Microstructure Studies of Interdiffusion Behavior of U_3Si_2 /Zircaloy-4 at 800 and 1000°C

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ABSTRACT

Fuel swelling during normal reactor operations could lead to unfavorable chemical interactions when in contact with its cladding. As new fuel types are developed, it is crucial to understand the interaction behavior between fuel and its cladding. Diffusion experiments between U_3Si_2 and Zircaloy-4 (Zry-4) were conducted at 800 and 1000°C up to 100 hours. The microstructure of pristine U_3Si_2 and U_3Si_2 /Zry-4 interdiffusion products were examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with an energy dispersive X-ray spectroscopy (EDS) system. The primary interdiffusion product observed at 800°C is ZrSi_2 , with secondary phases of U-Zr in the Zry-4, and Fe-Cr-W-Zr-Si phases at Zry-4/ ZrSi_2 interface and Fe-Cr-U-Si phases at ZrSi_2 /U-Si interface. The primary interdiffusion products at 1000°C were Zr_2Si , U-Zr-Fe-Ni, U, U-Zr, and a low melting point phase U_6Fe .

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1. Introduction

Triuranium disilicide (U_3Si_2) has higher uranium density and higher thermal conductivity compared with UO_2 and thus, has the potential to replace UO_2 in future Light Water Reactors (LWR) fuel designs [1-4]. Previous efforts in this area have demonstrated that high density U_3Si_2 pellets can be produced by conventional powder metallurgical processes [2,3].

The structural integrity of a fuel element is of significant importance during the operation of a nuclear reactor [5,6]. During normal reactor operation, fuel can swell and make contact with the cladding, resulting in interdiffusion and formation of potentially unwanted phases. This fuel cladding chemical interaction (FCCI) can thin the cladding and produce strength reducing diffusion zones as well as low melting phases. This can affect the structural integrity and potentially cause a breach of a fuel rod. Thus, it is important to understand the interdiffusion behavior between the promising nuclear fuel, U_3Si_2 , and cladding material. Early work on the interdiffusion of U_3Si_2 was focused on the U_3Si_2 dispersion fuels in the Al matrix. The interaction between the U_3Si_2 fuel particles and the Al matrix resulted in the formation of a $\text{U}(\text{Al}, \text{Si})_x$ ($x=3, 4.6, 5.25$) layer [7-9]. To the best of authors' knowledge, there has been no interdiffusion study for bulk U_3Si_2 published.

The work presented summarizes the microstructure observations of interdiffusion behavior of U_3Si_2 /Zircaloy-4 (Zry-4) diffusion couples at 800 and 1000°C. It will reveal the compatibility between U_3Si_2 and Zry-4 and help inform decisions on the acceptability of U_3Si_2 as a potential replacement for UO_2 . Zircaloy-4 is used in this work and is assumed to be an acceptable surrogate for many different, more contemporary, alloys of zirconium such as Zirloy®.

2. Experimental

The polycrystalline depleted U_3Si_2 sample pellets used in the present work were fabricated at Idaho National Laboratory following the procedure given in [3]. The density of sintered U_3Si_2 pellets is 11.8 g/cm^3 (96.9% theoretical density). The pellets were sliced into ~2 mm thick, 8.2 mm diameter disks with a high speed saw, SiC blade in a radiological hood. Zry-4 strapping was also machined into disks of ~2 mm thick and 8.2 mm diameter disks. The surfaces of both U_3Si_2 and Zry-4 disks were polished down to a $1 \text{ }\mu\text{m}$ roughness using diamond suspension prior to diffusion tests. The composition of Zry-4 is 98.5 wt.% Zr, 0.07-0.13 wt.% Cr, 0.18-0.24 wt.% Fe, 0.09-0.16 wt.% O, and 1.20-1.70 wt.% Sn.

The diffusion couples composed of a U_3Si_2 disk and a Zry-4 disk were fixed in an Invar alloy jig. Tantalum foils were used to prevent any chemical reaction between the diffusion couple and jig. The diffusion tests were conducted in a RD Webb “Red Devil” vacuum furnace at 800°C and 1000°C for 30 hours and 100 hours at $<5 \times 10^{-6}$ Torr. After the thermal cycle, the diffusion couples were mounted in epoxy and polished for microstructure characterization. Temperatures higher than normal operation conditions (fuel cladding temperature of $300\text{-}400^\circ\text{C}$ is nominally expected) were chosen for these tests to accelerate diffusion and simulate accident conditions. Neutron irradiation may also accelerate interdiffusion [10,11]. Kim et al. found that the interaction layer between U-Mo and Al is proportional to the square root of the fission fragment damage rate [11]. Therefore, it is necessary to test the unirradiated system at more extreme conditions than expected in operation. The microstructure of the samples after diffusion tests was examined by scanning electron microscopy (SEM) and transmission electron microscopy

(TEM). The cross sectional microstructure of diffusion couples was evaluated using a JEOL 7600 field emission SEM equipped with an energy-dispersive X-ray spectrometer (EDS). A Rigaku X-ray diffraction (XRD) with Cu K α radiation was used to identify the phases in the diffusion couples tested at 1000°C for 100 hours. The XRD was collected on bulk sample using PB-focus mode (microXRD). The scanning step of 0.04° and the scanning speed of 1° /min were used. TEM samples were prepared by a dual-beam focused ion beam (FIB, Quanta 3D FEG, FEI Company) system at the Center for Advanced Energy Studies. Platinum coating was deposited to protect the oxide surface before cutting. TEM lamellas were created by coarse trenching 20 $\times$ 15 $\times$ 15 μm^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. FIB damage was cleaned with a final polish using 2 kV at 27 pA ion emission current. A 300 kV Tecnai TF30 scanning transmission electron microscope (STEM) equipped with EDS system, was used for structure and composition analysis of the diffusion couples.

3. Results

3.1 Microstructure of pristine U_3Si_2

Figure 1 shows typical TEM images of as-sintered U_3Si_2 pellets. Small UO_2 grains (marked by arrows) and medium size USi grains (relatively darker than U_3Si_2 matrix) coexist with large U_3Si_2 grains in the FIB lamella. This is very consistent with early SEM observation, which shows roughly 84-88 wt.% U_3Si_2 , 8-13 wt.% USi and 2-4 wt.% UO_2 determined by XRD [3]. The oxygen is from the surface oxides of powders as well as the O_2 impurity in Ar gas. The oxidation of U causes the formation of Si-rich USi phases when using U and Si powers in a

stoichiometric ratio of U_3Si_2 . UO_2 and U_3Si_2 grains are nearly free of defects (Fig. 1(b) and 1(d)), while the USi grains show numerous stacking faults (Fig. 1(c)). The diffusion of diffraction spots also confirmed these planar defects.

3.2 Interdiffusion at 800 °C

Figure 2 shows an SEM image and EDS map of $\text{U}_3\text{Si}_2/\text{Zry-4}$ diffusion couple annealed at 800°C for 100 hours. There is a distinct diffusion zone of $7.4 \pm 0.6 \mu\text{m}$ wide formed between U_3Si_2 and Zry-4. This zone is rich in Zr and Si and has been ascertained to be ZrSi_2 by EDS. The impurities of UO_2 in U_3Si_2 can also be readily identified in the O map (Fig. 2(d)). At both interfaces of $\text{U}_3\text{Si}_2/\text{ZrSi}_2$ and $\text{ZrSi}_2/\text{Zry-4}$, new phases containing Fe and Cr have precipitated (Figs. 2(f) and 2(g)). This indicates that Fe and Cr, alloying components in the Zry-4, diffused towards U_3Si_2 . In the Zry-4 near the $\text{ZrSi}_2/\text{Zry-4}$ interface, a U-rich phase was found (Fig. 2(e)), indicating that U diffused into Zry-4 at 800°C.

Figure 3(a) shows an SEM image of a lamella lifted out from the yellow and dashed rectangular region in Fig. 2. Three main phases, Zry-4, ZrSi_2 and U_3Si_2 and their interfaces, Zry-4/ ZrSi_2 and $\text{ZrSi}_2/\text{U}_3\text{Si}_2$ were marked. The lamella was further thinned until perforation for TEM observation (Fig. 3(b)). Figure 3(c) shows the STEM image of the lamella with adjusted contrast at three regions to reveal the multiple phases. The bright phases in Zry-4 (U-rich phases in SEM/EDS) are exclusively rich in U and Zr from the STEM/EDS measurements and the atomic ratio of U to Zr is close to 3 : 7, which should be $\delta\text{-UZr}_2$. $\delta\text{-UZr}_2$ could exist in a Zr at.% window of approximately 71-79 according to the U-Zr binary phase diagram [12,13]. In the matrix of Zry-4, lots of lath structure can be found and similar features in Zircaloy have been studied by

others [14,15], which should correspond to the zirconium hydride. Water was used as a cooling agent when the Zry-4 bar was cut into disks, and subsequently stored in ethanol, which could have induced hydrogen in the Zry-4 to form zirconium hydride. The Fe- and Cr-rich phases at the interface of Zry-4/ZrSi₂ and ZrSi₂/U₃Si₂ as well as the interdiffusion layer of ZrSi₂ were further characterized using STEM/EDS (Figs. 4-6).

Figure 4 shows the STEM image of the Zry-4/ZrSi₂ interface and the EDS mapping of the rectangular region. The bright grains distributed at the interface are rich in Fe and Cr while depleted in U. These grains also contain Zr, Si, and W, which could be a Fe-Cr-Zr-Si-W compound. W is neither contained in the Zry-4 nor among the starting materials for fabricating U₃Si₂. The W impurity originates from U and Si powder processing in which an arc melter with a W electrode was used to form the U₃Si₂ compound [3]. The W electrode is considered non-consumable during welding, but some erosion (burn-off) can still occur [16] and a W concentration varying from 100 to 700 ppm can often occur in U₃Si₂ fabricated by this process [3].

Most equiaxed grains in the diffusion zone correspond to ZrSi₂, while some grains are exclusively composed of Zr. The first EDS profiles in Fig. 5(a) show the bright grain is composed of Zr (Fig. 5(b)). Si in U₃Si₂ diffused towards Zry-4 and attacked Zr to form ZrSi₂, but part of Zr grains was not attacked. In the ZrSi₂ matrix, there are several white nano-precipitates (Fig. 5(a)), which are rich in U (Fig. 5(c)), indicating that U diffused through ZrSi₂ to react with Zr and form U-Zr in the Zry-4.

As shown in Fig. 2, there are (Fe, Cr)-rich phases at the $\text{ZrSi}_2/\text{U-Si}$ interface. STEM/EDS shows the (Fe, Cr)-rich phases are mainly composed of Si, U, Fe, and Cr (Fig. 6), which also indicates that Fe and Cr moved out of Zry-4, passed the ZrSi_2 layer, and interacted with U_3Si_2 to finally form Fe-Cr-U-Si phases at the $\text{ZrSi}_2/\text{U-Si}$ interface. The U-Si near the diffusion zone may change from U_3Si_2 to some Si-rich U-Si phases, such as U_3Si_5 , thanks to high Si activity at the $\text{ZrSi}_2/\text{U-Si}$ interface (Fig. 6(b)).

3.3 Interdiffusion at 1000 °C

Figure 7 shows an SEM image and EDS map of the $\text{U}_3\text{Si}_2/\text{Zry-4}$ diffusion couple annealed at 1000°C for 30 hours. A diffusion zone width of $45 \pm 5 \mu\text{m}$ wide contained two main interdiffusion products, U-Zr and Zr-Si. Additionally, U-Zr phases were observed at the Zry-4 side of the diffusion zone. A TEM lamella was prepared at the rectangular region in Fig. 7(a). The STEM image of the lamella is shown in Fig. 7(f). All the phases were determined by EDS and labeled. The atomic ratio of Zr to Si in Zr-Si phases is 1.9 ± 0.1 , and they should be Zr_2Si . The atomic ratio of U to Zr in U-Zr phases in the Zry-4 region is 0.20 ± 0.01 , while that in the Zr-Si rich region is 0.12 ± 0.01 .

Figure 8(a) shows a low-magnification SEM image of the diffusion couple annealed at 1000°C for 100 hours. The marked regions 1, 2 and 3 were magnified and shown in Figs. 8(b), 8(c) and 8(d), respectively. The EDS mapping of Figs. 8 (b), 8(c), and 8(d) are shown in Figs. 9(a), 9(b) and 9(c), respectively. The curved edges observed on the diffusion couple indicate the deformation of diffusion couple occurred during the annealing cycle at 1000°C, possibly due to formation of low melting point phases. There is a bright band near the original center of the Zry-

4 disk (Fig. 8(a)). The band was largely composed of U-Zr, which is rich in U towards the fuel (Fig. 9(a)). On the right side of the band, Zr is dominant with numerous U-Zr branches extending into the bulk as well as some Fe-Ni containing phases. On the left side, no U-Si phases were detected; instead Zr-Si, U-Zr-Fe-Ni and U-rich phases were prevalent (Fig.8(c) and Fig. 9(b)). Figure 8(d) shows the microstructure of a region close to the edge of fuel. Three phases, Zr-Si, Fe-U and U-Zr-Fe-Ni can be identified by the EDS mapping (Figure 9(c)).

Figure 10(a) is a TEM lamella prepared from the region close to Fig. 8(c). The EDS quantification results of 1-5 phases marked in Fig. 10(a) are summarized in Table 1. In the U-rich region, bright U straps (Phase 2), less than 1 μm in width, are embedded in the dark U-Zr matrix (Phase 1). The U content in Phase 1 (U:Zr = 31.7:64.0) is less than that in U-Zr band (Phase 4, U:Zr = 47.7:52.2). There are 15.6 at.% Fe and 6.3 at.% Ni found in the U-Zr-Fe-Ni phase (Phase 3) and the Ni characteristic peak near 7.5 keV is marked on the EDS spectrum (Fig. 10(b)). The atomic ratio of Zr to Si in the Zr-Si phase (Phase 5) is close to 3:2 and the Zr-Si phase could be Zr_3Si_2 . However, the XRD pattern (Fig. 12) implies that Zr_2Si is one of the main phases (other main phases are U_6Fe and U-Zr) in the diffusion couple. Some minor diffractions (marked “?”) have not been assigned and they could correspond to U-Zr-Fe-Ni phase. It follows that besides Zr_2Si , other Zr rich Zr-Si phases, like Zr_3Si_2 may also exist in the interdiffusion products. Near the edge of the fuel, the Fe-containing and U-rich phase should correspond to U_6Fe .

The observation of Ni in the diffusion couple was unexpected since Ni is not found in Zr_2Si or U_3Si_2 . It follows that Ni and possibly some additional Fe diffused from an external source. The

likely source being the jig (48 wt.% Ni and 52 wt.% Fe). Figure 11 shows a picture of the jig after diffusion testing at 1000°C for 100 hours. Localized melting of the jig occurred near the diffusion couple, and although a Ta foil was used to separate the jig and the diffusion couple, Ni and Fe managed to diffuse into the diffusion couple.

4. Discussion

It has been shown in many out-of-pile and in-pile experiments that UO₂ fuel can be reduced by Zry-4 cladding at high temperatures under good solid state contact conditions to form oxygen-stabilized α -Zr(O) and metallic U [17-19]. Similar to the interaction between UO₂ and Zry-4 system, the solid state interaction between U₃Si₂ and Zry-4 could lead to the formation of Zr-Si compounds and U.

The U atoms diffused through ZrSi₂ layer (Fig. 5) and further towards Zry-4 cladding forming a U-Zr phase in the Zry-4 (Fig.3). Zr-rich Zr-Si phases, such as Zr₂Si formed near the Zry-4 (Fig. 7(f)). The U concentration in the reaction front (U-Zr in the Zry-4 regions) is higher than that in the diffusion zone (U-Zr in Zr-Si regions). U atoms near the interface only lead to the development of the reaction zone, resulting in a higher concentration of U at the front end of the reaction zone. Recent work on interdiffusion between U-UO₂ cermet fuel and T91 cladding shows that U₆(Fe,Cr) is close to T91 cladding and U(Fe,Cr)₂ is next to U₆(Fe,Cr) [19]. At the front end of the reaction zone, fuel and cladding constituents form U-rich intermetallic phases. The deep penetration of U atoms into Zry-4, resulting in the formation of numerous U-Zr branches in the Zry-4 (Fig. 7) implies the significant enhancement of U diffusion at 1000°C. Annealing the sample at 100 hours enhanced the interdiffusion of U₃Si₂ and Zry-4 leading to the

formation of a U-rich U-Zr band. This U-rich region acted as a reservoir providing consistent U to interact with Zr forming a U-Zr phase in the Zry-4. The formation of U-Zr due to the outward diffusion of U to Zry-4 may deteriorate the performance of cladding, which should be inhibited in the future. Further long term and lower temperature work is needed and the potential impact of fission products on fuel cladding interaction is yet to be studied.

At 800°C, Fe and Cr moved out of Zry-4 cladding and diffused towards U_3Si_2 . They first interacted with Zr-Si layer and formed Fe-Cr-W-Zr-Si at Zry-4/Zr-Si interface. W was from U_3Si_2 fuel and introduced by the arc-melting process [3], which will not be discussed here. Some Fe and Cr diffused through the Zr-Si layer and further interacted with the fuel and formed Fe-Cr-U-Si phases at Zr-Si/U-Si interface. At 1000°C and 30 hours, the segregation of (Fe,Cr)-containing phases at these interfaces was not readily observed from the EDS maps (Fig. 7), which indicates that some Fe and Cr diffused into the fuel and formed associated compounds there. At a longer annealing time (100 hours), U-Si fuel suffered serious attack from Zr and Fe as well as Ni and no U-Si phases remained in the diffusion couple. The gradual formation of low melting point U-Fe should be mainly responsible for the creep and serious deformation of the diffusion couple at 1000°C, which eventually led to a direct contact between the diffusion couple and the jig. In addition, the rate of element diffusion in the diffusion couple was remarkably increased when liquid phase U-Fe occurred. Ni and Fe from the Invar alloy jig could diffuse into the diffusion couple and form U-Zr-Fe-Ni and U_6Fe phases ($T_m = 831^\circ C$), which caused the localized melting of the jig contacting the diffusion couple. If more Fe diffuses from jig to the diffusion couple, UFe_2 may form, which can induce a eutectic reaction between UFe_2 and U_6Fe

at 719°C [21]. The eutectic reaction may cause a catastrophic melting of the jig and the diffusion couple. In addition, there is a low temperature eutectic reaction between Zr and Fe at 928°C [22], which could also prevent higher temperature investigations of this system using the current jig.

5. Conclusions

In this work, the microstructure of the interdiffusion behavior of U_3Si_2 and Zry-4 was investigated. At 800°C, the main interdiffusion product was a ZrSi_2 layer between the fuel and cladding; U in U_3Si_2 diffused into Zry-4 to form U-Zr; Fe and Cr in Zry-4 diffused towards U_3Si_2 to form Fe-Cr-W-Zr-Si at the Zry-4/ ZrSi_2 interface and Fe-Cr-U-Si phases at the ZrSi_2 /U-Si interface. At 1000°C, the diffusion rate of U was greatly enhanced, which caused U interactions with Zry-4 that formed a U-Zr band at the disc interface as well as numerous U-Zr branches in Zry-4. The main interdiffusion products were Zr_2Si , U_6Fe , U-Zr-Fe-Ni, U-Zr, and U. The formation of low melting point U-Fe caused the deformation of the diffusion couple at 1000°C, which led to a direct contact between the diffusion couple and the Invar alloy jig and their localized melting at the contact region. At 800°C, there does not appear to be any unexpectedly severe interdiffusion that would prevent the utilization of Zircaloy cladding with U_3Si_2 ; at 1000°C, the formation of low melting point U-Fe phase may cause a serious problem for the diffusion couple. Further work on the diffusion kinetics and more detailed microstructure characterization is planned. A neutron irradiation experiment is planned to further study the interaction of U_3Si_2 with cladding material at prototypic PWR temperatures (300-400°C).

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Table 1 EDS quantification results of U, Zr, Si, Fe, and Ni for phase 1-5 in Fig. 10 (unit: at%)

Phase	U	Zr	Si	Fe	Ni
1	31.7±2.3	64.0±1.4	3.3±3.8	0.8±0.4	0.2±0.3
2	98.0±1.8	2.0±1.8	0	0	0
3	13.6±1.0	63.6±1.9	0.9±0.7	15.6±2.0	6.3±0.7
4	47.7±2.0	52.2±2.0	0	0.1±0.1	0
5	0	60.3±0.9	39.3±1.0	0.1±0.1	0.3±0.1

Figure captions

Fig. 1 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 $[210]$. (d) 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.

Fig. 2 SEM image (a) and its EDS mapping (b-h) of a $\text{U}_3\text{Si}_2/\text{Zry-4}$ diffusion couple annealed at 800°C for 100 hours. A TEM lamella (Fig. 3a) was prepared from the yellow and dashed rectangular region.

Fig. 3(a) and (b) SEM images of a TEM lamella before and after the final thinning, respectively, (c) STEM image of the TEM lamella with various contrast at different regions. The main phases of Zry-4, ZrSi_2 , U_3Si_2 and their interfaces, $\text{Zry-4}/\text{ZrSi}_2$ and $\text{ZrSi}_2/\text{U}_3\text{Si}_2$ are marked.

Fig. 4 STEM image of $\text{Zry-4}/\text{ZrSi}_2$ interface for the TEM lamella in Fig. 3(c) and EDS mapping of the rectangular region.

Fig. 5 (a) STEM image of the diffusion zone in the TEM lamella in Fig. 3(c); (b) and (c) are the EDS line scan profiles along the line 1 and line 2, respectively.

Fig. 6 (a) STEM image of $\text{ZrSi}_2/\text{U-Si}$ interface; (b) EDS line scan profiles along the line in (a).

Fig. 7 SEM image (a) and its EDS mapping (b-e) of a $\text{U}_3\text{Si}_2/\text{Zry-4}$ diffusion couple annealed at 1000°C for 30 hours. (f) STEM image of a FIB lamella prepared at the rectangular region in (a).

Fig. 8 (a) Low magnification SEM image of a $\text{U}_3\text{Si}_2/\text{Zry-4}$ diffusion couple annealed at 1000°C for 100 hours. A U-Zr band was marked. (b) SEM image of a U-Zr band region (Mark 1 in (a)). (c) SEM image of a region near the left side of U-Zr band (Mark 2 in (a)). (d) SEM image of a region near the edge of the fuel (Mark 3 in (a)).

Fig. 9 EDS mapping of the region in Fig. 8(b)-Fig. 8(c).

Fig. 10 (a) STEM image of the $\text{U}_3\text{Si}_2/\text{Zry-4}$ diffusion couple annealed at 1000°C for 100 hours. The EDS quantification results for phase 1-4 are summarized in Table 1. (b) Representative EDS spectrum of phase 3.

Fig. 11 Picture of Invar jig after the diffusion testing at 1000°C for 100 hours.

Fig. 12 XRD pattern of the $\text{U}_3\text{Si}_2/\text{Zry-4}$ diffusion couple annealed at 1000°C for 100 hours. The diffractions of Zr_2Si , U_6Fe , (U, Zr), Sn and unassigned phases are marked.

(a) **(b)** UO_2 [101] **(c)** USi [210] **(d)** U_3Si_2 [100]

Zr La1

Si Ka1

O Ka1

U Ma1

Fe Ka1

Cr Ka1

C Ka1_2

Zry-4

ZrSi₂

500 nm

(a)

(b)

Localized melting of jig