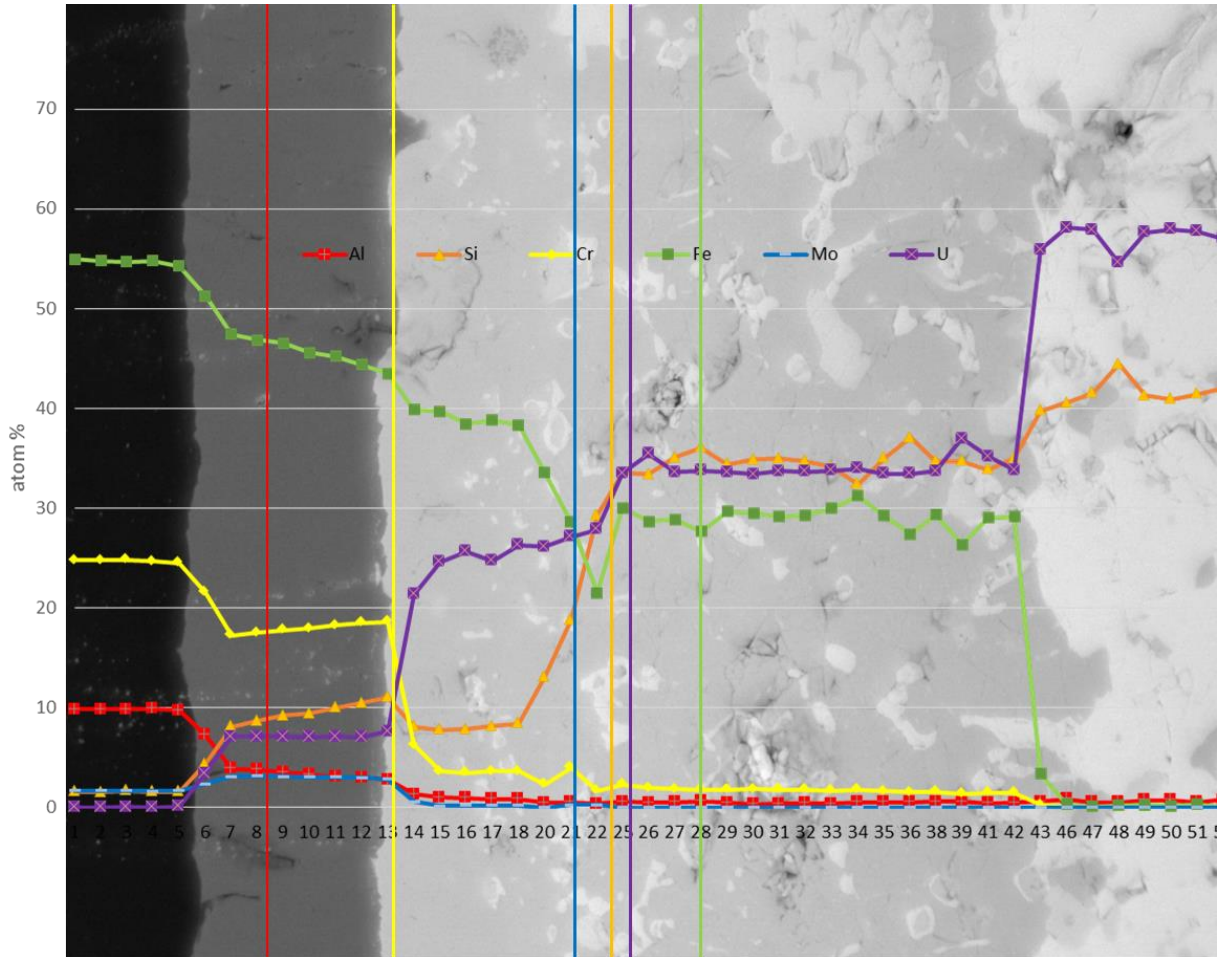


Fig. 4.7 Calculated location of the Matano plane represented by solid vertical lines for each element in the system from the composition profile in atom % overlaid on the SEM BSE micrograph near where the actual data was collected.

If the concentration gradients in each phase are considered negligible due to noise in the data, a simplified composition profile and therefore simplified flux profile can be displayed. False gradients at the interfaces may be a result of the interaction volume of the electron beam at the sample interphase that compose the two neighboring phases. A modified concentration profile, Fig 4.8a), and corresponding

calculated diffusion flux, Fig. 4.8b), for each element in the system was constructed from seven EDS line spectra, each about 20 individual points, taken parallel to the material interface and averaged. The concentration differences in these parallel lines were negligible except when a point landed on a secondary phase within the layer matrix. From this data, summarized in table 4.2, it was determined that layer C was likely $\text{U}_2\text{Fe}_3\text{Si}$ with some UFe_2 regions. This UFe_2 phase was later confirmed with TEM characterization, section 4.2. Both false and actual concentration gradients were eliminated in the modified profile, but are clearly seen in both the map, Fig. 4.3, and original concentration profile, Fig. 4.4a). Layer D has a primary matrix UFeSi with other U-Fe-Si and U-Si phases. The interdiffusion layer matrix composition is illustrated nicely in the modified concentration profile, Fig. 4.8a).

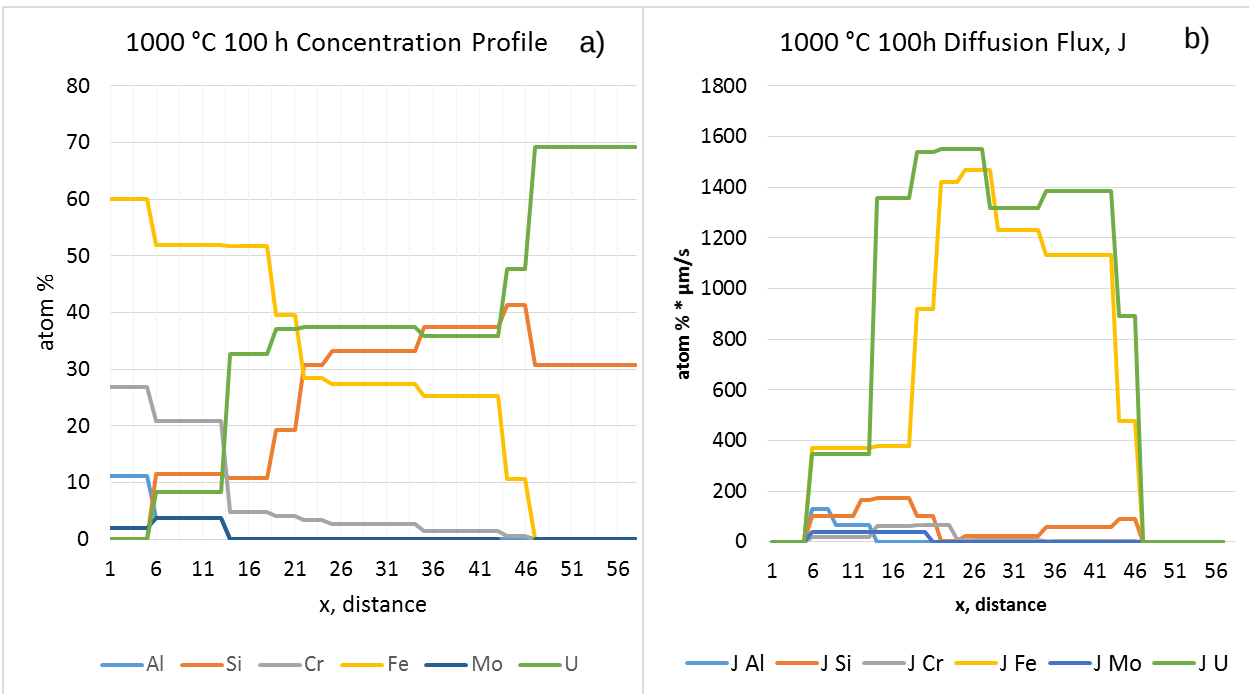


Fig. 4.8 a) A modified composition profile of each major element in the system from points perpendicular to the material interface given in atom percent and **b)** corresponding diffusion flux calculated from the B-M method of the interdiffusion zone of the diffusion couple heated at 1000 °C for 100 h.

Table 4.2**Width and elemental composition of layers in 1000 °C 100 h diffusion couple.**

Layer	FeCrAl (A)		B Fe-Cr-Si-U-Al-Mo		C U ₂ Fe ₃ Si/UFe ₂		D UFeSi		U ₃ Si ₂ (E)	
Width			25.8 ± 1.9 μm		19.1 ± 1.1 μm		67.4 ± 4.7 μm			
	Normalized Percent Composition									
	wt.	at.	wt.	at.	wt.	at.	wt.	at.	wt.	at.
U	0	0	46.6	8.3±0.28	68.2	32.9±1.5	90.5	37.7±7.2	96.6	57.6±1.7
Fe	61.8	59.1±0.2	33.0	52.3±1.7	26.0	51.2±1.1	6.0	30.7±6.5	0.43	0.4±0.1
Cr	27.9	26.5±0.1	11.5	20.7±0.7	2.5	4.9±0.3	0	0	0	0
Al	4.9	10.7±0.2	1.2	3.9±0.5	0	0	0	0	0	0
Si	1.0	1.8±0.2	2.8	11.2±1.5	3.2	11.1±0.9	3.5	31.6±6.8	3.01	42.0±1.6
Mo	4.3	1.9±0.0	4.9	3.7±0.1	0	0	0	0	0	0

Along the right side of layer C a U-Fe-Si-Cr phase, similar to the composition of layer B developed in some sections of the diffusion couple, Fig. 4.9. Several EDS point spectra were gathered on these areas with very similar results. The average compositions in wt. % was U: 77.93, Fe: 16.56, Si: 3.37, and Cr: 2.24. There was also some W formation along the left side of the D layer, seen in Fig. 4.8. This W formation was also observed in the 800 °C 30 h diffusion couple, section 4.2, where a detailed STEM analysis confirmed the presence of W.

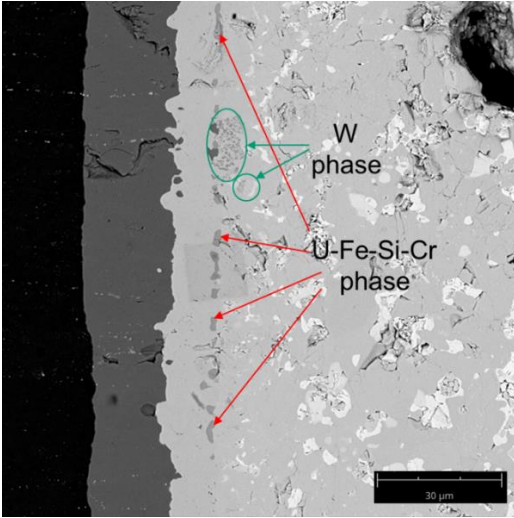


Fig. 4.9 Backscatter electron micrograph of diffusion couple annealed at 1000 °C for 100 h highlighting features along the C-D boundary.

In tests heated to 800 °C and higher, U rich spots are visible in the FeCrAl section, layer A, and also slightly visible in layer B, Fig. 4.3a). Characterization of pristine FeCrAl showed the presence of Si rich white spherical spots homogenously dispersed, Fig. 3.3c). The spots containing U or Si have a similar appearance in BSE images of diffusion couple tests. Elemental composition was only achieved with EDS measurements. An example of this EDS analysis is provided in Fig. 4.10. Lighter colored features were present in the diffusion couples at lower temperatures, but do not necessarily have U in them, as was explained in section 3.2 for the diffusion couple heated to 600 °C for 100 h.

Element Symbol	Atomic Conc.
U	23.36
Fe	20.99
O	37.35
Cr	8.94
Al	9.36

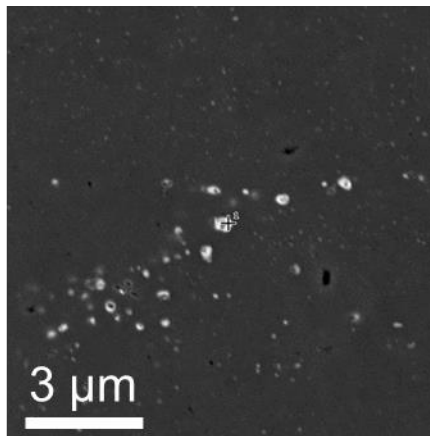


Fig. 4.10 Composition of U phase in FeCrAl material of diffusion couple heated to 1000 °C for 100 h.

Because the spots are submicron size, the point quantification includes information about material surrounding the spot as well. When the FeCrAl composition is subtracted from the gathered composition

the spots appear to be U_6Fe . U_6Fe is liquid down to $719^{\circ}C$ according to the U-Fe binary phase diagram, Fig. 2.2, and is the least stable phase in the U-Fe system. There is an allotropic phase transformation from alpha U to beta U at $668^{\circ}C$ that is likely a factor in the growth of this U_6Fe phase. (Huang, 2012)

EDS spectra gathered near the center of the U_3Si_2 disk, the point farthest away from the FeCrAl, showed an Fe rich phase, with a composition resembling that of U_2FeSi_3 , that permeated the fuel. A phase containing Fe was observed via SEM in diffusion couple tests down to the $800^{\circ}C$ with the percent Fe in the fuel matrix for each test increasing with increasing heating temperatures, as expected. As stated in the theory section 2.3, initial boundary conditions for calculating the chemical diffusivity require the terminal ends of the system be unaffected by the diffusion process. This boundary condition was not met, and further studies would need to increase the thickness of the material or decrease the test duration in order to properly calculate the interdiffusion parameters for the system. An approximation of the diffusivity localized to the interdiffusion layer region was calculated instead.

4.2 1000 °C 30 h

An optical image of diffusion couple heated at $1000^{\circ}C$ for 30 h reveals an excellent bond formation at the interface after annealing. However, the existence of a reaction zone was not continuous along the interface, as shown in Fig. 4.11.

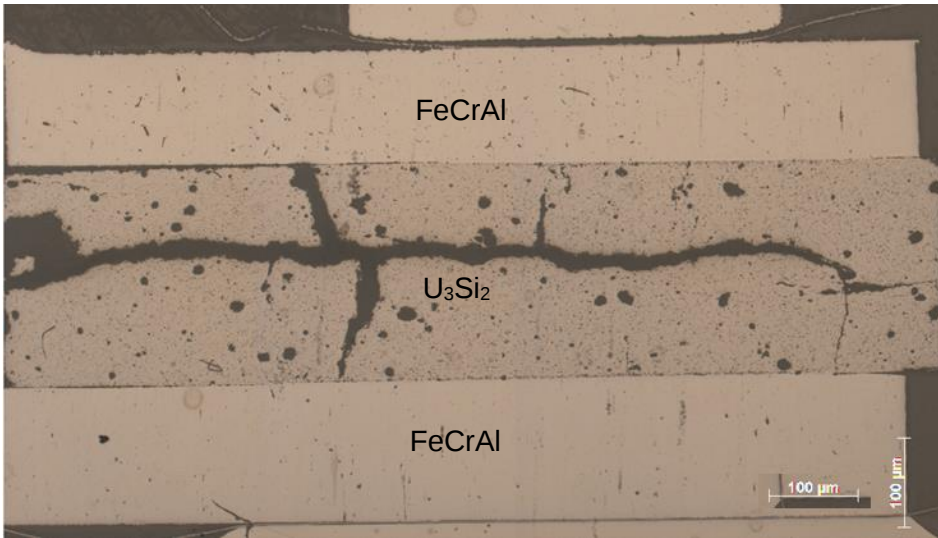


Fig. 4.11 Optical image of diffusion couple annealed at 1000 °C for 30 h.

Along the U_3Si_2 side of the original interface a row of porosity developed, and can be seen in both optical and electron images, Fig. 4.12 a,b). The observed porosity is thought to be a general phenomenon of the diffusion process, known as Kirkendall porosity, described in section 2.3. (Seitz, 1953) This pore formation was only observed in the test at 1000 °C for 30 h, but may be an indication of the atomistic diffusion process taking place in the U_3Si_2 - FeCrAl system.

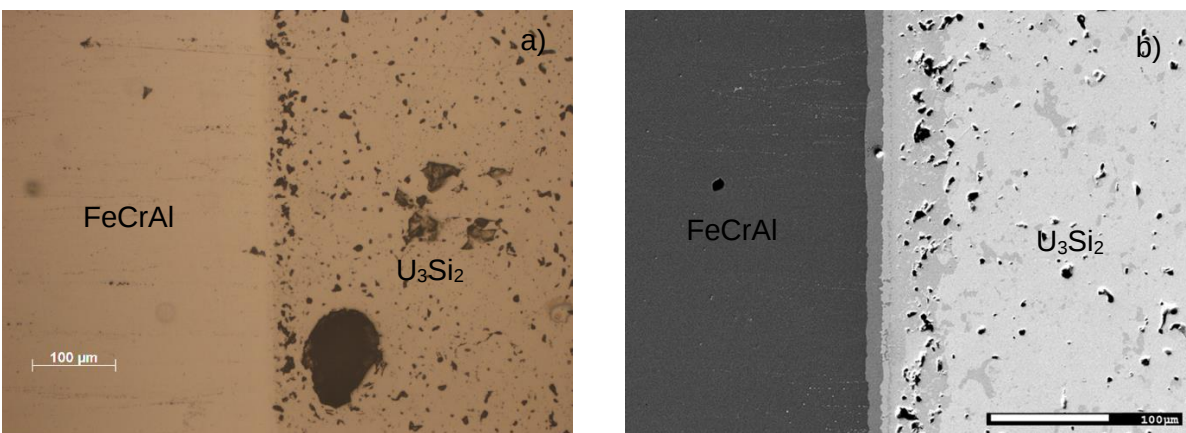
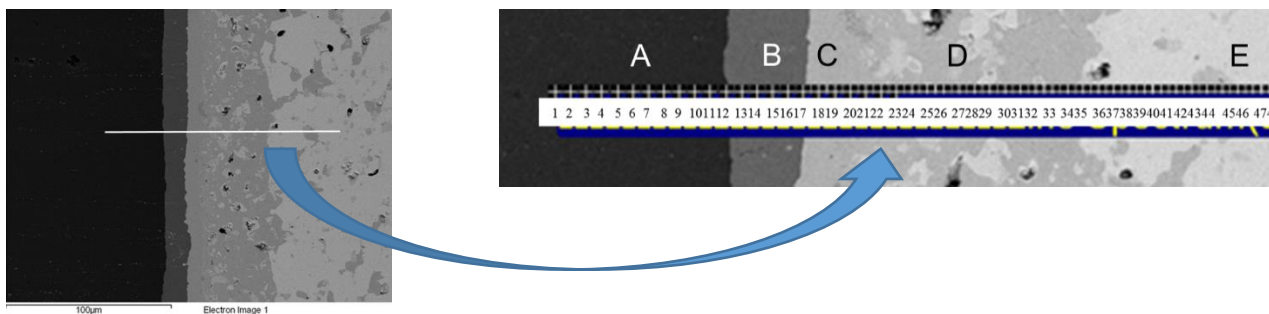


Fig. 4.12 Kirkendall porosity in diffusion couple annealed at 1000C for 30 h. **a)** Optical image **b)** SEM backscatter micrograph taken on a similar location on the diffusion couple.

In the region of interaction three distinct interdiffusion zones were identified, similar to the diffusion couple annealed at the same temperature for 100 h. The thickness of interaction layers were uniform and the interface between each layer were planar. An EDS map of the interdiffusion zone is provided in Fig. 4.13 with the top right image in the figure labeled with the numbered location of the EDS point spectra and labels A through E to identify the interdiffusion layers. Layer A is the FeCrAl side of the diffusion couple and Layer E, the U_3Si_2 , is on the opposite side, with the interaction layers labeled B, C, and D in the middle. Fig. 4.13 is very similar to Fig. 4.3 and is included here to show the proportional increase in diffusion layers resulting from time at temperature. A quantitative comparison is also provided in Tables 4.2 and 4.3 where the measured thickness of individual diffusion layers are provided.

The concentration profile, Fig. 4.14a), derived from the EDS point spectra labeled in Fig. 4.13; corresponding diffusion flux profile, Fig. 4.14b); and calculated chemical diffusivities (as a function of concentration), Fig. 4.15, were plotted and included here for comparison to the same test run for a longer heating time described in section 4.1. The agreement between calculation methods for the diffusivity values was much better for the 30 h test than the 1000 °C test. The diffusivity values were all in the range of 10^{-14} m²/second on the 30 h test.



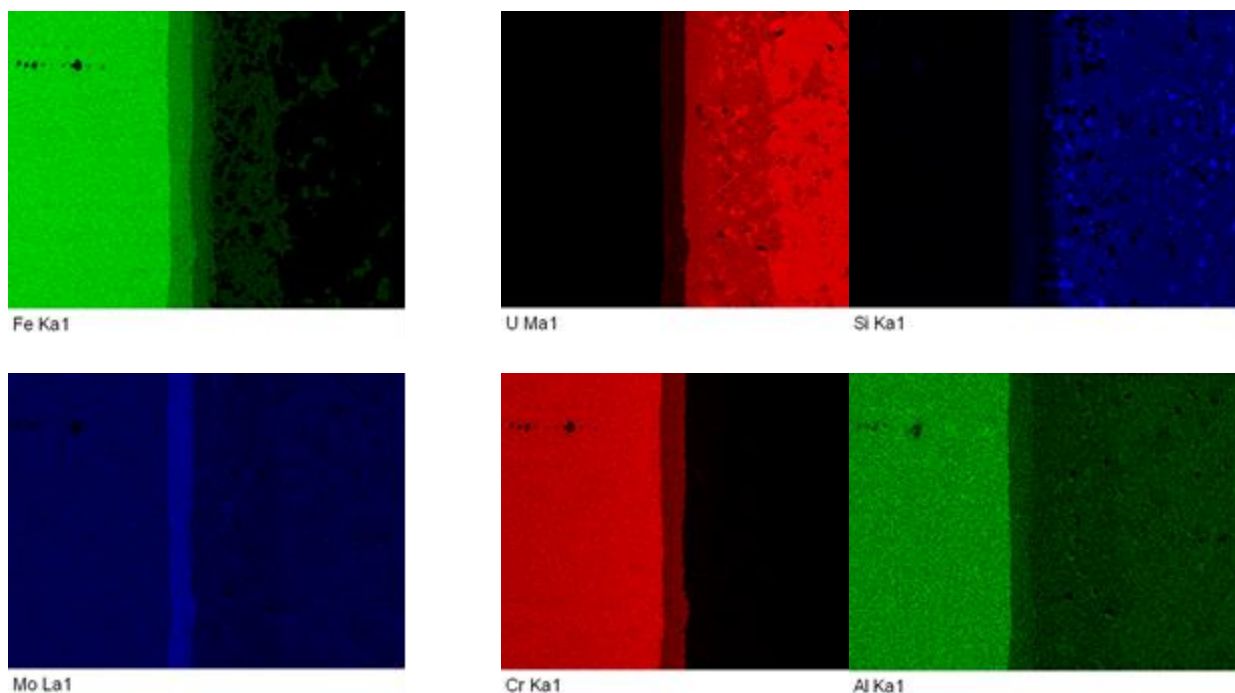


Fig. 4.13 A secondary electron micrograph of a diffusion couple annealed at 1000 °C for 30 h with the intensity map for U, Si, Fe, Cr, Al, and Mo. The lighter hue indicates higher concentration.

Table 4.3

Width and elemental composition of layers in 1000 °C 30 h diffusion couple.

Layer	FeCrAl (A)		B Fe -Cr-Si -U- Al-Mo		C U ₂ Fe ₃ Si/UFe ₂		D UFeSi		U ₃ Si ₂ (E)	
Width			13.7 ± 1.3 μm		9.9 ± 0.9 μm		40.9 ± 3.1 μm			
	Normalized Percent Composition									
	wt.	at.	wt.	at.	wt.	at.	wt.	at.	wt.	at.
U	0	0	29.5	8.4±0.1	70.0	32.6±1.2	76.3	35.3±1.2	92.5	58.8±1.1
Fe	63.1	60.1±1.6	43.5	52.7±1.2	24.5	50.5±3.2	15.2	29.8±.6	0	0.3±0
Cr	26.1	26.3±1.0	15.8	20.6±0.4	2.4	5.4±0.7	0	0	0	0
Al	5.6	1.2±0.6	1.7	4.1±0.2	0	0	0	0	0	0

Si	3.5	1.6±0.2	4.5	10.7±0.8	3.0	10.3±0.4	8.4	34.9±0.9	7.5	40.9±1.5
Mo	0.8	1.9±0.0	5.1	3.7±0.1	0	0	0	0	0	0

Table 4.3 lists the composition, reported in both weight and atom percent. The results are an average of a semi-quantitative EDS 50 point spectra that was taken on this diffusion couple over the range of interaction indicated on the top right image in Fig. 4.13 perpendicular to the material interface.

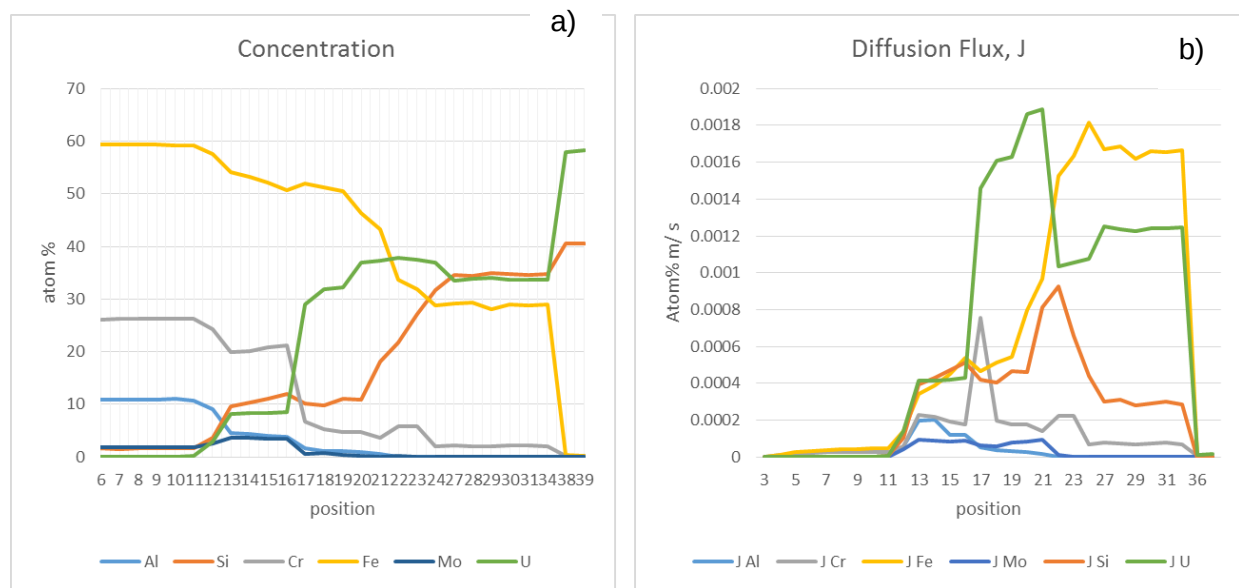


Fig. 4.14 a) Concentration plot for diffusion couple annealed at 1000 °C for 30 h, and the **b)** corresponding diffusion flux on the right.

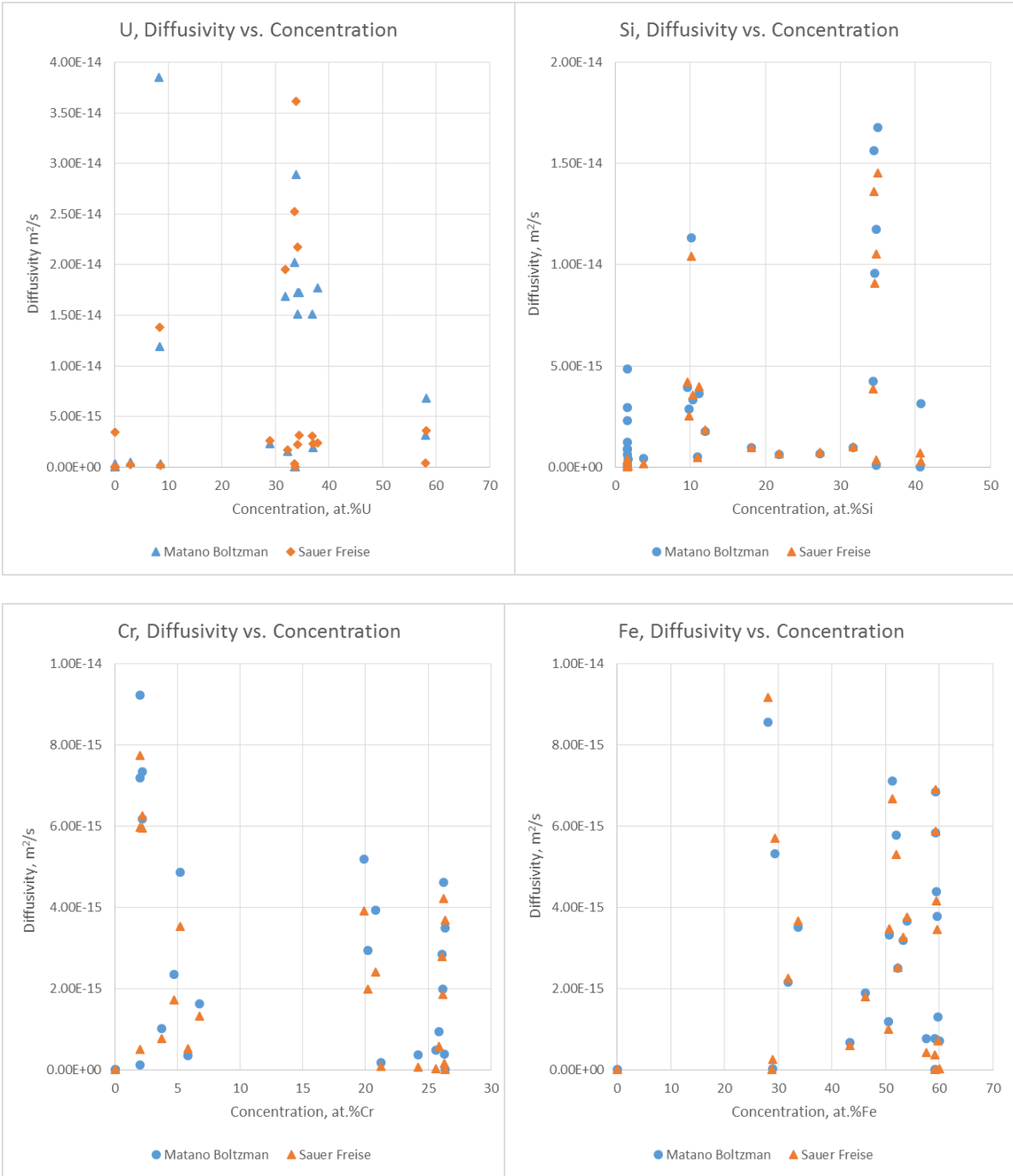


Fig. 4.15 Comparison of diffusivity calculations with respect to concentration using B-M and S-F methods for the diffusion couple heated to 1000 °C for 30 h.

4.3 800 °C 100 h

A diffusion zone was observed with the SEM in a small section where the diffusion couple maintained contact. A line scan and intensity profile with EDS, Fig. 4.16, showed that a small amount of diffusion occurred and that it followed the same basic intensity/diffusion pattern as what was seen in the 30 h test at the 800 °C.

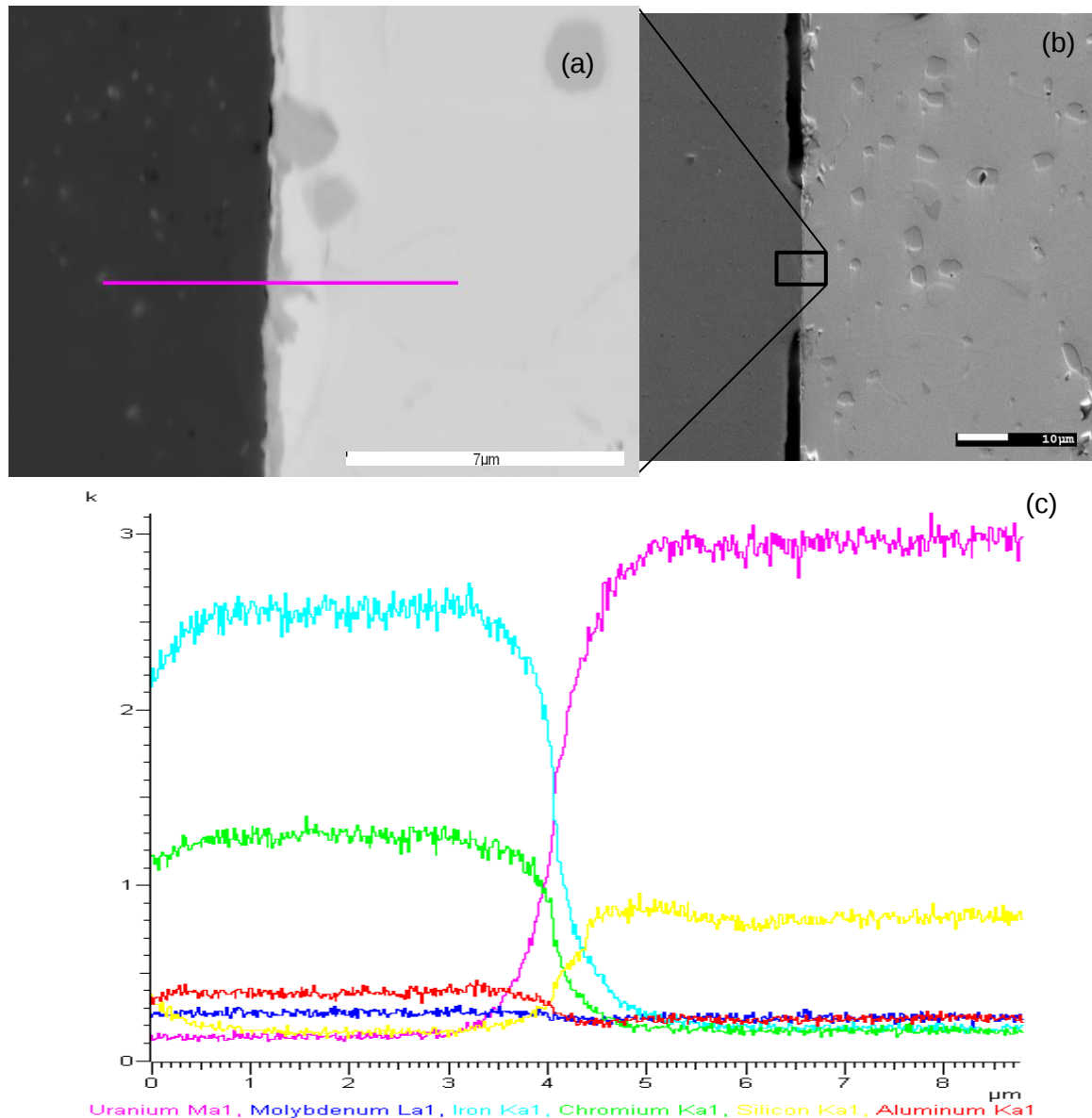


Fig. 4.16 EDS line scan and intensity profiles from a diffusion couple annealed at 800 °C for 100 h. a) Enlarged backscatter electron micrograph of the contact/interaction zone with a pink horizontal line indicating where the measurement was taken. b) SEM BSE image of the contact zone. c) EDS intensity profile for the constituent elements: U, Mo, Fe, Cr, Si, and Al.

The average diffusion zone was about 4 μm wide. Another section in the diffusion couple, where the materials had lost contact at some point, showed some slight diffusion, Fig. 4.17. The longer annealing time should be associated with a greater diffusion zone, but in this instance the poor diffusion was a result of poor contact in the old style jig during annealing.

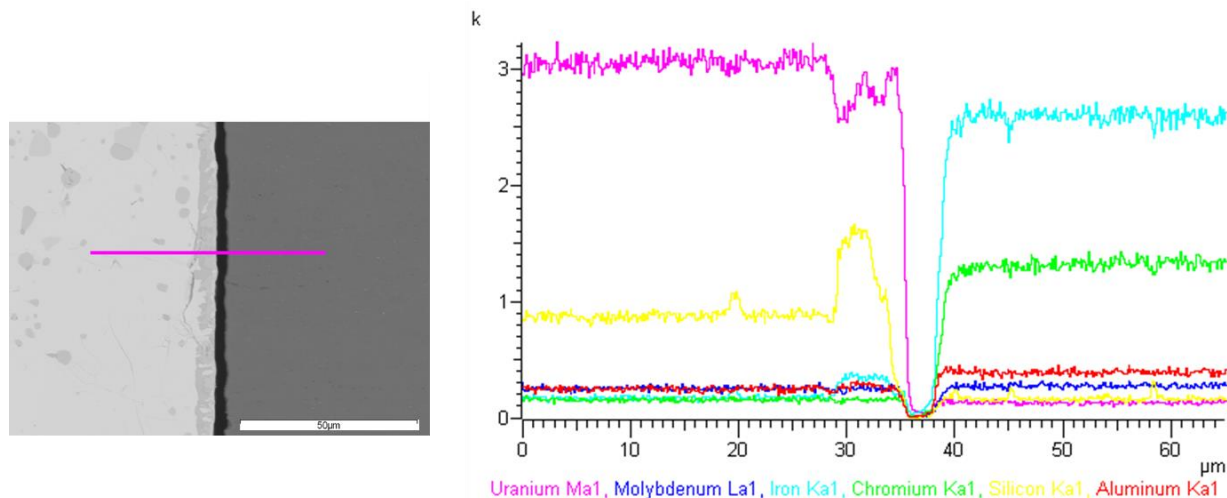


Fig. 4.17 EDS line scan and intensity profiles from a diffusion couple annealed at 800 $^{\circ}\text{C}$ for 100 h. SEM BSE micrograph of the diffusion zone with a pink horizontal line indicating where the measurement was taken. EDS intensity profile for the constituent elements: U, Mo, Fe, Cr, Si, and Al

The material interface edge of the U_3Si_2 had accumulated a silicon rich phase as well as an oxygen rich phase, shown in Fig. 4.18. Point quantification using EDS distinguishes the USi and UO_2 . The region labeled with an X is 3.13 O, 0.17 Al, 14.54 Si, 0.15 Cr, 5.90 Fe, and 76.12 U in weight percent, and possibly correlates to a U – Fe – Si intermetallic compound.

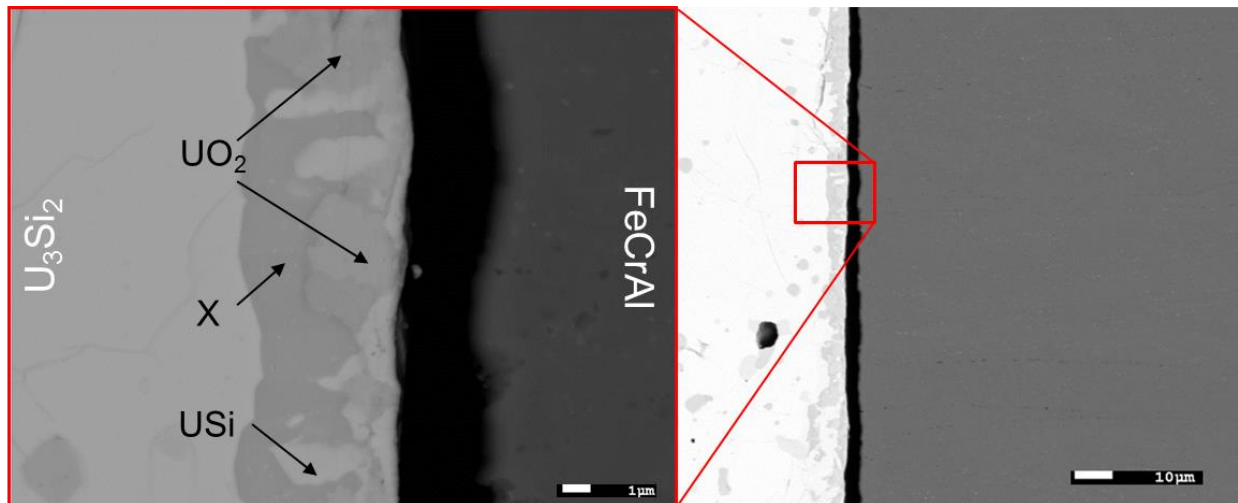


Fig. 4.18 SEM BSE micrograph of the material interface in the diffusion couple annealed at 800 °C for 100 h.

4.4 800 °C 30 h

A diffusion zone, with an average width of 13.2 μm , shown in Fig. 4.19, was identified using an SEM BSE detector. The interaction zone was only present on one side of the diffusion couple, and only for a section in the middle. The disruption from mounting seems to have broken the bond that occurred in the diffusion zone. The diffusion couple likely separated at the original material interface.

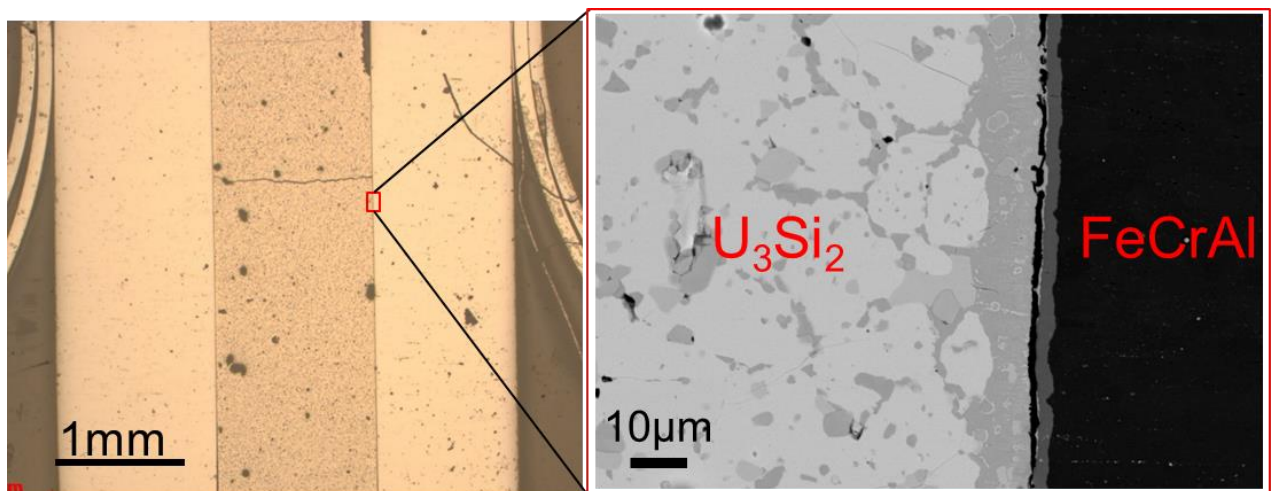


Fig. 4.19 The picture on the right is an optical image of the polished diffusion couple annealed at 800 °C for 30 h. The enlarged portion shows the diffusion zone detected with SEM, depicted with a backscatter electron micrograph.

An SEM EDS scan along the line XY, Fig. 4.20, and mapping, Fig. 4.21, shows an iron rich phase penetrating into the fuel matrix, also some penetration of U and Si into the FeCrAl. The Si and O rich phases within the U_3Si_2 illustrated in the Si and O maps are a characteristic of the as sintered fuel. Cr was fairly stable with a slight amount of diffusion toward the fuel.

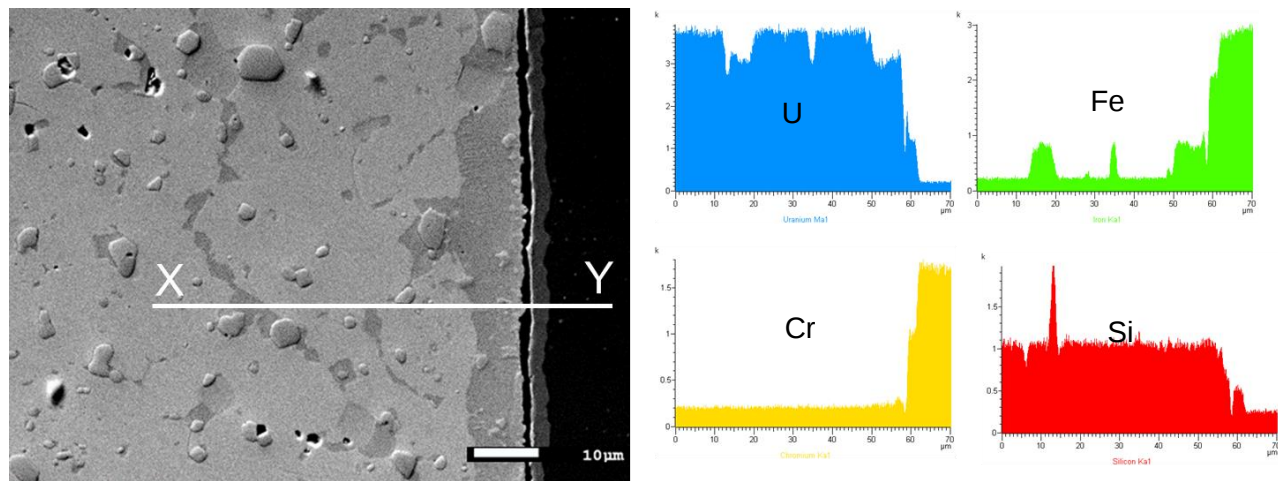


Fig. 4.20 SEM BSE of a diffusion couple annealed at 800 °C for 30 h with the intensity profile for U, Fe, Cr, and Si recorded along the line labeled XY.

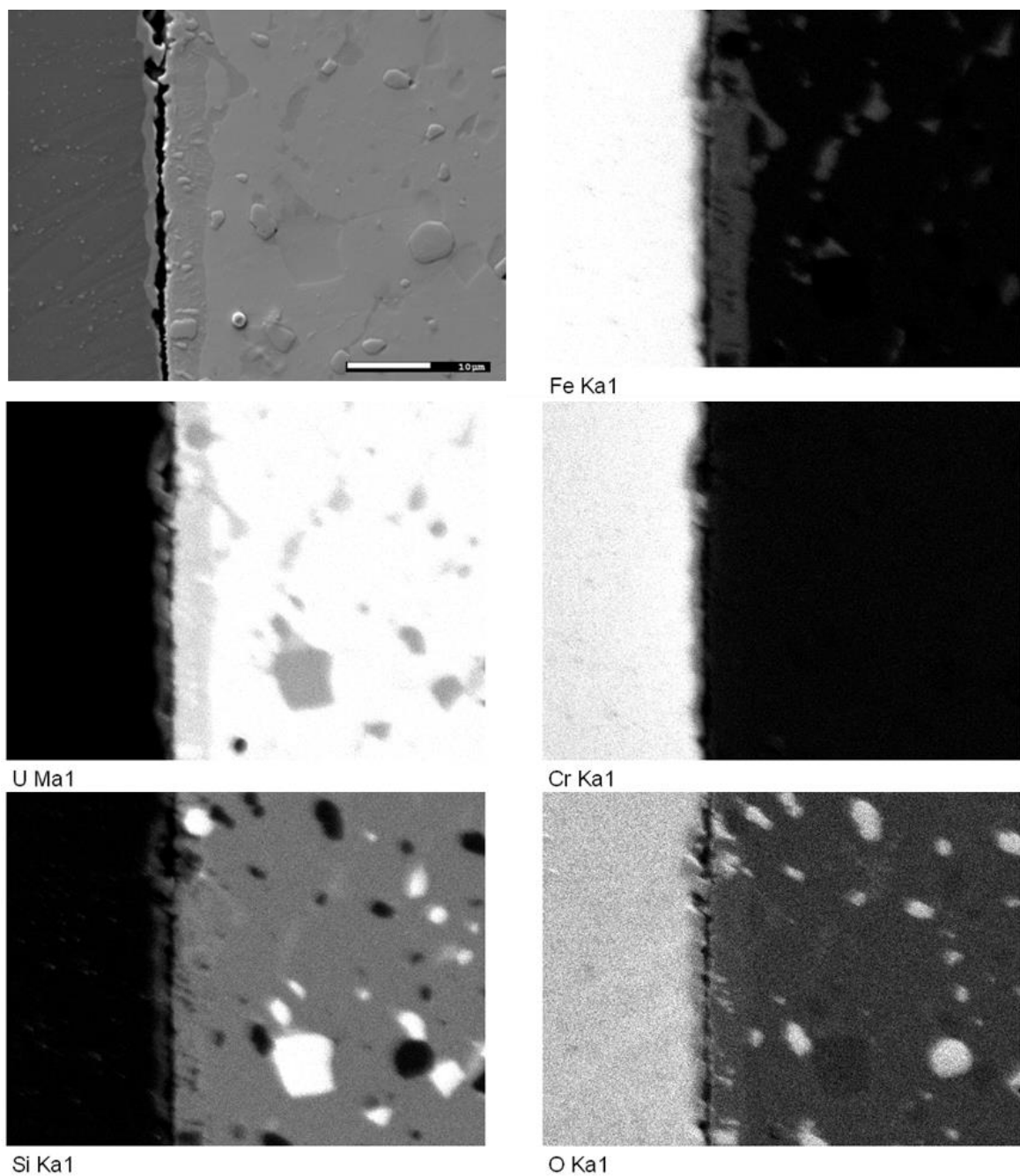


Fig. 4.21 A secondary electron micrograph of a diffusion couple annealed at 800 °C for 30 hours with the intensity map for U, Si, Fe, Cr, and O. The lighter hue indicates higher concentration.

The composition of multiple regions were quantified in the diffusion zone using SEM non standardized EDS point spectra, Fig. 4.22.

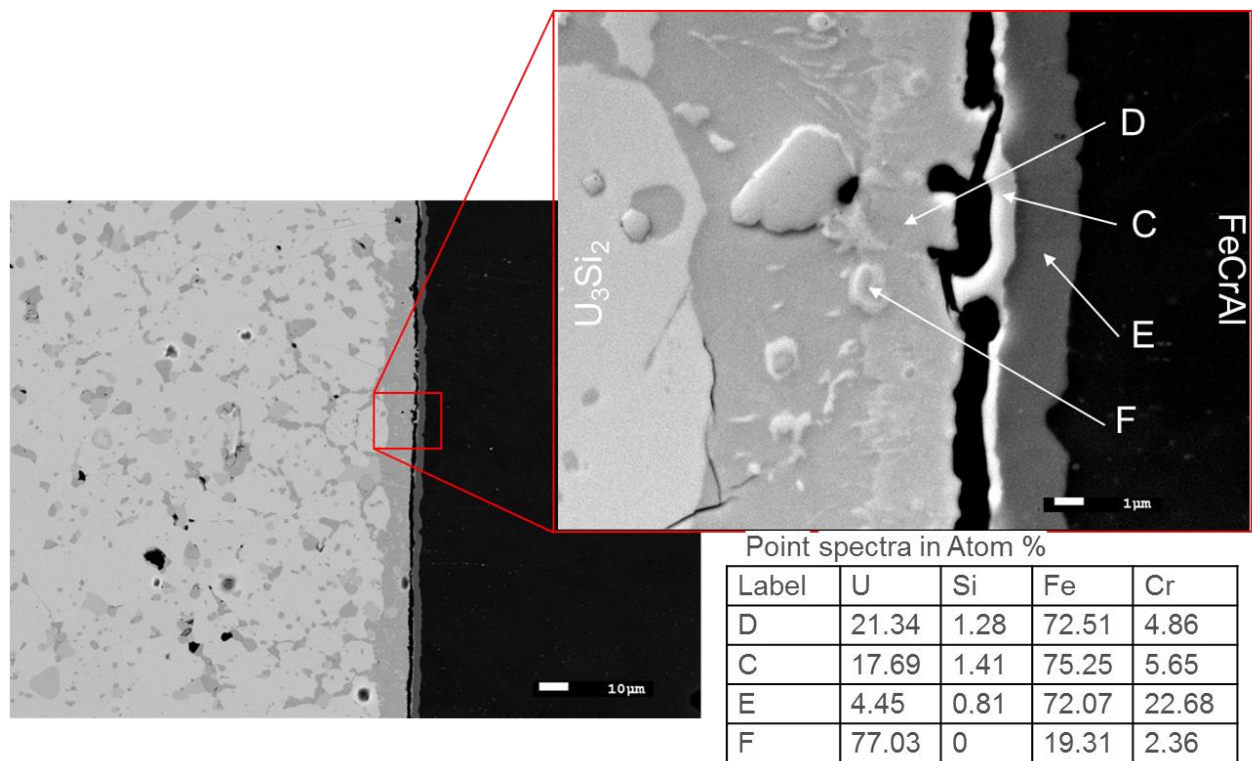


Fig. 4.22 Quantification of different regions within the diffusion zone.

A detailed composition verification was done via TEM on this diffusion couple as well. Fig. 4.23 shows a) an SEM image of the material interface with a rectangle indicating where the FIB lift out occurred, b) an SEM image of the TEM lamella, c) an STEM image of the TEM lamella where subsequent phase validation was done, d) a TEM image labeled with the identified phases, and the corresponding indexed diffraction patterns for the crystalline structures present. The region containing signal from each element in the system (Fe-Cr-Al-Mo-U-Si), corresponding to the B layer in the diffusion couples heated at 1000 °C (Section 4.1-2), was not indexed due to the complexity of a potentially six component phase. It was similar in structure to UFe_2 .

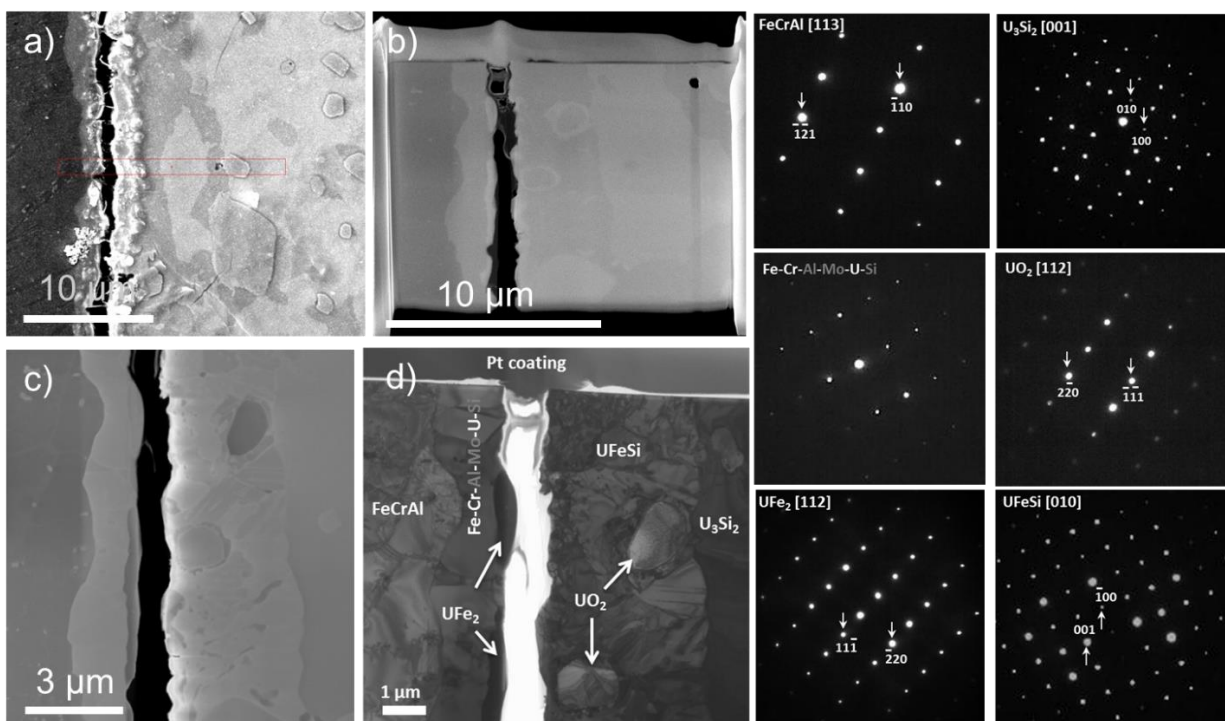


Fig. 4.23 a) SEM micrograph of the interdiffusion zone in the diffusion couple heated at 800 °C for 30 h. with a rectangle indicating where FIB lift-out occurred. **b)** SEM and **c)** STEM image of TEM lamella. **d)** TEM image labeled with identified phases, and corresponding indexed diffraction patterns on the right side.

A TEM EDS line scan, Fig. 4.24, shows individual components/layers of the diffusion couple materials represented in normalized atom percent. This line scan illustrates, both quantitatively, qualitatively, and in higher resolution compared with the SEM data, Fig. 4.20, the phases present at the material interface. Below the charted line scan data is a cut – out of Fig. 4.23 c) where the line scan was taken. The concentration profile is similar composition profile to the diffusion couples annealed at 1000 °C. The diffusion layers were much smaller and less pronounced in the diffusion couple heated at the lower temperature. TEM was required to see the details of the interdiffusion zone in the 800 °C test that were more clearly formed in the 1000 °C tests.

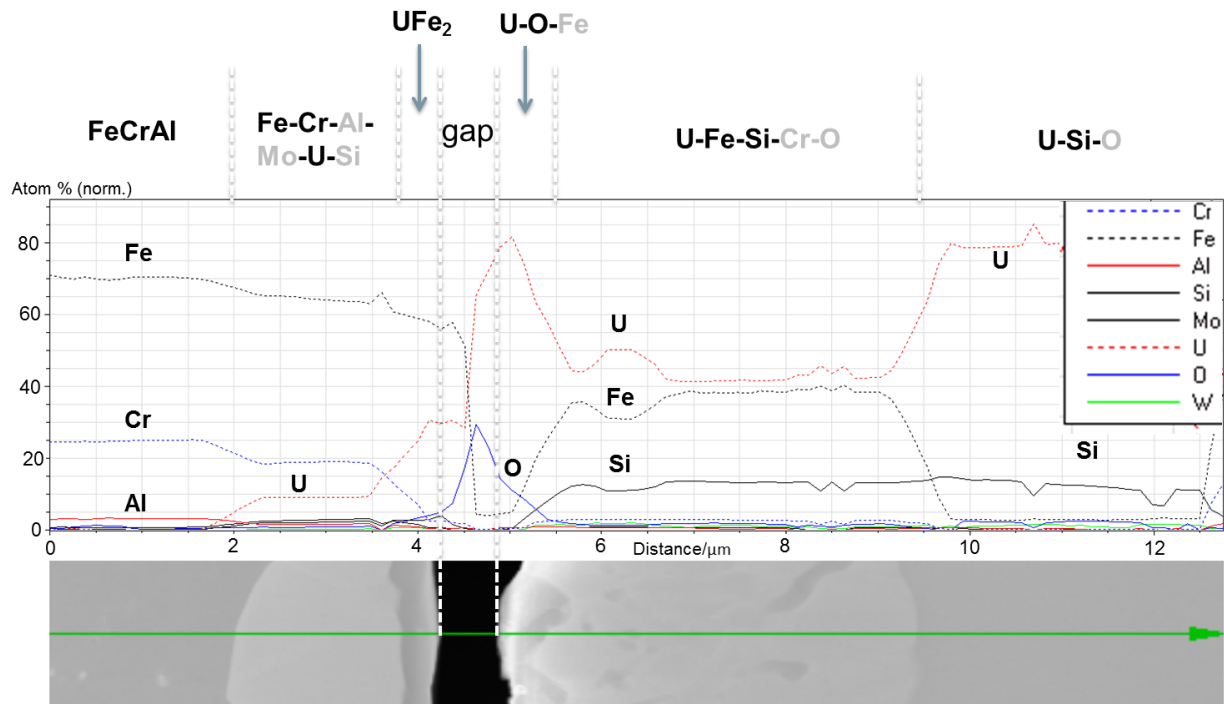


Fig. 4.24 A TEM image cut-out of Fig. 4.21 c) with EDS line scan representing the concentration in normalized atom percent of individual components of the diffusion couple materials with interdiffusion layers labeled along the top.

Plate like crystals arranged in parallel fashion, characteristics of eutectic microstructure are shown in an SEM image, Fig. 4.25 a). (Mishra, 2016) This structure was likely caused by the Fe-U eutectic at 725 °C (Chatain, 2006), and was located sporadically along the material interface. An STEM image, Fig. 4.24 b), gives an enlarged view of the eutectic interaction region. TEM EDS mapping and quantitative analysis of the amorphous region indicate that there are two separate compositions present. The coarser features are likely a phase primarily composed of U_6Fe while the finer lines are likely a U-W phase, also observed in the diffusion couples annealed at 1000 °C, Fig. 4.8. W contaminants were found in the characterization of as-sintered U_3Si_2 fuel, likely introduced during fabrication process. The Si map shows depletion at the eutectic feature confirming the W phase is not a result of peak overlap with Si. Mo shows a higher intensity within the eutectic features. The U-Mo binary system has a low melting eutectic

at 550 °C that likely enhances the diffusion of Mo into the U_3Si_2 .

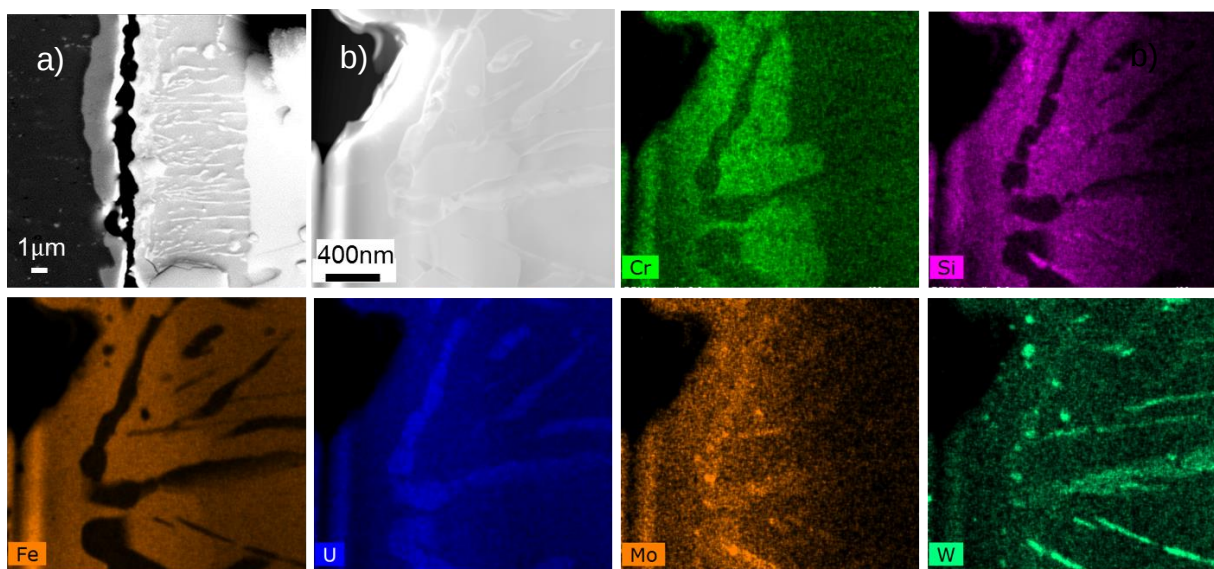


Fig. 4.25 Interaction zone of diffusion couple heated at 800 °C for 30 h. **a)** SEM BSE micrograph, **b)** STEM high angle annular dark field micrograph and corresponding elemental maps.

EDS analysis shows iron within the fuel matrix indicating that iron migrated from the FeCrAl into the fuel. An SEM EDS point spectra analysis of the Fe rich phase at the center of the U_3Si_2 fuel matrix, ie. the farthest distance from the FeCrAl interface was 13.39 w% Si, 7.24 w% Fe, 78.77w% U, with trace amounts of Al and Cr. An EDS map for U, Si, Fe, and O of the same region, Fig. 4.26, indicates an iron rich phase penetrating the fuel matrix. The smaller white specs in the Si map would be polishing contamination. The larger Si regions as well as the O map show phases inherent to the fuel makeup.

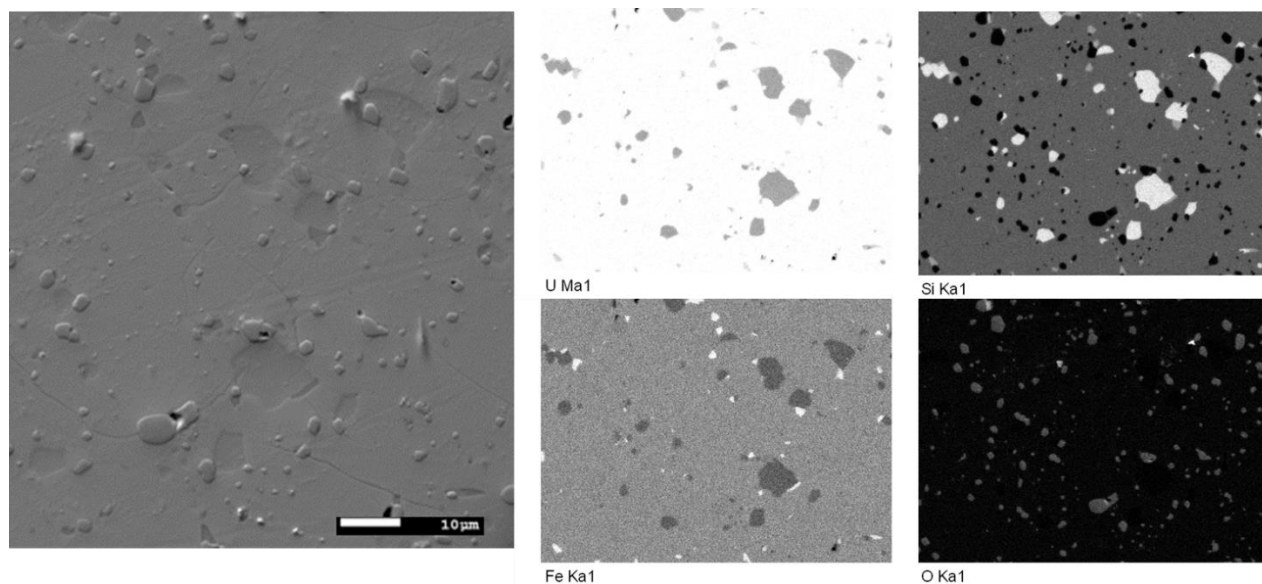


Fig. 4.26 A secondary electron micrograph of the diffusion couple heated at 800 °C for 30 h at the center of the U_3Si_2 on the left with corresponding elemental concentration maps on the right. The lighter hue indicates a higher concentration.

UFeSi , similar to that found at the material interface, was identified as the Fe rich phase at a center region of the U_3Si_2 with TEM diffraction. Fig. 4.27 shows an STEM image of the TEM lamella with a darker iron rich phase located at the triple point of a grain boundary. A UO_2 phase was also present within the lamella. Corresponding indexed diffraction patterns for the identified phases are included. A line scan, representing element concentrations in atomic percent, taken across the UFeSi phase, indicated by a yellow arrow on the STEM image, illustrates the presence of iron, and also the increase in Si over that phase.

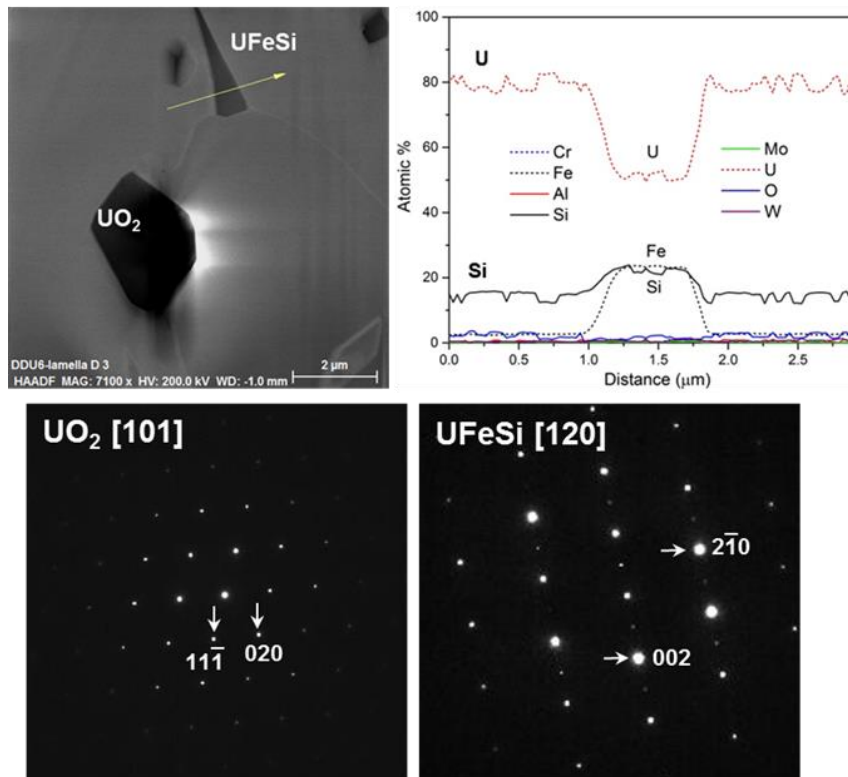


Fig. 4.27 STEM micrograph and corresponding line scan and diffraction patterns of Fe rich and UO_2 phase further back into the U_3Si_2 disk.

4.5 600 °C 100 h

This diffusion couple heated at 600 °C for 100 h maintained good contact along the material interface. A small interdiffusion zone with an average width of $3.0 \pm 1.1 \mu\text{m}$, Fig. 4.28, was identified with a high magnification backscatter electron image.

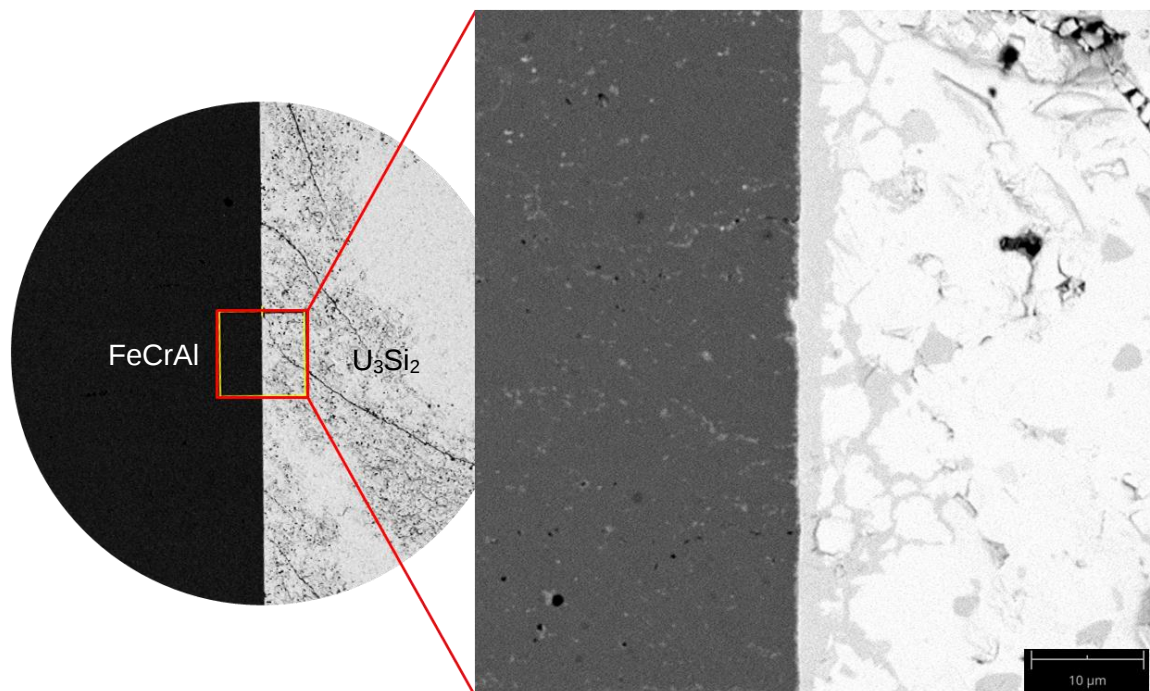


Fig. 4.28 Backscatter electron micrograph of diffusion couple annealed at 600 °C for 100 h.

The small white features in the FeCrAl side of the diffusion couple in Fig. 4.28 are a Mo –Si rich phase, as illustrated by an SEM EDS line scan in Fig. 4.29. A line on the BSE micrograph indicates where the scan was taken. A higher magnification of the line scan region is provided below the line scan signal, represented in atom percent. No uranium was detected in this region. 600 °C is below the known eutectic point for the Fe-U system, diffusion is not expected.

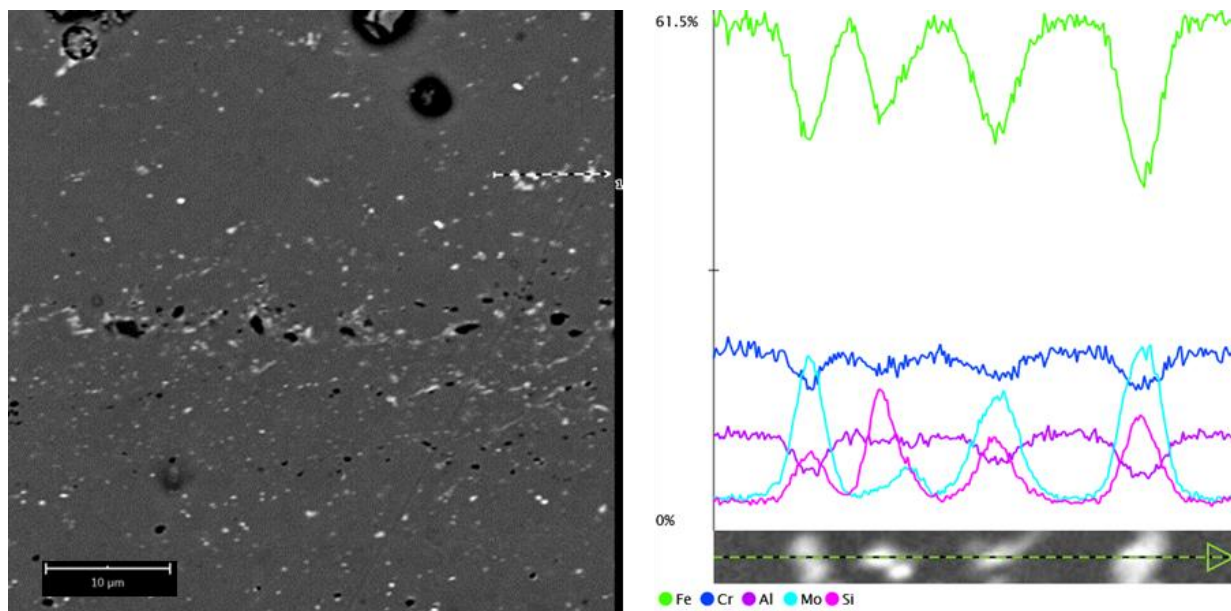


Fig. 4.29 SEM BSE micrograph of the FeCrAl side of the diffusion couple heated at 600 °C for 100 h and corresponding EDS line scan over the region indicated by an arrow on the micrograph.

4.6 500 °C 100 h

There was no visible diffusion zone for the diffusion couple test at 500 °C for 100 h, Fig. 4.30. This diffusion couple was taken out of the original jig before mounting. Upon removal from the jig the diffusion couple came apart, but it looked like there may have been some weak bonding. EDS showed a weak iron signal along the U_3Si_2 material interface, indicating there may have been some diffusion from the FeCrAl into the U_3Si_2 .

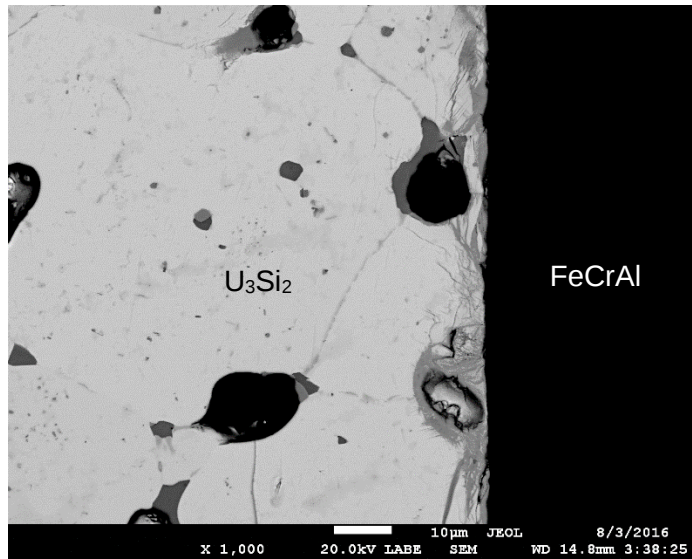


Fig. 4.30 SEM BSE micrograph of material interface of diffusion zone heated to 500 °C for 100 h.

4.7 500 °C 30 h

This diffusion couple was the first done with the new jig. It maintained contact of the fuel and cladding material. No diffusion was detected with the SEM or STEM as seen in Fig. 4.31. Fig. 4.31 has an a) STEM image of the material interface with a line indicating where the lamella was taken, b) SEM image of the TEM lamella, c) STEM image of the lamella where the line scan was taken, d) enlarged cut out where the line scan data was gathered, and e) resultant EDS line scan indicating atom percent composition of each component across the material interface. This analysis was duplicated with the SEM providing a larger scale illustration of the lack of diffusion. Fig. 4.32 has a backscattered electron micrograph of the material interface with a line indicating where an EDS line scan was taken along with corresponding major element concentration in terms of EDS signal, giving qualitative composition across the interface. The slight composition slope at the interface is likely an artifact of the EDS spot size and volume interaction at the interface.

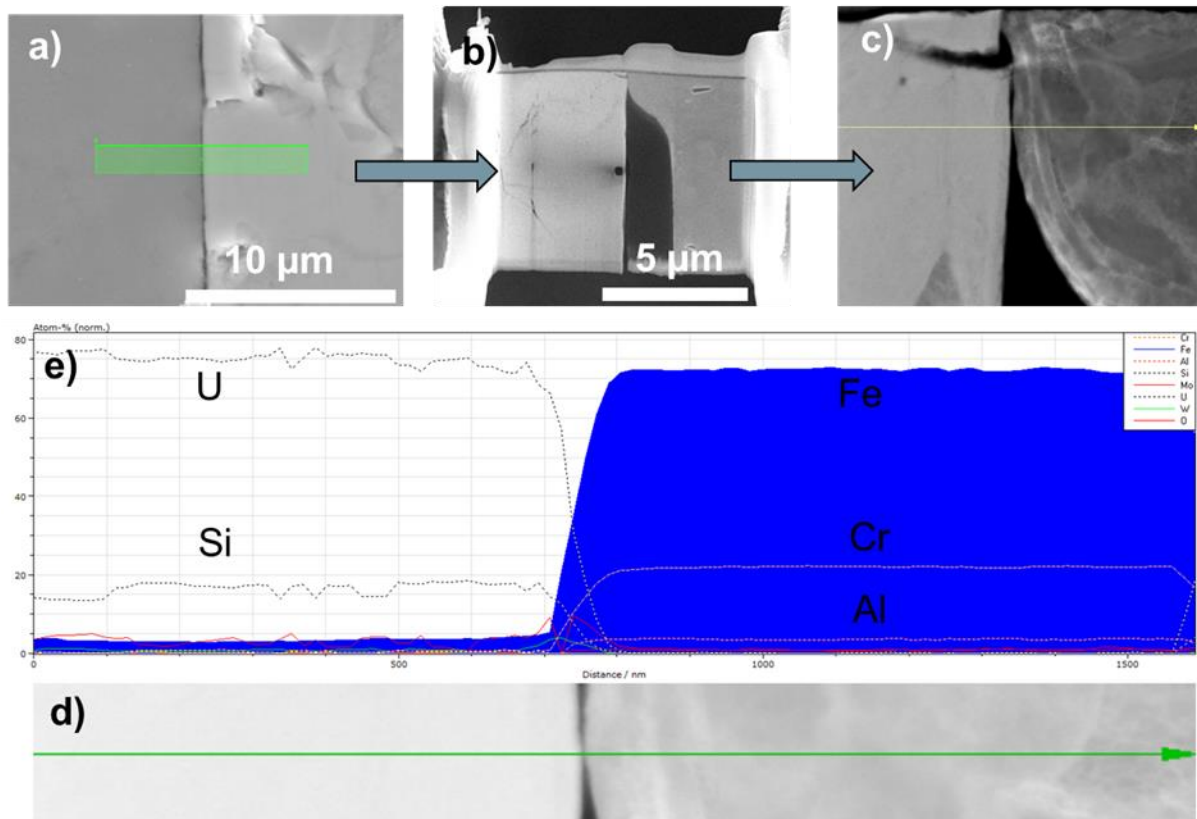


Fig. 4.31 STEM images **a)** U_3Si_2 diffusion couple heated at 500 °C for 30 h with a rectangle indicating where FIB lamella was extracted, **b)** FIB lamella, **c)** enlarged section of the lamella where the line scan was taken, **d)** enlarged section where the line scan data was gathered, and **e)** resultant EDS line scan indicating atom percent composition of each component across the material interface.

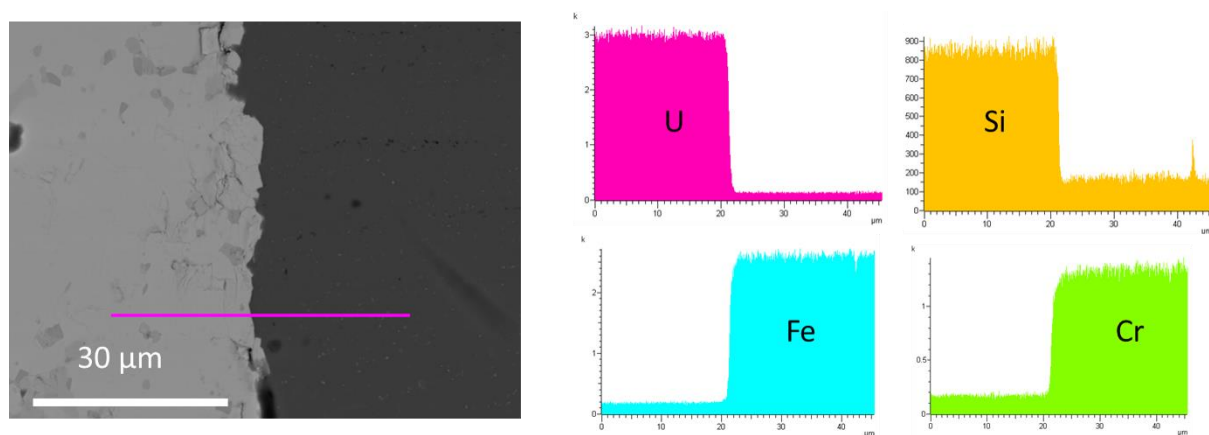


Fig. 4.32 SEM backscattered electron micrograph of the diffusion couple heated at 500°C for 30 hours

with a line across the material interface where and EDS line scan was taken. The corresponding major element (U, Si, Fe, and Cr) concentrations, in terms of EDS signal, provide a qualitative composition of the elements present.

5.0 Discussion

Fuel-cladding interaction and the formation of fuel-cladding bonding layers with specific chemical, physical and mechanical properties are of importance regarding the evolution of thermal conductivity as well as in the context of fuel cladding chemical interaction (FCCI). It is also important in the framework of long-term storage of spent fuel where the phases formed at the fuel-cladding boundary are considered to be the first to be leached in case of cladding failure. (Van den Berghe, 2005) This bonding may have detrimental effects on fuel rod behavior under irradiation, ie., preventing the axial transport of fission gases in a fuel rod and inducing a severe pellet-cladding mechanical interaction. (Nogita, 1997)

The overall performance of the FeCrAl- U_3Si_2 system may not be greatly affected by the presence of different phases in the interaction region. A comparison of U_3Si_2 , UFe_2 and FeCrAl's individual experimentally measured specific heat capacities, found in literature, is given in Fig. 5.1. While the measured heat capacity values for UFe_2 are higher than that of U_3Si_2 , they are well below the reported values for FeCrAl.

The melting point of the overall system is, however, reduced by the presence of the U-Fe eutectic phases. The migration of U into FeCrAl is especially damaging to the fuel system as it will decrease not only the melting point of the clad, but the overall mechanical strength as well.

The rate of growth of each layer is inversely proportional to its thickness due to a decreased diffusion flux with increased layer thickness. The growth constant, k , defined (Paul, 2017) as, $k = \sqrt{2 * t / \Delta x}$, where t is the length of heating and x is the width of the layer, was calculated for each layer. The k values for tests that produced the 3 distinct layers are presented in Table 5.1. The values of the 800°C 30 h test have a high uncertainty because the layer thickness and presence was not uniform, and

the layer interface was less easily identified. When comparing the diffusion couple heated for 100 h vs. the diffusion couple heated for only 30 h, interaction layers were identified in both tests, but were wider in the longer test. The width of layers B, C, and D increased by about 47%, 48%, and 39% respectively from 30 h to 100 h. The growth constants from 30 h to 100 h increased roughly 2.8% and 5.7% for the B and C layer respectively and decreased by about 10.7% for the D layer. The D layer is notably wider than the B and C layers. Huang (Huang, 2012) listed several factors that may influence the different growth rates in the individual interaction layers including the calculated diffusivity and heat of formation of the phase. The UFeSi phase was the largest interdiffusion phase corresponding to the largest diffusivity values for U, Fe, and Si at that composition. UFeSi may have a greater thermodynamic stability and greater driving force for formation than the C and E layers. The C layer, made up of $\text{U}_2\text{Fe}_3\text{Si}$ and UFe_2 , and was the thinnest layer in each test. The calculated diffusivity values for uranium and iron correspond to diffusivity values in the UFe_2 , $\text{U}_2\text{Fe}_3\text{Si}$ compositions lower than that of UFeSi, but higher than any other composition. UFe_2 is the most stable compound in the U-Fe binary system, and its crystal structure is dissimilar to that of the surrounding layers which may have reduced its growth rate.

Table 5.1

Proportionality constants of interaction layers in selected diffusion couples.

Layers	B	C (UFe_2)	D (UFeSi)	Time (h)	Temperature ($^{\circ}\text{C}$)
Width (μm)	2.4 ± 0.3	0.6 ± 0.2	10.3 ± 1.2	30	800
Width (μm)	25.8 ± 1.9	19.2 ± 1.1	67.4 ± 4.7	100	1000
Width (μm)	13.7 ± 1.3	9.9 ± 0.9	40.1 ± 3.1	30	1000
Growth constant ($\mu\text{m/s}$)	0.31	0.07	1.32	30	800
Growth constant ($\mu\text{m/s}$)	1.82	1.35	4.76	100	1000
Growth constant ($\mu\text{m/s}$)	1.77	1.28	5.27	30	1000

The U-Fe system has been well investigated, but much less is known about the U - Fe- Si system. The microstructures of the U_3Si_2 vs FeCrAl diffusion couple appeared similar to that of the more simple U vs Fe and U vs. Fe-Cr systems studied earlier by Huang, however the UFe_2 layer identified by Huang behaved differently than what was observed in the present study. While the temperatures Huang tested were generally lower than temperatures tested here, comparison at roughly the same temperatures shows that the U_3Si_2 -FeCrAl interaction layers are much smaller than those of pure U and Fe. The U-Fe test carried out by Huang at 700 °C for 96 h had a total interaction zone of over 100 μm while the maximum diffusion zone recorded in the present work was less than 100 μm in the test at 1000 °C for 100 h, about 300 degrees higher than the Fe-U eutectic temperature.

A main advantage of the U_3Si_2 – FeCrAl fuel system is its superior thermal conductivity in comparison to the UO_2 – Zry fuel system. A useful measurement would then be that of the thermal conductivity of the interaction layers and/or phases identified, like $UFeSi$, and at a range of temperatures relevant to LWR operating conditions to determine how they would affect the overall thermal conductivity of the system at elevated temperatures. Measurement of the thermal properties of $UFeSi$ would be especially instructive in determining the impact of its presence on the system.

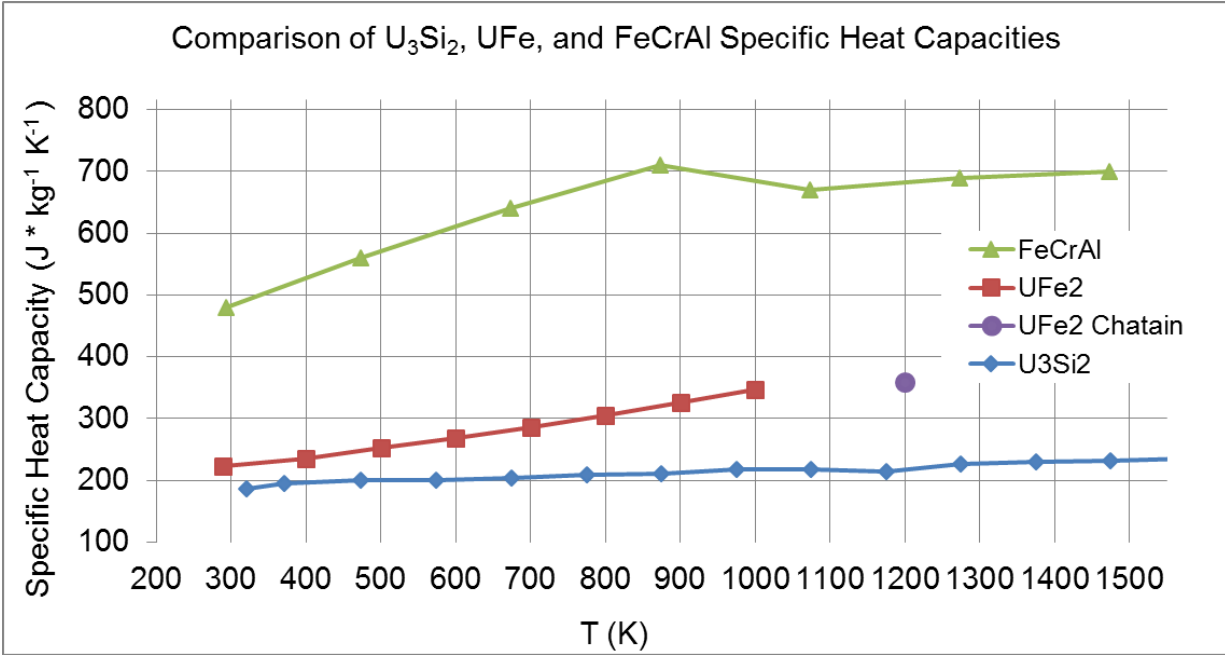


Fig. 5.1 Experimentally measured specific heat capacities of U_3Si_2 , UFe_2 , and $FeCrAl$ from literature.

It is unknown how the presence of interaction layers will affect fuel performance. The U_3Si_2 – $FeCrAl$ fuel system is theoretical at present with little data on the performance of either component in LWR conditions. Only one other investigation on the diffusion of bulk U_3Si_2 with Zry has been published; (He,2017) no other comparable data exists. The data generated in this study will help to inform modeling of this new fuel system at normal operation and in accident scenarios to further elucidate implications of interaction regions at normal and higher than normal operating temperatures. In other fuel system models (Karahan, 2010) input data included: the concentration of atoms and diffusion coefficients at the material interface. Phases present in the interdiffusion zone and their individual properties are also important input parameters for future modeling. Modelers can use the experimentally measured width and composition of interdiffusion layers (Tables 4.2, 4.3, and 5.1) to validate, and potentially, extrapolate predictions to LWR operating conditions.

This study approximates LWR conditions, and represents a graded approach. This simplified

diffusion couple experiment allowed for primary tests to determine the degree of interaction in non-reactor conditions. A repeat of these tests doping the diffusion couple materials with fission products/lanthanides would be a path to extract more information and provide a greater approximation to LWR operating conditions from fresh/non-irradiated fuel testing.

5.1 Conclusions

In a non-irradiated U_3Si_2 – FeCrAl fuel system, annealing at temperatures greater than 500 °C with direct contact causes chemical diffusion. Well known Fe – U eutectics contribute to the formations of Fe – U rich interactions layers. At higher annealing temperatures (800 °C – 1000 °C) three distinct interaction layers were observed with an SEM BSE detector. These layers were similar to those formed in a binary U-Fe system, but significantly thinner. U traveled into the matrix of the FeCrAl in small U rich phase circular/spherical uniform spots, and likely formed a composition of U_6Fe . The presence of this phase in the FeCrAl is significant because it lowers the melting point of the fuel/cladding system and potentially decreases the structural integrity of the cladding. Fe also traveled far into the matrix of the U_3Si_2 and formed irregularly shaped Fe rich phases, similar in composition to that of layer D (UFeSi), the interaction layer closest to the U_3Si_2 matrix. This Fe rich phase was smaller and less abundant further away from the material interface. Tungsten, a contaminant present in the U_3Si_2 as a result of the fabrication process for the specimens tested, was also present in the interaction layers in a eutectic formation. The determination of phases present in the interaction regions from this study can be used to validate computer modelling predictions.

Weak EDS signal from lesser constituents in the system, including Al and Mo, leave uncertainty on the extent of their diffusion. A more quantitative composition profile using standardized EDS or electron probe micro analysis would help to ensure the accuracy of the calculated results. A microprobe for composition of interaction layers was not available, but would have been a nice compliment to the

data gathered. A re-test at 800 °C for 100 h conducted in the new jig would also complete the data collected in this study. It was hard to determine the migration of the Fe in the fuel matrix due to weak Fe EDS signals far back into the matrix that may have been a result of signal overlap.

Interdiffusion coefficients and diffusion flux for each component in the system at different hold times, heating temperatures, and compositions was calculated from composition profiles. From these calculations the effective penetration depth of each component can be assessed. The interdiffusion behavior of the individual components, and under changing conditions/different test parameters, can be compared numerically, but because the boundary conditions for the diffusivity equation was not met the values calculated here do not reflect the true diffusivity values. Future tests should either increase the width of the U_3Si_2 to ensure the maximum diffusion depth of Fe and U diffusion can be determined, or reduce the duration of the test at the elevated temperature to reduce the extent of diffusion..

While no commercial vendors are pursuing the FeCrAl- U_3Si_2 fuel system at this time, FeCrAl's interaction with uranium at elevated/accident scenario temperatures in U_3Si_2 may also indicate a potential interaction with UO_2 at normal operating temperatures. A future test investigating the interaction between FeCrAl and UO_2 would fill a gap in the knowledge of this new cladding material.

Other candidate cladding materials have been planned for similar analysis. In parallel with this study, a study on the interaction of U_3Si_2 with Zry - 4 has been performed, and a similar study of the interaction of U_3Si_2 with SiC is under way. (He, 2017) Planned irradiation tests include diffusion couple systems pairing U_3Si_2 with three potential cladding candidates: FeCrAl, Zry – 4, and SiC to study material interaction under reactor conditions is currently being fabricated. These tests will help to ultimately determine the attractiveness and acceptability of the U_3Si_2 – FeCrAl fuel system as a future ATF.

REFERENCES

- S. Bragg-Sitton et al., Advanced fuels campaign light water reactor accident tolerant fuel performance metrics, Prepared for U. S. Department of Energy, 2014, INL/EXT-13-29957.
- G. Campbell, "The Thermodynamic Properties of UFe_2 : Agreement with the Campbell Correlation of Laves Phase Compounds," Metallurgical Transactions A, 8A (1977) 1493.
- S. Chatain, et al., U-Fe Phase Diagram, ASM Alloy Phase Diagram Database P. Villars, editor-in-chief; H. Okamoto and K. Cenzual, section editors; ASM International, 2006, retrieved from: <http://mio.asminternational.org/apd/> (May 19, 2017).
- M.A. Dayananda, Y.H. Sohn, Average effective interdiffusion coefficients and their applications for isothermal multicomponent diffusion couples, Scr. Materialia, 35 (1996) 15.
- M.A. Dayananda, An examination of a multicomponent diffusion couple, J. of Phase Equilibria and Diffusion, 27 (2006) 572-581.
- F.J.A. den Broeder, Scripta Metall., 3 (1969) 321-25.
- L. S. Darken, Diffusion, mobility and their interrelation through free energy in binary metallic systems, Member AIME, New York Meeting, February 1948.
- D.D. Ellis, R.B. Rebak, Passivation characteristics of ferritic stainless materials in simulated reactor environments, Paper C2016- 7452, Corrosion/2016 (NACE International, Houston, TX)
- Finlay, MR, GL Hofman, and JL Snelgrove. Irradiation Behavior of Uranium Silicide Compounds, J. Nucl. Mater. 325.2 (2004) 118-128.
- B. Fultz and J. M. Hove, Transmission Electron Microscopy and Diffractometry of Materials, Graduate Texts in Physics (Springer, Berlin, Heidelberg, 2013).
- J. Gan, et al., Microstructure of the irradiated $\text{U}_3\text{Si}_2/\text{Al}$ silicide dispersion fuel, J. Nucl. Mater. 419 (2011) 97-104.

N.M. George, K. Terrani, J. Powers, Neutronic analysis of candidate accident-tolerant iron alloy cladding concepts, Tech. Rep. ORNL/TM-2013/121, Oak Ridge National Laboratory, 2013.

N.M. George, et al., Neutronic analysis of candidate accident-tolerant iron alloy cladding concepts in pressurized water reactors, J. Nucl. Mater. 75 (2015) 703-712.

J.R. Greer, Fick's law and macroscopic diffusion, Lecture Notes, MS 133 Kinetics of Solid Phase Transformations, California Institute of Technology, 2016, retrieved from: <http://www.jrgreer.caltech.edu/content/teaching/MS133Files/Notes/Lect3MS133JRG.pdf> (May, 19, 2017).

J.M. Harp, P.A. Lessing, R.E. Hoggan, Uranium silicide pellet fabrication by powder metallurgy for accident tolerant fuel evaluation and irradiation, J. Nucl. Mater. 466 (2015) 728-738.

L. He, et. al., Corrosion and Interdiffusion Studies of U_3Si_2 , Top Fuel Conference presentation, Boise, ID, September 10, 2016.

L. He, et. al., Microstructure studies of interdiffusion behavior of U_3Si_2 /Zircaloy-4 at 800 and 1000°C, J. Nucl. Mater. 486 (2017) 274-282.

G.L. Hoffman, A short note on high density dispersion fuel, Argonne National Laboratory, 1996, retrieved from: <http://www.rertr.anl.gov/ADV-FUELS/GHHD.PDF> (May 19, 2017).

X. Hu, et al., Hydrogen permeation in FeCrAl alloys for LWR cladding application, J. Nucl. Mater. 461 (2015) 282-291.

K.E. Huang, Diffusion and reaction in selected uranium alloy systems, University of Central Florida, Masters Thesis, 2012.

International Atomic Energy Agency (IAEA), Thermophysical properties database of materials for light water reactors and heavy water reactors, 2006, retrieved from: http://www-pub.iaea.org/MTCD/publications/PDF/te_1496_web.pdf (May 19, 2017).

S.K. Kailasam, J.C. Lacombe, and M.E. Glicksman, Evaluation of the methods for calculating the

concentration-dependent diffusivity in binary systems, Metall and Mat Trans A, 30 (1999) 2605.

Kanthal APMT, Material data sheet, retrieved from: <http://www.kanthal.com/en/products/material-datasheets/tube/kanthal-apmt/> (May 19, 2017).

A. Karahan and J. Buongiorno, Modeling of thermos-mechanical and irradiation behavior of mixed oxide fuel for sodium fast reactors, J. Nucl. Mater. 396 (2010) 272-282.

K. Kim, et al., Thermal compatibility studies of U_3Si_2 dispersion fuels prepared with centrifugally atomized powder, J. Nucl. Mater. 270 (1999) 315-321.

Y.S. Kim, Uranium intermetallic fuels (U–Al, U–Si, U–Mo). In: Konings R.J.M., (ed.) Comprehensive Nuclear Materials, volume 3, pp. 391-422 Amsterdam: Elsevier, 2012.

E.J. Leeds, M.R. Johnson. Order to modifying licenses with regard to requirements for mitigation strategies for beyond-design-basis external events (EA-12-049), United States Nuclear Regulatory Commission, 2012.

A. Leenaers, et al., Microstructure of U_3Si_2 fuel plates submitted to a high heat flux, J. Nucl. Mater. 327 (2004) 121-129.

P. Martin, et al., Pellet-clad interaction in water reactor fuels, Organisation for Economic Co-operation and Development, Nuclear Energy Agency, Seminar Proceedings, Aix-en-Provence, France. March 9-11, 2004.

C. Matano, On the relation between the diffusion-coefficients and concentrations of solid metals (The Nickel-Copper System), Japanese J. of Phys. 8 (1933) 109.

H. Mehrer, Diffusion in Solids. Fundamentals, Methods, Materials, Diffusion-Controlled Processes. Mechanics, Springer Series in Solid-State Sciences, (2007) 163-164.

S. Mishra, et al., Compatibility study between U- UO_2 cermet fuel and T91 cladding." J. Nucl. Mater. 481 (2016): 1-12.

K. Nogita, K. Une, Formation of pellet-cladding bonding layer in high burnup BWR fuels, J. of Nucl. Sci. and Technol. 34 (1997) 679-686.

L.J. Ott, Advanced severe accident response models for BWR application, J. Nucl. Mater. 115 (1989) 289-303.

A. Paul, The Kirkendall effect in solid state diffusion, Technische University Eindhoven PhD Thesis, 2004.

A. Paul, S. Divinski, Handbook of Solid State Diffusion, Cambridge, MA, 1 (2016) 128-129.

E. Perez, Interdiffusion Analysis For Nicocraly And Nial Vs. Various Superalloys, University of Central Florida, Masters Thesis, 2005.

B.A. Pint, et al., High temperature oxidation of fuel cladding candidate materials in steam–hydrogen environments." J. Nucl. Mater. 440.1 (2013) 420-427.

R.B. Rebak, N.R. Brown, K.A. Terrani, Assessment of advanced steels as accident tolerant fuel cladding for commercial light water reactors, 17th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, Paper 227, Ottawa, Ontario, Canada (Canadian Nuclear Society, Toronto), August 9-12, 2015.

R.B. Rebak, K.A. Terrani, R.M. Fawcett, FeCrAl alloys for accident tolerant fuel cladding in light water reactors, ASME 2016 Pressure Vessels and Piping Conference, Volume 6B: Materials and Fabrication Vancouver, British Columbia, Canada, (July 17–21, 2016).

K.R. Robb, Analysis of the FeCrAl accident tolerant fuel concept benefits during BWR station blackout accidents, 16th International Topical Meeting on Nuclear Reactor Thermal hydraulics, Chicago, IL, USA, 2015.

F. Sauer, V. Freise, Z. Elektrochem., 66 (1962) 353–63.

- F. Seitz, On the porosity observed in the Kirkendall Effect, *Acta Metallurgica*, 3 (1953) 355–369.
- J.A. Turnbull, C.A. Friskney, The diffusion coefficients of gaseous and volatile species during the irradiation of uranium dioxide, *J. Nucl. Mater.* 107 (1982) 168-184.
- S. Van den Berge, et al., Observation of a pellet-cladding bonding layer in high-power fuel, Pellet-clad interaction in Water Reactor Fuels, Conference Book, 37 (2005) 265-275.
- C.M. Walter, L.R. Kelman, The interaction of iron with molten uranium, *J. Nucl. Mater.* 20 (3) (1966) 314-322.
- J.T. White, A.T. Nelson, Thermal conductivity of UO_{2+x} and U_4O_{9-y} , *J. Nucl. Mater.* 443 (2013) 342-350.
- J.T. White, et al., Corrigendum to “Thermophysical properties of U_3Si_2 to 1773 K” [*J. Nucl. Mater.* 464 (2015) 275–280] 484 (2017) 386-387.
- X. Wu, et al., Preliminary safety analysis of the PWR with accident-tolerant fuels during severe accident conditions, *Annals of Nucl. Energy*. 80 (2015) 1-13.
- S.J. Zinkle, et al., Accident tolerant fuels for LWRs: A perspective, *J. Nucl. Mater.* 448 (2014) 374–379.
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