10. ^N^NPHYSICO-CHEMICAL STUDIES OF Fe-Cr-Al-CLAD FUEL SYSTEMS

(7076)

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The objective of this program, which was terminated at the end of FY-66, was to define and to understand the reactions which can occur between oxidation-resistant Fe-Cr-Al-base alloys and UO₂ in the temperature region from 500° to 1200°C.

Early attempts to use Fe-Cr-Al-base alloys as cladding for UO₂ or metal-UO₂ fuels resulted in the appearance of uranium as surface contamination on specimens tested in air at elevated temperatures for extended periods of time. The tentative explanation of this result was that UO₂ was reduced by aluminum in the cladding, thus producing uranium which diffused to the surface. Final work on this program during CY-67 included diffusion studies and fueled capsule tests. A summary of the conclusions derived from the overall work program is presented.

10.1 DIFFUSION STUDIES

Fe, Cr, AND Al DIFFUSION

Diffusion couples of Fe-Cr-Al versus Fe and Fe-Cr-Al versus Cr were studied to determine the rate of influx of cladding alloy constituents, such as Al, into the core area, which normally contains a cermet fuel of Fe-UO₂ or Cr-UO₂. The couples were fabricated from 2.54-cm-long by 1.27-cm-diameter rods of the Fe-Cr-Al alloys listed in Table 10.1. A 0.32-cm-diameter axial hole was drilled into the rods and the core portion of the diffusion couple (usually Fe or Cr) press-fitted into the opening in the cladding. The diffusion capsules were completed by fitting a closure rod of the same alloy as the cladding into the top of the capsule and sealing by electron-beam welding in vacuum. After checking for leaks, the capsules were autoclaved for 2 hours at 1000°C and 700 kg/cm² gas pressure to insure core-cladding contact. Sufficient couples were placed on test at 1000°C that a complete set could be removed for destructive analysis after 100, 300, and 1000 hours.

The initial results of transverse electron microprobe analyses presented previously¹ were not quantitatively accurate; trends in the data, however, indicated that cladding materials containing greater quantities of Al will increase the distance Al diffuses into Fe cores, and that Cr most effectively curtails the diffusion of cladding constituents. The diffusion couples were re-examined using the electron microprobe in the step-scan scaling mode with fixed-time counting. Corrections were applied to the data and plots made of the normalized concentrations as a function of radial distance.² A solution of the diffusion equation, appropriate for the geometry of the test specimens, was determined and

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¹"Sixth Annual Report - High-Temperature Materials Program, Part A," GE-NMPO, GEMP-475A, March 31, 1967, pp. 178-179.

²"AEC Fuels and Materials Development Program Progress Report No. 67," GE-NMPO, GEMP-67, June 30, 1967, pp. 79-86.

numerical values for diffusion coefficients of Fe, Cr, and Al in Fe-base alloys were calculated (Table 10.2). No diffusion coefficients were calculated for samples with Cr cores. The markedly lower diffusion rates in Cr were apparent from a qualitative examination of the plots.

URANIUM DIFFUSION

The objective of the uranium diffusion studies was to determine the manner in which the U-bearing reaction products formed in the core were transported through the cladding to the surface. An attempt was made to determine the diffusion coefficient of U in Fe-Cr-Al alloys and to differentiate between volume diffusion and grain boundary diffusion of U in these alloys.

Determination of the diffusion coefficients of U in Fe-Cr-Al alloys was hampered by the lack of an accurate method for measuring very small concentrations of U in these alloys. Initially, the electron microprobe and spark-source mass spectrograph were used in attempts to measure U concentration gradients and solubilities. The extremely low U solu-

TABLE 10.1

COMPOSITIONS^a OF ALLOYS FABRICATED FOR PROGRAM USE

Fe - 5Cr - 4Al	Fe - 5Cr - 7Al	Fe - 5Cr - 10Al	Fe - 4Al
Fe - 15Cr - 4Al	Fe - 15Cr - 7Al	Fe - 15Cr - 10Al	Fe - 10Al
Fe - 25Cr - 4Al	Fe - 25Cr - 7Al	Fe - 25Cr - 10Al	Fe - 5Cr
			Fe - 25Cr

^aNominal compositions are in weight percent.

TABLE 10.2

DIFFUSION COEFFICIENTS AT 1000°C

Nominal Composition, wt % Core	Cladding	Time, hr	Diffusion Coefficient, cm ² /sec		
			D _{Fe}	D _{Cr}	D _{Al}
Fe	Fe - 4Al	100	— ^a	—	6.5 x 10 ⁻¹⁰
Fe	Fe - 4Al	300	—	—	5.0 x 10 ⁻¹⁰
Fe	Fe - 10Al	100	7.8 x 10 ⁻¹⁰	—	6.7 x 10 ⁻¹⁰
Fe	Fe - 10Al	300	—	—	8.0 x 10 ⁻¹⁰
Fe	Fe - 25Cr	100	2.9 x 10 ⁻¹⁰	3.1 x 10 ⁻¹⁰	—
Fe	Fe - 25Cr	300	—	9.0 x 10 ⁻¹⁰	—
Fe	Fe - 5Cr - 4Al	100	—	2.9 x 10 ⁻¹⁰	5.8 x 10 ⁻¹⁰
Fe	Fe - 5Cr - 10Al	100	6.3 x 10 ⁻¹⁰	2.8 x 10 ⁻¹⁰	5.3 x 10 ⁻¹⁰ to 21.0 x 10 ⁻¹⁰
Fe	Fe - 25Cr - 4Al	100	2.9 x 10 ⁻¹⁰	2.4 x 10 ⁻¹⁰	9.5 x 10 ⁻¹⁰
Fe	Fe - 25Cr - 10Al	300	8.1 x 10 ⁻¹¹	3.5 x 10 ⁻¹⁰	1.3 x 10 ⁻⁹
Fe - 10Al	Fe - 5Cr - 10Al	1000	—	5.5 x 10 ⁻¹⁰	—
Fe - 10Al	Fe - 25Cr - 10Al	100	4.7 x 10 ⁻¹⁰	3.4 x 10 ⁻¹⁰	—
Fe - 25Cr	Fe - 25Cr - 4Al	100	—	—	3.5 x 10 ⁻¹⁰
Fe - 25Cr	Fe - 25Cr - 4Al	300	—	—	4.0 x 10 ⁻¹⁰
Fe - 25Cr	Fe - 25Cr - 10Al	100	—	—	6.8 x 10 ⁻¹⁰

^aNot measured.

bilities in Fe-Cr-Al alloys (~ 0.1 wt %) were at or below the detection limit of the electron microprobe, and the relatively low spatial resolution of the spark-source mass spectrograph rendered it unsuitable for accurate analysis of a solid diffusion couple.

The high sensitivity and accuracy of the X-ray fluorescence spectrograph in determining microgram quantities of U on the surface of Fe-Cr-Al-clad fueled specimens (discussed later), prompted an investigation of this instrument as a potential tool in determining U diffusion coefficients. As originally fabricated, the diffusion couple to be analyzed consisted of two solid right cylinders of Fe-5Cr-4Al-1U and Fe-5Cr-4Al (both wt %) butted together and sealed in Fe-Cr-Al tubing. The couple was autoclaved at 1000°C to insure contact and then heat treated for 3450 hours at 1000°C . Parallel sections were removed by machining and analyses were made perpendicular to the specimen length with the periphery masked to eliminate surface effects. A graph of the U concentration as a function of distance (shown in Figure 10.1) agreed with pertinent chemical analyses, microprobe, and metallographic data; however, part of the experimental data in the region of the interface appeared suspect and would need to be verified. Also, the

Fig. 10.1 — Uranium concentration profile in Fe-5Cr-4Al-1U versus Fe-5Cr-4Al (wt %) diffusion couple after 3450 hours at 1000°C .

unsymmetrical shape of the data points in the vicinity of the interface does not fit available solutions of the diffusion equation. However, the extended length of diffusion time and the length of the diffusion zone may partly compensate for experimental errors. The maximum diffusion distance measured by this technique correlates well with data obtained from the fission track etching method (discussed later). This correlation adds credence to the present data and prompted calculating an approximate value of the diffusion coefficient for U in the Fe-5Cr-4Al alloy. Using a semi-infinite diffusion model with an extended source, the diffusion coefficient was determined to be in the range 10^{-9} to 10^{-10} cm^2/sec , or approximately the same as the coefficients determined for Fe, Cr, and Al. Although supporting data are necessary before this coefficient can be considered accurate, the results

do show the potentialities of the X-ray fluorescence spectrograph to perform difficult and sensitive analyses. It is believed that improved sectioning and standardizing techniques could significantly increase the accuracy of this technique for future diffusion studies of this type.

An attempt was made to differentiate between volume and grain boundary diffusion of U in Fe-Cr-Al alloys using the fission track etching technique.³ Diffusion couples of the type Fe-Cr-Al-U versus Fe-Cr-Al were heat treated for 500 and 1000 hours at 1000°C and 100 hours at 1050°C. These specimens were longitudinally sectioned, metallographically polished, and shipped to a reactor site where they were coated with plastic and irradiated. After irradiation, the location of U in the Fe-Cr-Al side of the couple was determined in relation to existing grain boundaries. This method showed that U diffusion through Fe-Cr-Al alloys at 1000° to 1050°C is by volume diffusion, unaffected by grain boundaries. This method also confirmed the existence of U in the U-depleted zone of the original Fe-Cr-Al-U portion and an abrupt decrease of U at the depleted zone – Fe-Cr-Al-U boundary. Because of the relatively small number of diffusion couples irradiated and the failure of several to develop reliable fission track patterns, no diffusion constant was obtained; however, maximum U diffusion distances were measured and are shown in Figure 10.2 together with the maximum distance of U penetration as measured by X-ray fluorescence on Fe-5Cr-4Al-1U versus Fe-5Cr-4Al after 3450 hours at 1000°C. These data verify that the diffusion of U is unaffected at 1000°C by grain boundaries and is independent of Fe-Cr-Al composition (within the limits studied).

Fig. 10.2 — Maximum penetration of uranium in Fe-Cr-Al-base alloys at 1000°C as measured from the interface by fission track etching or sectioning methods

³H. S. Rosenbaum and J. S. Armijo, "Fission Track Etching as a Metallographic Tool," Journal of Nuclear Materials, Vol. 22, April 1967, pp. 115-116.

10.2 FUELED CAPSULE TESTS

Capsule tests were performed to quantitatively determine the rate of U accumulation on the surface of Fe-Cr-Al-clad UO_2 -containing cermet fuel specimens as a function of the cladding and core composition. The specimens in these tests were 2.5-cm-diameter discs approximately 0.25 cm thick, with 0.038-cm-thick cladding on one flat side and 0.076-cm-thick cladding on the other. The cladding compositions were those listed in Table 10.1 and the fueled cores were predominantly $\text{UO}_{2.00}$, $\text{UO}_{1.989}$, and Fe - 40 $\text{UO}_{2.00}$ (vol %) sintered to densities exceeding 95 percent of theoretical. A few Cr - 40 $\text{UO}_{2.00}$ (vol %) cores clad with 0.051-cm-thick Fe - 25Cr - 4Al (wt %) were fabricated. The capsules were evacuated, sealed by electron-beam welding, and autoclaved at 600°C and 140 kg/cm² gas pressure to achieve uniform core - cladding contact during testing. Testing was done under 2 atmospheres of argon gas containing 3 volume percent oxygen to maintain core - cladding contact, oxidize any U diffusing to the cladding surface, and prevent catastrophic oxidation of the low-alloy claddings.

Partial results from testing capsules at 1200°C and 800°C were reported previously,⁴ together with information for a series of capsules containing Fe - 40 $\text{UO}_{2.00}$ cores and $\text{UO}_{1.989}$ cores which completed 1000 hours at 600°C. Analysis for surface U was by X-ray fluorescence spectrograph with a 7 to 9 microgram U/cm² lower limit of detection.

Two series of clad specimens completed 1000 hours at 1200°C; one series contained $\text{UO}_{2.00}$ cores and the other $\text{UO}_{1.989}$ cores. Figure 10.3, which shows the quantity of U on the surface of specimens containing $\text{UO}_{1.989}$ cores, demonstrates that free U (present in the core) diffuses completely through the cladding within 6 hours at 1200°C. The quantity of Al present in the Fe-Cr-Al cladding appeared to have little, if any, influence on the rate of accumulation of surface U; however, complete absence of Al from the cladding (Fe - 5Cr and Fe - 25Cr) decreased the U diffusion rate. The presence of U in the claddings had a detrimental effect on the cladding or cladding - core interface and resulted in many cladding failures due to radial cracking.

Results for representative capsules containing $\text{UO}_{2.00}$ cores during 1000 hours at 1200°C are shown in Figure 10.4. Only minor differences arising from different cladding thickness are indicated, the first detection of surface U on the 0.76-mm-thick cladding occurred 20 to 40 hours after the first indication on the 0.38-mm-thick side (13 hours). No definite relationship was established between the quantity of Al in the Fe-Cr-Al cladding and the amount of surface U contamination. The data show that binary Fe-Al claddings will produce greater amounts of U on the surface than Fe-Cr-Al alloy claddings and claddings containing no Al will produce no detectable U during 1000 hours testing at 1200°C. Thus, it appears that Al in the cladding does produce subsequent U contamination on the surface, probably due to reducing UO_2 to U. The comparatively high U concentration on the capsules without Cr in the cladding may indicate that Cr has an inhibiting effect on the diffusion of Al. A slight but similar trend was noted among the Fe-Cr-Al-clad capsules; those with 25 percent Cr had smaller surface concentrations than those with 5 percent Cr, even though the Al concentrations of the claddings were the same. In this group of specimens, there was no evidence of oxidation or cracking in any of the claddings as in the group of substoichiometric specimens.

The preceding observations were in agreement with the diffusion results on Cr and Al and suggested that the diffusion of Al into the core (containing $\text{UO}_{2.00}$) could be curtailed or eliminated with a Cr barrier layer; thus, no U would be produced to diffuse to the surface of the cladding. Accordingly, several capsules were fabricated from 0.51-mm-thick Fe - 25Cr - 4Al (wt %) cladding and Cr - 40 $\text{UO}_{2.00}$ (vol %) fuel was fabricated as the usual

⁴GEMP-475A, pp. 181-182.

Fig. 10.3 — Concentration of U on surface of various claddings after 1000 hours at 1200°C (clad specimens contained $UO_{1.989}$)

Fig. 10.4 — Concentration of U on surface of various claddings after 1000 hours at 1200°C (clad specimens contained $UO_{2.00}$)

disc-shaped core. A 0.08-mm-thick layer of Cr separated the core and cladding. Capsules were tested in the usual manner at 1200°C with control capsules and a capsule containing a substoichiometric $\text{UO}_{1.989}$ core separated from the Fe - 25Cr - 4 Al cladding by a Cr barrier. Results from the control capsules duplicated previous results (Figures 10.3 and 10.4). The capsule containing the $\text{UO}_{1.989}$ core showed no improvement over previously tested capsules with no Cr layer; hence, a Cr barrier does not impede the diffusion rate of U through the cladding after U is formed. Results from capsules containing Cr- $\text{UO}_{2.00}$ fuel and Cr barriers showed no surface U in 900 hours at 1200°C plus 125 hours at 1300°C. This appears to be a significant improvement over non-Cr-barrier capsules, but the extent was difficult to assess because of the lower limit of detection of 7 to 9 micrograms U/cm² and the usual range of U concentration formed on Fe-Cr-Al-clad capsules (10 to 20 micrograms U/cm²) after 1000 hours at 1200°C.

When examined, a metallurgical bond between the Cr and the core and cladding made the exact interface difficult to determine. There were a few small voids and oxide particles in the interface area, fewer than in capsules containing Fe- $\text{UO}_{2.00}$ or Cr- $\text{UO}_{2.00}$ with no Cr barrier. From this limited amount of testing, it appears that a Cr barrier impedes the inward diffusion of Al to the UO_2 core and thus prevents the formation of U; it does not, however, prevent the outward diffusion of U if it is already present in the fuel.

Two series of capsules containing Fe - 40 $\text{UO}_{2.00}$ (vol %) cores and $\text{UO}_{1.989}$ cores were initially tested at 600°C for 1000 hours in argon containing 3 percent oxygen. Intermediate analyses by X-ray fluorescence during and after the test showed no surface U contamination on any of the capsules. The temperature was increased to 800°C and the same specimens were tested an additional 1000 hours. Intermediate and final analyses indicated again that no surface U was on the claddings (within the 7 to 9 micrograms U/cm² detection limit of the instrument).

The capsules were returned to test at 1000°C. After 100 hours, analyses showed U on all Fe-Cr-Al- and Fe-Al-clad $\text{UO}_{1.989}$ core capsules. The amount varied from 10 to 60 micrograms U/cm² and increased regularly with time until after 1000 hours it ranged from 30 to 380 micrograms U/cm². The results were similar to the previous test at 1200°C in that no definite relationship was established between Cr or Al content of the cladding and the amount of U measured. No U was detected on the cladding alloys which did not contain Al; thus corroborating 1200°C test data showing enhanced U diffusion rates through cladding alloys containing Al. There were no cladding failures due to cracks during this 1000°C test as there were at 1200°C; however, metallographic examination disclosed that U diffusing through the claddings had a detrimental effect. Most of the claddings bore evidence of intergranular oxidation; oxide penetration up to 0.35 mm was found in some specimens.

Analyses of the series of clad capsules containing Fe - 40 $\text{UO}_{2.00}$, both during and after the 1000-hour test at 1000°C, detected no U on the surface of any capsule. Post-test metallographic examination showed no deterioration of the cladding (as occurred with substoichiometric fuels) and good core-to-cladding contact with a thin discontinuous film, approximately 3 microns thick, of Al_2O_3 at the interface.

10.3 CONCLUSIONS

Aluminum in Fe-Cr-Al-base cladding alloys reduces UO_2 in cermet fuels, beginning in the temperature range between 1000° and 1200°C. Free U formed in this reaction dissolves in and diffuses rapidly through the cladding to the surface where it is converted to an oxide. At 1000°C and below, no reaction of Al with UO_2 takes place within the lower limits of detection of the surface analytical method used (7 to 9 micrograms U/cm²). Oxygen liberated during the reduction of UO_2 combined with Al from the cladding to form Al_2O_3 at the clad-

ding - core interface. This stable compound inhibits subsequent diffusion of Al into the UO_2 -containing fuel and consequently limits the quantity of U formed. This process of Al_2O_3 barrier formation indicates that increasing the Al content of the cladding above 4 weight percent, to increase oxidation resistance, would not significantly influence the amount of surface U contamination.

The diffusion coefficient of Al in Cr was found to be significantly lower than other elements in the Fe-Cr-Al-U system and led to the development of a Cr barrier between the fuel and cladding to reduce Al- UO_2 interaction and potentially eliminate surface U contamination.

If free U is initially present in the fuel, for example, as substoichiometric UO_{2-x} , or if free U is formed in the fuel during operation, then the U would diffuse through 0.38-mm-thick cladding within 100 hours at 1000°C or within 6 hours at 1200°C . Uranium diffusion through binary Fe-Cr alloys is curtailed in comparison with ternary Fe-Cr-Al alloys, in which the diffusion rate is virtually unaffected by the composition of the cladding (within the composition limits of this study 5 to 25% Cr and 4 to 10% Al). No U was detected on the surface of any specimen after 1000 hours at 600°C or after the test temperature was increased to 800°C for an additional 1000 hours. At 1000°C , U solubility in Fe-Cr-Al alloys is 0.1 to 0.2 percent, and its diffusion coefficient is in the range 10^{-9} to 10^{-10} cm^2/sec .