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INTERDIFFUSION BETWEEN
URANIUM-5 w/o FISSION ALLOY
AND TYPE 304 STAINLESS STEEL

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ABSTRACT

The compatibility of U-5 w/o Fs* with Type 304 stainless steel was investigated in the temperature range from 550 to 700°C. Appreciable interdiffusion bands were detected, but only about 5% of the band was into the stainless steel while the bulk of the diffusion was into the fuel. When the data obtained at the reference operating temperature of 550°C for EBR-II, Core I was extrapolated to the proposed recycle time of 7.8×10^6 sec (90 days), a value of 6.4×10^{-3} cm was found for the total band width. As the temperature increased, the diffusion band widened rapidly, more than doubling with each 50°C temperature increment until at 650°C it becomes 3.6×10^{-2} cm in 7.8×10^6 sec (90 days).

The total band width, as determined metallographically, was taken as the depth of diffusion penetration. Electron microprobe analysis served to corroborate these findings.

INTRODUCTION

The diffusion of fuel through the cladding while in a reactor could result in contamination of the coolant stream and loss of fissionable material. Appreciable diffusion may also severely affect pertinent mechanical and thermal properties of the fuel cladding. For these reasons it is necessary to know the amount of interdiffusion that occurs between the fuel and the cladding in any reactor loading.

The materials and the conditions of time and temperature selected for the study herein were based on the utilization of the Core-I loading of the Experimental Breeder Reactor II (EBR-II). The fuel is U-5 w/o Fs* and the clad is AISI Type 304 stainless steel. Although the maximum planned interface temperature between fuel and clad is 550°C, this study was extended to 700°C to determine the maximum useful temperature for this combination of materials.

*Fissium (Fs) is an equilibrium concentration of fission product elements left by the pyrometallurgical reprocessing cycle designed for EBR-II. The major constituents of fissium are zirconium, molybdenum, palladium, ruthenium, and rhodium.

Although work has been done in the past on closely related systems, the interdiffusion of the above two materials has not been studied. Kittel,⁽¹⁾ using a picture-frame method, studied the interdiffusion of uranium and Type 347 stainless steel. Weil and Paine⁽²⁾ also studied the interdiffusion of uranium and Type 347 stainless steel, but used a slightly different experimental procedure.

Both represented their data by the general parabolic rate equation $X^n = Kt$, where X is the diffusion depth in centimeters, K is a constant in cm^n/sec , t is the time at temperature in seconds, and n is the exponent of X found from the slope of a log-log plot of X versus t . Both sets of rate equations are given in Table I. Kittel's equations are for the total diffusion band width. The equations given by Weil and Paine represent data only for the uranium-rich layer, which was by far the wider of the two zones encountered, because they believed it was difficult to calculate diffusion coefficients for multiphase systems. In the Weil and Paine couples, the iron-rich phase was about 10% of the total diffusion band width at 500°C and about 25% of the band width at 700°C.

Table I

COMPARISON OF RATE EQUATIONS OF THE FORM
 $X^n(\text{cm}) = K(\text{cm}^n/\text{sec})t(\text{sec})$ FOR INTERDIFFUSION
 BETWEEN URANIUM AND TYPE 347 SS

Temp (°C)	Kittel (Total Band)	Weil and Paine (U-rich Band)
500	$X^{2.9} = 1.9 \times 10^{-15} t$	$X^{1.952} = 1.770 \times 10^{-12} t$
550		$X^{2.033} = 4.337 \times 10^{-12} t$
600	$X^{2.5} = 1.7 \times 10^{-12} t$	$X^{2.108} = 1.041 \times 10^{-11} t$
650		$X^{2.178} = 2.417 \times 10^{-11} t$
700		$X^{2.242} = 5.522 \times 10^{-11} t$

We believe that the number of significant figures presented in Weil and Paine's equations is unwarranted because of the inherent problems of diffusion-band measurement. For instance, the exponents obtained in their equations could probably have been rounded off at one place to the right of the decimal point.

At 600°C and for 8.6×10^5 sec (10 days), Kittel's and Weil and Paine's work agreed quite well ($X = 4.6 \times 10^{-3}$ cm and 4.0×10^{-3} cm, respectively). Their data do not agree at 500°C for 8.6×10^5 sec ($X = 4.1 \times 10^{-4}$ cm and 1.0×10^{-3} cm, respectively). They also report activation energies (17.7 kcal/mol by Kittel, and 42.6 kcal/mol by Weil and Paine) that are in poor agreement.

The discrepancy in activation energy may be explained by considering work done by Van Horn⁽³⁾ in which he analyzes the relationships between the diffusion constant K , the exponent n of the modified general parabolic law, and the activation energy for diffusion of phase boundaries. The relationship he finds when n varies with temperature is much more complicated than that used in the analysis of the above data. Because of this, Van Horn considers it fallacious to use the general parabolic law $X^n = Kt$, as it stands, to obtain an activation energy.

Kittel and Weil obtained approximately the same penetrations at 600°C, but because of their differences in n and K and their variation with temperature, the quantities they calculated as activation energies were far different and really have little physical significance.

Even when one is considering the interdiffusion between two metals having complete mutual solid solubility, care must be exercised in obtaining an activation energy for diffusion from the slope of $\log D$ versus $1/T$, as is pointed out by Hilliard.⁽⁴⁾

In view of the above we will not calculate an activation energy, but will only plot $\log K$ (penetration coefficient) versus $1/T$ to show the variation of K with temperature T . We will, however, determine from this plot the appropriate constants used in an equation relating X , t , and T .

Weil and Paine also studied the effect of irradiation on the interdiffusion rate between uranium and Type 347 stainless steel. They found that there was no measurable effect with neutron fluxes up to 3×10^{12} nV for runs up to 1.4×10^6 sec (16 days). The neutron dose obtained in their experiments is much lower than that expected in EBR-II Core I, which should have a central core flux of 3.7×10^{15} nV for 7.8×10^6 sec (90 days).⁽⁵⁾

EXPERIMENTAL PROCEDURE

Specimen Preparation

The analysis of the U-5 w/o Fs and of the Type 304 stainless steel used in these experiments is given in Table II.

Table II
ANALYSIS OF U-5 w/o Fs AND AISI TYPE 304 SS
USED FOR DIFFUSION COUPLES
(w/o)

Element	Material		Element	Material	
	U-5 w/o Fs	304 SS		U-5 w/o Fs	304 SS
Mo	2.51		Si		0.63
Pd	0.203		P		0.023
Rh	0.279		S		0.008
Zr	0.0554		C	0.036	0.08
Ru	1.94		N	0.079	0.005
Ni		9.30	O	0.071	0.03
Cr		17.87	H	0.0033	
Mn		0.49			

Each diffusion-couple assembly consisted of a disk of U-5 w/o Fs between two disks of 304 stainless steel, each 0.635 cm in diameter by 0.477 cm thick, stacked on top of one another and fitted snugly into a molybdenum picture frame (see Fig. 1). Molybdenum was used because of its low coefficient of thermal expansion, $5 \times 10^{-6}/^{\circ}\text{C}$,⁽⁶⁾ and its good elevated temperature strength. These features were desirable because we wanted positive pressure on the couple during heat treatment.

36780

Fig. 1. Diffusion-couple Assembly

The surfaces which were to become diffusion interfaces were carefully polished flat by use of 4/0 emery paper on a glass plate and a special specimen holder (see Fig. 2). After two 304 stainless steel specimens and one U-5 w/o Fs specimen were polished, they were immediately assembled in the molybdenum picture frame and the assembly was squeezed under a 6400-kg load (about 6300 kg/cm^2). The couple was then placed in a vacuum desiccator and evacuated. The time lapse between surface preparation and insertion into a vacuum was no more than 3 min.

36781

Fig. 2. Specimen Holder for Polishing Diffusion Surfaces

Encapsulation for Heat Treatment

The couples were transferred to stainless steel capsules, which were in turn loaded with enough NaK to immerse the couples, back-filled to $\frac{1}{2}$ atm (absolute) with helium and sealed.

The apparatus used to encapsulate and load with NaK was located in a glovebox containing a protective nitrogen atmosphere.⁽⁷⁾ The NaK was added to the capsules for the following two reasons: 1) the presence of NaK in the capsule as a good heat transfer media assures one of more even temperature across the couple. 2) the actual reactor fuel is thermally bonded to its stainless steel cladding with sodium.

Heat Treatment

Heat treatments were carried out at 550, 600, and 650°C for 7, 14, and 35 days, and at 700°C for 35 days. Temperatures in the furnaces were controlled to better than $\pm 3^\circ\text{C}$.

Metallography

After the annealing, the diffusion couples were removed from their picture frames and sectioned. Standard mechanical grinding and polishing techniques were used (grinding on 180 through 600 grit papers, and polishing with 6- and 1- μ diamond paste). An electrolytic etch containing 5 parts ethylene glycol, 5 parts phosphoric acid, and 8 parts ethyl alcohol, by volume, was used on all couples at about 25 V for 10-45 sec. Photomicrographs of representative areas were taken at 200X (see Figs. 3 and 4), and all measurements of the diffusion depth were made directly from these photographs. Uniform bands were found in all cases, indicating that good bonding had occurred.

Electron Microprobe Analysis

Because metallography may not bring out all the compound bands or solid-solution diffusion areas, additional data were required. To obtain these, electron microprobe analysis was performed, with a Cambridge unit by IIT Research Institute, with two specimens [550°C for 3.0×10^6 sec (35 days) and 650°C for 3.0×10^6 sec]. The analyses indicated that significant penetration did not occur beyond that shown in the photomicrographs.

Fig. 3. Photomicrographs of U-5 w/o Fs vs. 304 SS Diffusion Couples all at 200X

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200X

Fig. 4. U-5 w/o Fs vs. 304 SS Annealed at 700°C for 35 Days

RESULTS AND DISCUSSION

The penetration data obtained are summarized in Table III and plotted in Fig. 5 (as log of the penetration time versus log of the penetration depth at 550, 600, and 650°C). Though an appreciable interdiffusion band was detected, only about 5% of the band was into the stainless steel, the remainder being into the fuel. If the curve for 550°C (the expected fuel-cladding interface temperature of EBR-II, Core I) is extrapolated to 7.8×10^6 sec (90 days), which is the recycle period, a value of 6.4×10^{-3} cm is obtained for the penetration. About 3×10^{-4} cm of this would be into the 2.3×10^{-2} cm cladding. However, these bands are chiefly composed of compounds of uranium with iron, chromium, and nickel - the low thermal conductivities and brittleness of which could affect performance of the fuel and the cladding.

Table III

TOTAL DIFFUSION BAND WIDTHS
BETWEEN U-5 w/o Fs AND 304 SS

Temp (°C)	Band Width (cm x 10 ³)		
	6.0 x 10 ⁵ -sec (7-day) Anneal	1.2 x 10 ⁶ -sec (14-day) Anneal	3.0 x 10 ⁶ -sec (35-day) Anneal
550	1.9	2.6	4.2
600	4.5	5.9	9.5
650	9.9	14	22
700	-	-	53

Fig. 5. Penetration Time vs. Total Band
Width of U-5 w/o Fs vs. 304 SS

The slope of the log-log plot in Fig. 5 gives a value for n in the general parabolic equation $X^n = Kt$, where X is the band width in cm, K is the penetration coefficient, and t is the time in seconds.⁽⁸⁾ The value of n obtained is about 2, which gives a rate law of $X^2 = Kt$ and the following equations:

$$550^\circ\text{C}: X^2 = (5.7 \times 10^{-12} \text{ cm}^2/\text{sec}) t;$$

$$600^\circ\text{C}: X^2 = (3.1 \times 10^{-11} \text{ cm}^2/\text{sec}) t;$$

$$650^\circ\text{C}: X^2 = (1.6 \times 10^{-10} \text{ cm}^2/\text{sec}) t.$$

A plot of the log of the penetration coefficient calculated from the above equation against the inverse of the absolute temperature (see Fig. 6) gives a fairly straight line. The data obtained at 700°C were not plotted since they may not be reliable in a diffusion analysis. This question arises because at 700°C our fuel-cladding combination is very close to the temperature at which it will form a low-melting eutectic (an eutectic forms in the uranium-iron system at 725°C).⁽⁹⁾ The U-5 w/o Fs/304 SS system probably forms an even lower-melting material.

Fig. 6. Penetration Coefficient vs. the Inverse of the Temperature for U-5 w/o Fs vs. 304 SS

From Fig. 6 a value of K for any temperature between 500 and 650°C may be estimated, and the equation $X^2 = Kt$ may be used to calculate the band width for a given time. The following equation may also be used to calculate X :

$$X = 10.3 (t)^{1/2} \exp - \frac{1.26 \times 10^4}{T}.$$

Because of the complexity of this system, no attempt was made to calculate an activation energy from the slope of the $\log K$ versus $1/T$ plot.

Figure 7 is a comparison of the data obtained with uranium against Type 347 stainless steel by Kittel and by Weil and Paine with the data in the present investigation of U-5 w/o Fs against 304 stainless steel. Although Kittel's and Weil and Paine's work is with the same materials, they have very different results; only at about 600°C do their data agree.

Fig. 7. Total Thickness of Diffusion Layers Formed in 10 Days (8.6×10^5 sec)

The use of metallographic examination of diffusion zones is a common way to determine interdiffusion between two materials which form compounds. There are, however, some very serious shortcomings to this method. The first is the possibility of not bringing out with the etchant all of the compound layers present. The second is the possibility of substitutional solid-solution diffusion in systems which exhibit extensive solid solubility. One may not be able to bring out this solid-solution penetration with an etchant. There is also the possibility that diffusion of impurities or of small amounts of alloying elements cannot be detected metallographically. It is therefore desirable to have a more positive identification. The microprobe analysis performed in this investigation served as a check on the metallographic results. There was no evidence for penetration deeper than was seen metallographically by either iron, chromium, and nickel into the U-5 w/o Fs, or of uranium, molybdenum, and ruthenium into the 304 stainless steel.

CONCLUSIONS

(1) At 550°C for 7.8×10^6 sec (90 days) (the expected operating temperature and recycle time of EBR-II, Core I), a total band width of 6.4×10^{-3} cm was found. Of this, only 3×10^{-4} cm was into the 2.3×10^{-2} -cm 304 stainless steel cladding. This penetration, however, could affect the performance of the fuel and cladding.

(2) As the temperature increased, the diffusion band widened rapidly, more than doubling with each 50°C temperature increment, until at 650°C it became 3.6×10^{-2} cm in 7.8×10^6 sec (90 days).

(3) The experimental technique proved to be adequate, especially with respect to producing good bonding.

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