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CHARACTERIZATION OF INTERACTION LAYER IN U-MO/AL DIFFUSION-COUPLE

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Abstract

In this paper, the Interaction behavior of U-Mo/Al was studied with diffusion-couple method, and the couple was continuously jointed by hot-pressing with special device. Annealing experiments were accomplished in a Vacuum hot-pressing furnace, and temperature for 550～570□ at 5～21hours. The results show that: the Interaction Layer is uneven thickness and their interface is not smooth. The layer close to U-Mo side is composed of product (U, Mo)Al_3 and UMo_2Al_{20}, while the Al side is composed of (U, Mo)Al4 and UMo_2Al_{20}. Diffusion process of U-Mo/Al is Al immigrating over the Al / U-Mo original interface into U-Mo side and reacting with U-Mo, subsequently the interaction layer is growing into Al. The diffusion reaction behavior of U-Mo/Al is a diffusion-controlled process, parabolic law, which kinetics conforms to the parabola rule, namely interaction layer thickness is proportional to the square root of time. Along with temperature increasing and time prolonging, interaction layer thickness increases.

1. Introduction

U-Mo alloy is the most promising research experiment reactor fuel for the γ-U-Mo radiation stable performance, fuel uranium density and relatively simple reprocessing [1]. During 1999 to 2003 high temperature and high burn-up irradiation, U-Mo fuel and Al matrix excessively reacted to generate loose compounds (U, Mo)Al_x high Al content. These products is unable to bound fission gas, pore appeared at interaction layer/Al interfaces grow up and interconnect, making fuel core rupture and leading to severe swelling and deformation of the fuel [1, 2]. Obviously, (U-Mo)-Al Dispersion Fuel irradiation failure is caused by excessive reaction of U-Mo/Al and interaction between fission gas and reaction products.

The research work out of pile can not exactly simulate the dynamic interaction process of fission gases and interaction layer, but it is easy to know diffusion reaction process of fuel and matrix. Furthermore, the study of U-Mo/Al is helpful in knowing U-Mo/Al reaction mechanisms and laws. It reported that diffusion reaction of U-Mo/Al did not occur lower than 500□ in Reference [3]. In-pile irradiation, the temperature is lower than 200℃, and U-Mo/Al interaction is caused by fission-fragment damage [4]. Out of pie the reaction should mainly initiate by temperature.

In this paper, Characterization of interaction layer of U-10Mo/Al, such as morphology, thickness, composition, elemental concentration distribution and phase structure, was studied with hot-press diffusion-couple method. In addition, the result was compared with irradiation test results. Finally, interface of interaction layer and variation of atomic ratio and diffusion-reaction kinetic was discussed based on the analysis.

2. Experimental

2.1 U-Mo Alloy and Al

Material is U-10Mo (10wt. % Mo) laboratory vacuum-induction melted and pure Al market purchased. The ingot and Al were rolled into a 3mm thick sheet. Al composition (mass fraction) is for Al-99.7Si-0.06Fe-0.16Ca-0.17, the total impurity content of 0.254.

2.2 Experimental procedures

First, U-Mo and Al was cut into 20mm × 10mm × 3mm small pieces. Then, the pieces were rough and fine grinded and polished by hand, successively washed the surface with alcohol and dried with air cooler. After doing this, it was clamped together with the hot-pressing equipment, and placed in a vacuum hot-press furnace. In order to keeping U-Mo and Al close fitting, a pressure of 6~8MPa was applied in heat-treatment. A sample using clamping means, due to Al softened at high temperatures, and its clamping force can be ignored. Basing on exploring fine annealing conditions, experiments were planed shown as Table 1.

2.3 Testing

After annealing, metallographic samples was prepared for analyzing interaction layer characteristics. Using MeF3A optical microscope (OM) to observe interaction layer morphology and measure the layer thickness, with U.S. FEI's Sirion200 scanning electron microscopy (SEM) to further observe the morphology of the layer interface features and Noran System SIX NSS300-based energy dispersive spectrometer (EDS) to analyze the layer composition, D/MAX-1400 X-ray diffraction (XRD) to analyze the layer phase composition.

Table.1 U-Mo/Al vacuum diffusion annealing experiments

No.	Diffusion Couple	Annealing Condition			Vacuum (Pa)	Fitting means
		Temperature (℃)	Pressure(MPa)	Time(h)		
1	U-Mo/Al	570±5	0	10	10^{-3}-10^{-4}	clamping
2	U-Mo/Al	570±5	6	5	10^{-3}-10^{-4}	hot-pressing
3	U-Mo/Al	570±5	6	10	10^{-3}-10^{-4}	hot-pressing
4	U-Mo/Al	570±5	6	15	10^{-3}-10^{-4}	hot-pressing
5	U-Mo/Al	570±5	8	10	10^{-3}-10^{-4}	hot-pressing
6	U-Mo/Al	550±5	6	10	10^{-3}-10^{-4}	hot-pressing
7	U-Mo/Al	550±5	6	21	10^{-3}-10^{-4}	hot-pressing
8	U-Mo/Al	550±5	8	5	10^{-3}-10^{-4}	hot-pressing

3. Results

3.1 interaction layer morphology

F. Mazaudier et al [3, 5, 10] reported that U-Mo/Al interaction layer had an unsmooth interface and uneven thickness distribution and layered when it was thicker. In this study, U-Mo/Al interaction layer morphology is showed in Fig. 1. As seen from Fig. 1 (a) and (b), the layer thickness is uneven and the interface is not smooth. In Fig. 1 (c) even if the layer is up to 600um, it is not layered. In Fig. 1 (a) in local areas, the layer exhibits an island-like growth. This pattern imply inconsistent growth rate at different locations or prior growth in some interface. This inevitably leads to interaction layer unsmooth growing and thickness unevenly distributing when the layer is thin. This growth pattern has been reported in U/Al system [6].

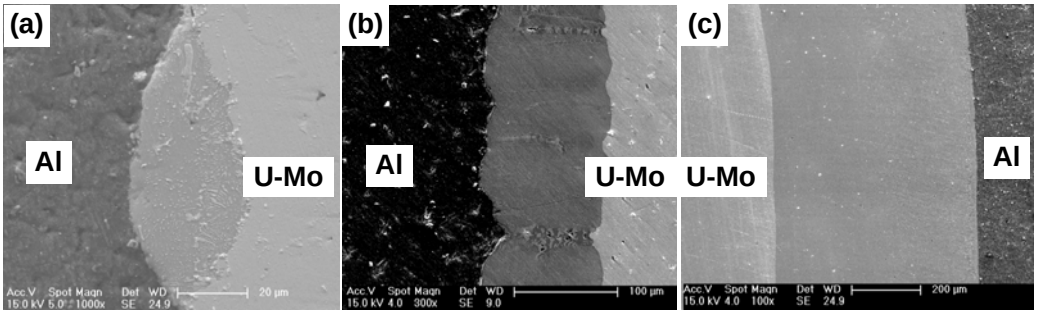

Fig.1 U-Mo/Al interaction layer SEM morphology
(a) 570℃×10h;(b) 570℃×6MPa×5h; (c) 570℃×8MPa×10h

3.2 Thickness of interaction layer

Table.2 U-Mo/Al Diffusion-couple Interaction Layer Thickness

Diffusion couple	Layer thickness (μm)						
	550℃×6MPa		550℃×8MPa	570℃×6MPa			570℃×8MPa
	10h	21h	5h	5h	10h	15h	10h
U-Mo/Al	16	293	103	138	580	820	593

The thickness of interaction layer is identified under the scope of the OM, and then area of diffusion zone and length of the interface direction of the layer is measured using software. Then, ratio of area/ length is mean thickness of interaction layer, which is shown in Table 2.

Be seen from the table, when temperature invariableness, the thickness increase over time to increase, and when time invariableness the thickness increase with temperature increasing. The thickness is lower the results which have reported by F. Mazaudier et al in U-7Mo/Al diffusion-couple [3]. This may be due to U-Mo alloy Mo content increased, and diffusion reaction rate decreases.

3.3 Composition of the interaction layer

Interaction layer composition is expressed with the form of (U, Mo)Al_x, where x is Al/(U + Mo) atomic ratio. EDS point scan image of U-Mo/Al diffusion couple interaction layer is showed in Fig. 2 (a), (b) and (c), and the composition is showed in Table 3.

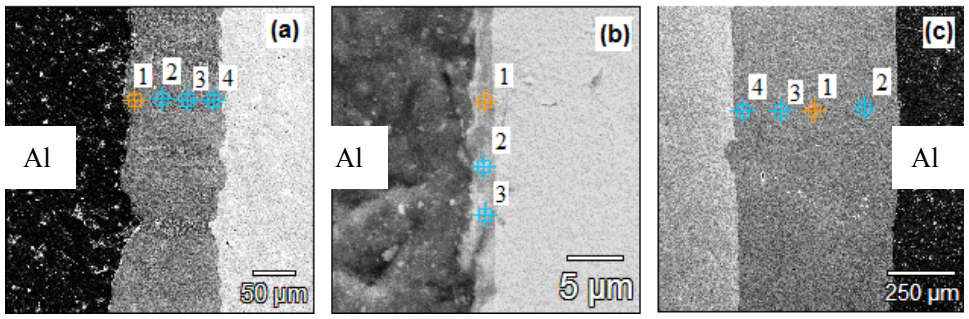

Fig.2 U-Mo/Al Interaction Layer EDS Point-scanning Composition Analysis
(a)570℃×6MPa×5h; (b)570℃×10h; (c)570℃×8MPa×10h

From Table 3, the interaction layer composition in Fig. 2(a) are (U, Mo) $Al_{5.5\sim3.7}$, where the x is greater than 3, and from the Al side to the U - Mo side Al content decreased gradually. In Fig. 2 (b) the layer composition is (U, Mo) $Al_{3.9\sim2.5}$, whose thickness is about 2um, where the x is about 3. In Fig. 2 (c) the layer thickness is about 600um, whose components are (U, Mo)$Al_{3.6\sim4.9}$. This result is conformed with irradiated test Al content 77~85 at.% Al and out pile study Al content of 70~90at.%Al which is respectively reported by G. hofman et al [7,8] and F. Mazaudier et al [3,5,8,10].

Table.3 U-Mo/Al Diffusion-couple Interaction Layer EDS Point-Scanning Composition

Point	Atom Fraction (at.%)			Composition	Atomic ratio		
	Al	U	Mo	Al/(U+Mo)	Al/U	U/Mo	Al/Mo
(a)-1	84.0	12.1	3.9	(U, Mo)Al5.3	6.9	3.1	21.5
(a)-2	84.7	11.2	4.1	(U, Mo)Al5.5	7.6	2.7	20.7
(a)-3	84.3	11.1	4.6	(U, Mo)Al5.4	7.6	2.4	18.3
(a)-4	78.7	15.9	5.4	(U, Mo)Al3.7	4.9	2.9	14.6
(b)-1	71.6	19.8	8.6	(U, Mo)Al2.5	3.6	2.3	8.3
(b)-2	77.2	15.8	7.0	(U, Mo)Al3.4	4.9	2.3	11.0
(b)-3	79.6	13.6	6.8	(U, Mo)Al3.9	5.9	2.0	11.7
(c)-1	78.3	15.8	5.9	(U, Mo)Al3.6	5.0	2.7	13.3
(c)-2	83.1	12.8	4.0	(U, Mo)Al4.9	6.5	3.2	20.8
(c)-3	77.7	16.3	6	(U, Mo)Al3.5	4.8	2.7	13.1
(c)-4	78.6	15.7	5.7	(U, Mo)Al3.7	5.0	2.8	13.8

From the table.3, when the ratios of Al/U are equal or approximate, correspondingly the values of Al/(U+Mo) are close. The ratio Al/U has the same changing trend with Al/Mo as well as Al/(U+Mo). Namely, the value of Al/U increases with Al/Mo as well as x value of (U, Mo)Al_x and Al/U decreases with Al/Mo as well as x value of (U, Mo)Al_x.

We can speculate that U-Mo/Al diffusion reaction should form (U, Mo)Al_3 type compounds firstly, and then form (U, Mo)Al4 type compounds. Therefore, UAl_3 may be U-Mo side in XRD and UAl_4 detected in Al side.

3.4 Concentration Distribution of interaction layer

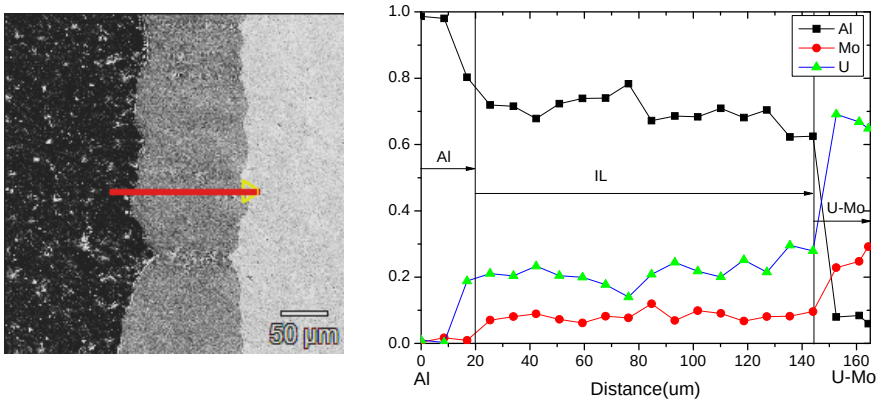

Fig.3 U-Mo/Al Interaction Layer EDS Line-scanning Elements Concentration Distribution

The concentration distribution of U-Mo/Al interaction layer EDS line scanning is shown in Fig. 3. As seen from the Fig. 3, from Al side to U-Mo side, Al content sharply decline at the Al/IL interface and then slowly reduce in IL; U and Mo gradually increase in the IL and then rapidly increase at the IL/U-Mo interface. The content of Al, U, and Mo is mutational at the interface of Al/IL and IL/U-Mo.

3.5 Phase of interaction layer

In order to detect the phase, the sample is removed Al with sandpaper to get U-Mo side interaction layer, and torn Al to get Al side interaction layer.

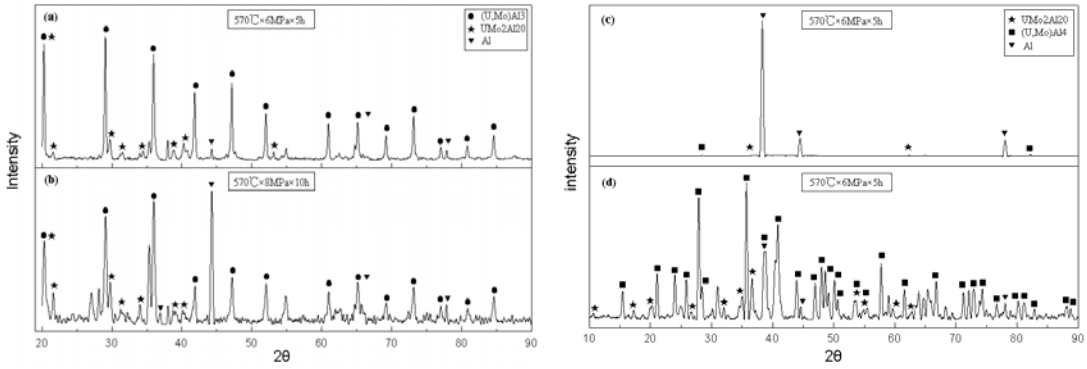

Fig.4 U-Mo/Al Diffusion-couple Interaction Layer XRD Analysis

XRD result is shown in Fig.4, which (a) and (b) respectively present the result of 570℃ ×6MPa×5h and 570℃×8MPa×10h U-Mo side interaction layer and (c) and (d) present the result of 570℃× 8MPa×10h and 570℃× 8MPa×10h U-Mo side interaction layer. As seen from Fig.4, near the U-Mo side the phase is composed of (U, Mo)Al_3 and UMo_2Al_{20}, which is main (U, Mo)Al_3 phase; close to Al side at the IL/Al interface the phase is composed of (U, Mo)Al_4 and UMo_2Al_{20}. These results are consistent with EDS composition and speculated conclusion. Because peak of UMo_2Al_{20} is infrequent in Fig.4 (a) and (b), the interaction layer of U-Mo side may be a mixture of (U, Mo)Al_3 and UMo_2Al_{20} or only (U, Mo)Al_3.

In the XRD detection, the result of Fig.4 (a) and (b) is UAl_3 (lattice constant: a = b = c = 4.24, Pm-3m space group structure) 2θ right shifted, taking into account the results of EDS and abroad results the phase should be (U, Mo)Al_3. Fig. 4 (c) and (d) to detect is UAl_4 (lattice constant: a = 4.400, b = 6.250, c = 13.716, Lmma space group structure), and consequently it is determined as (U, Mo)Al_4. In all samples, UMo_2Al_{20} (lattice constant a = b = c = 14.51, Fd3m space group structure) is detected, however, there is no evidence to indicate $U_6Mo_4Al_{43}$ existence which have reported by F. Mazaudier et al [3].

4. Discussions

4.1 U-Mo/Al diffusion interface

It is well known that the higher melting point metals and alloys the stronger binding force between atoms be, and the more difficult atom is activated to migrate. The Al melting point is 660℃ which is far lower than the U-10Mo alloy melting point (1150℃), so Al atoms are easier to migrate. Thus, in the diffusion processes of U-Mo/Al, Al atom is easier to be activated and takes the lead in passing through the interface between U-Mo and Al and migrating into U-Mo side. To observe the migration of the original interface of U-Mo/Al in the diffusion process, a Mo wire was placed at the interface between U-Mo and Al. After 570℃× 6MPa×15h annealing, the wire is fond at IL/Al interface, which is shown as Fig. 5(a). This means that the IL/Al interface is the original interface of U-Mo/Al. Therefore, diffusion reaction process of U-Mo/Al

is actually Al migrating into U-Mo side, in consequence interaction layer grown and Al consumed.

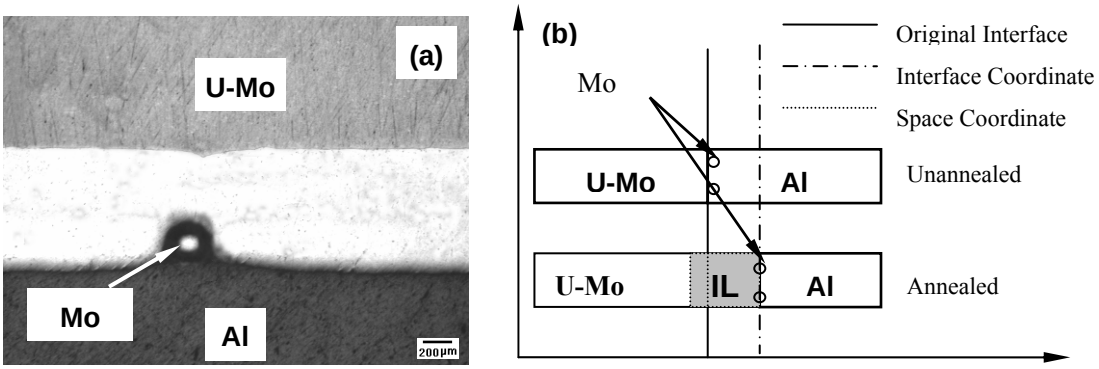

Fig.5 Initial Interface Immigration and Schematic Diagram (570℃×6MPa×15h)

If original interface where the molybdenum wire is placed is established interface reference coordinate, then the diffusion reaction process of U-Mo/Al is the Al diffusing into U-Mo side and solid-state reaction tacking place. It is reported that volume of product increase 10~15% comparing with reactant in diffusion behavior of U/Al and U/Al-Si [6]. In Fig.1 (a) the interaction layer is land-like growth, that is, mostly in the Al side and partly in U-Mo side, this may explain that the product of (U, Mo)Al_x expands to Al side. If original interface is established experimental space coordinate, the diffusion process is an inter-diffusion process of U (Mo) and Al. the original interface reference coordinate and the space experimental coordinate is shown in Fig.5 (b).

4.2 Variation of atomic ratio of interaction layer

Variation of atomic ratio of interaction layer in table 3 is shown In Fig. 6 (a). From Al side to U-Mo side, the ratio of Al/(U+Mo) has the same trend with Al/U. The ratio of U/Mo has a small-scale fluctuation. This shows that in the study of U-Mo/Al diffusion reaction, U and Mo can be deal with an element U (Mo). The distribution of interaction layer composition is shown in Fig.6 (b), which is concentrating on (U, Mo) $Al_{3\sim5.6}$.

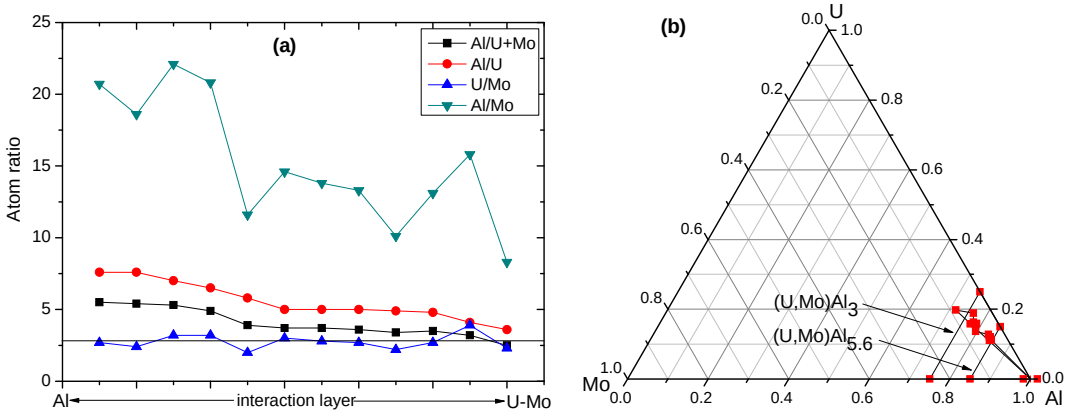

Fig.6 U-Mo/Al Diffusion-couple Interaction Layer Atomic Ratio and Composition Distribution

4.3 Diffusion kinetics of interaction layer

Diffusion reaction has two processes including phase interface diffusing and reacting. Reaction kinetics is controlled by the slowest process. When the diffusion velocity is much larger than reaction rate, then the reaction kinetics is controlled by the reaction rate; however, the diffusion rate is much smaller than reaction rate, then the reaction kinetics is controlled by the diffusion. It is reported that in U-Mo/Al system the diffusion kinetics is controlled by diffusion process as well as U/Al and U/Al-Si system [11]. Under normal circumstances controlled by diffusion process, interaction layer of the growth conforms to parabolic law. Using "Jander diffusion reaction model", it can be described as:

$$x^2 = Dt \tag{1}$$

Where, *x*-is interaction layer thickness; *D*-is diffusion coefficient; *t*-is annealing time. Interaction layer thickness and time in Table 2 was substituted in equation (1), obtaining the diffusion coefficient of 570 ℃ ×6MPa×(5~15)h $16.7\times10^{-12}m^2/s$ and 550 ℃ ×6MPa×(10h~21h) $2.16\times10^{-12}m^2/s$. the coefficient is much smaller than the diffusion coefficient of U-7Mo/Al D(550 ℃) =(2.5± 0.3)10^{-11} m^2/s and D(550℃)=4.78×10^{-11} m^2/s reported in literature[11].

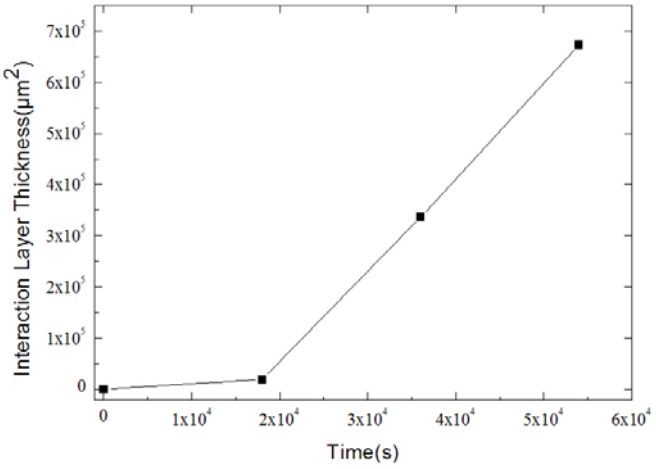

Fig.7 U-Mo/Al Diffusion Reaction Kinetics Curve (570℃×6MPa)

The relation of the interaction layer thickness and time is showed in Fig.7. From the Fig.7, the square of interaction layer thickness is proportional to time annealing 5~15h, which shows that U-Mo/Al diffusion reaction is a diffusion-controlled process during the period of 5~15h. "Multi-phase structure" of (U, Mo)Al_3, UMo2Al20 and (U, Mo)Al_4 has no effect on the growth of interaction layer. Additionally, the curve may be indicate that the diffusion reaction of U-Mo/Al has a long induction period or can be divided into two periods which diffusion reaction rate is different.

5. Conclusions

(1) The interaction layer of U-Mo side is composed of (U, Mo)Al_3 or a mixture of (U, Mo)Al_3 and UMo_2Al_{20}, and Al side is composed of (U, Mo)Al_4 and UMo_2Al_{20}. From Al side to U-Mo

side, Al content decrease, and U and Mo content increases; at interface Al, U and Mo content is mutational.

(2) The diffusion reaction process is Al passing through the original interface of Al/U-Mo and migrating into U-Mo side, which interaction layer grows to Al side. Taking interface coordinate as reference, the U-Mo/Al diffusion reaction is a process of Al diffusing to U-Mo side; Taking space coordinate as reference, the diffusion is a process of inter-reaction. In the process, the ratio of U/Mo is basically unchanged, so U-Mo/Al diffusion can be simplified to U(Mo)/Al binary diffusion.

(3) The diffusion reaction is controlled by diffusion, which kinetic conforms to parabolic law. Namely, the square of interaction layer thickness is proportional to time, and as time and temperature increased the layer thickness is increasing.

Acknowledgements

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