CHEMICAL INTERACTION OF METALLIC FUEL WITH AUSTENITIC AND FERRITIC STAINLESS STEEL CLADDING*

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ABSTRACT

The combination of metallic fuel and stainless steel cladding in a fuel element forms a complex multi-component diffusion couple at elevated temperatures. Interdiffusion of fuel and cladding components can in principle lead to several phenomena that could affect the reliable performance of a fuel element. These phenomena include; the formation of strength reducing diffusion zones in the cladding, intergranular penetration of fuel components into the cladding, and the formation of compositional zones with melting points below the anticipated operating temperatures.

A series of ex-reactor tests were performed to assess and study this potential problem in fuel elements consisting of U-Zr, U-Pu-Zr fuel clad in Ti stabilized austenitic stainless steel (D9) and ferritic stainless steel (HT-9). Diffusion couples of various combinations of fuel and the different steels were annealed at temperatures ranging from 650°C to 800° for up to 3000 h in an argon atmosphere. The post-test analysis of the diffusion couples included: metallographic examinations, scanning electron microscopy, and scanning Auger microscopy.

The initial results of this study may be summarized as follows: at 725°C and below the interdiffusion at the fuel cladding interface primarily involves zirconium and nitrogen. A zirconium layer, a few µm in thickness containing up to 20 at.% nitrogen is formed at the interface of all fuel-cladding combinations as well as a thinner layer of uranium-plutonium between the zirconium and the cladding. A large chemical potential gradient for zirconium plutonium and nitrogen in fuel and cladding is the likely driving force for the diffusion of these elements. The primary source of nitrogen appears to be the cladding, but experimental work to verify this is still in progress at this time.

It is proposed that the formation of the zirconium-nitrogen layer controls the interdiffusion of uranium-plutonium and iron and thus prevents or retards the formation of low melting alloys that exists in this ternary system. Diffusion anneals are in progress to determine the kinetics of the interface layer formation. U-10wt%Zr fuel was found to not significantly interact chemically with the cladding alloys. Diffusion couples tested at 650°C for 2880 hr and 750°C for 720 hr indicated that essentially no fuel/cladding interdiffusion occurred. At 650°C the bulk interdiffusion was limited to several microns or less, and at 750°C the interdiffusion was limited to 5 microns or less.

The diffusion zones observed in the ternary combinations at higher temperatures are much more complex. For example, the ferritic steel (HT-9) and the 19% plutonium fuel diffusion couple has an 80 μm, multi phase, zone after a 300 hour anneal at 750°C. An interchange of the cladding and fuel components is evident with high uranium and plutonium phases at the cladding side of the diffusion zone and high iron and zirconium-rich phases at the fuel side. The zirconium-nitrogen band seen at 700°C is not present and a relatively large amount of iron and fuel component diffusion has taken place. The interdiffusion of iron and uranium-plutonium has now created a layer of about 15 μm at the cladding side of the diffusion zone which appears to be once-molten alloy. Evidence of melting is observed in all fuel-cladding combinations at various temperatures between 725°C and 800°C after 300 hour anneals. Melting occurs at lower temperatures in this range for high plutonium fuel in general and at the lowest temperature for low chromium ferritic steel and high plutonium fuel combinations.

It can be stated that based on these ex-reactor tests thus far conducted, no deleterious effects stemming from fuel-cladding interdiffusion are apparent up to temperatures of 725°C, which is well in excess of the maximum anticipated operating temperature of a fuel element and the formation of molten phases in the diffusion layers occurs at temperatures that lie in the off-normal operating range of the fuel. The kinetics and extent of zone formation and molten phase formation are being studied. A comparison of the ex-reactor data with fuel element irradiation results that are now becoming available is in progress.

I. INTRODUCTION

Chemical interaction between fuel and cladding is a concern in any fuel element design. This phenomena takes very different forms depending on the type of fuel. In the case of IFR metallic U-Pu-Zr alloy fuel, FCCI manifests itself as a multi-component metallic diffusion problem. Because Pu and stainless steel components such as Fe and Ni can form relatively low melting point compositions, the interdiffusion of these elements has to be either avoided or accompanied by third species that raise the reactivity of these Pu compositions well above the cladding operating temperatures.

Early diffusion tests [1] of Pu containing fuels and austenitic stainless steel identified Zr as an effective alloy addition to avoid low melting phase formation in the diffusion zone. In fact, the selection of the present U-Pu-Zr fuel composition is based on that work and subsequent irradiation tests.

The present work does not at this time address the kinetics of interdiffusion, but is limited to the determination of the temperature at which molten phase formation first takes place between heretofore untested combinations of U-Pu-Zr and austenitic and ferritic cladding materials.

II. EXPERIMENTAL RESULTS

The composition of the materials used is given in Table 1. Fuel and cladding samples were cut from cylindrical bars to ~2.8 mm thick slices. These slices were ground flat on 30 μm Al_2O_3 paper. Fuel and cladding samples were alternatingly stacked, in columns of up to 12 samples. The sample stacks were wrapped in Zr getter foil and placed in a Mo holder, which in turn was placed in a welded, Ar containing, Type 304 stainless steel capsule. The thermal expansion difference between the Mo holder and the sample stack ensured axial compressive loading of the samples at test temperature. The nominal test temperatures were 650°C-800°C and were controlled within 10°C. Annealing times of the majority of the tests was 300 h with a few tests ending at 3000 h. After annealing, the samples were prepared for optical metallography, Scanning Electron Microscopy (SEM) and Scanning Auger Microscopy (SAM) in a conventional manner.

TABLE 1. Fuel and Clad Compositions[a]

	Material Heat			
	U-8Pu-10Zr/ EFL029	U-19Pu-10Zr/ EFL036	HT9/ 91353 (Ferritic)	D9 83510 (Aus.)
Fe			Bal.	Bal.
Cr			12.02	13.45
Ni			0.57	15.61
Mo			1.03	1.65
Ti			0.002	0.32
V			0.34	<0.01
W			0.51	<0.01
Mn			0.50	2.05
Si			0.22	0.85
C			0.21	0.034
N			0.0037	0.0051
O			0.0058	0.0062
U	82.39	71.75		
Pu	8.41	19.25		
Zr	9.80	10.34		

[a]In wt.% except as noted

No sign of formation of liquid alloys was observed in any of the diffusion couples that were annealed at 650°C and 725°C. However, narrow bands at the cladding-fuel interface were present at all fuel-cladding combinations. Results of examinations of these bands with the SEM and SAM are summarized in Figs. 1 and 2. The data shown in Fig. 1 are representative of fuel-ferritic steel combinations. There is a typically 1 to 3 μ Zr layer on the fuel side

U-19Pu-10Zr

HT-9

$\frac{63 \text{ U}}{\frac{17 \text{ Pu}}{20 \text{ Zr}}}$

$\frac{75 \text{ Zr}}{25 \text{ N}}$
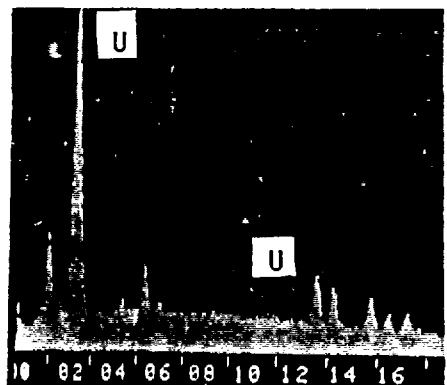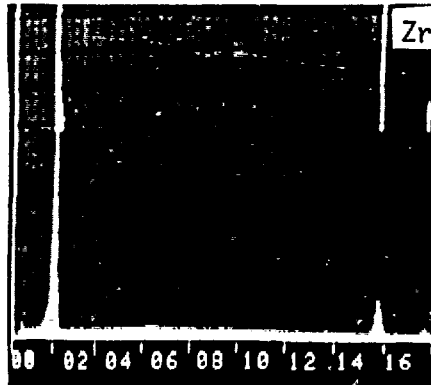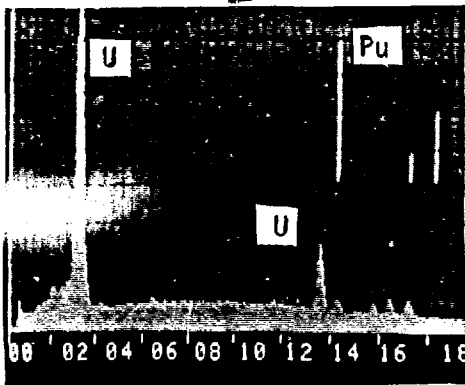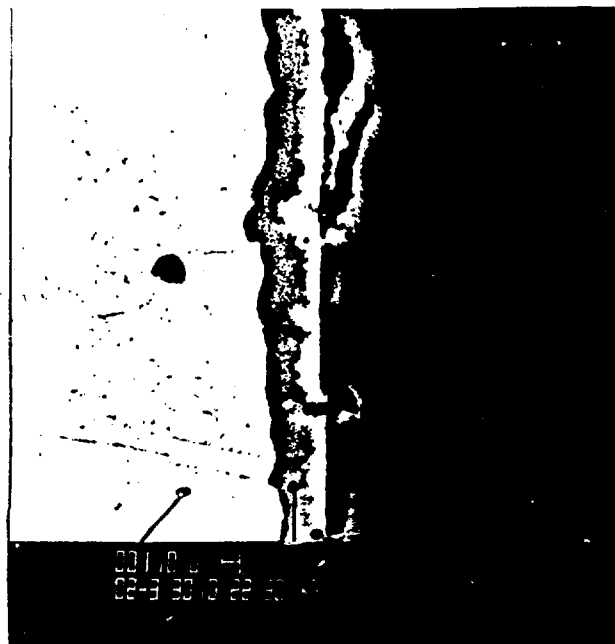
$\frac{\text{U}}{\frac{\text{Pu}}{\text{Zr}}} - \frac{\text{N}}{\frac{\text{O}}{\text{C}}}$

Fig. 1. Compositional Analysis of Interaction Zone in
(U-19Pu-10Zr)-(HT-9) Diffusion Couple After 300 h
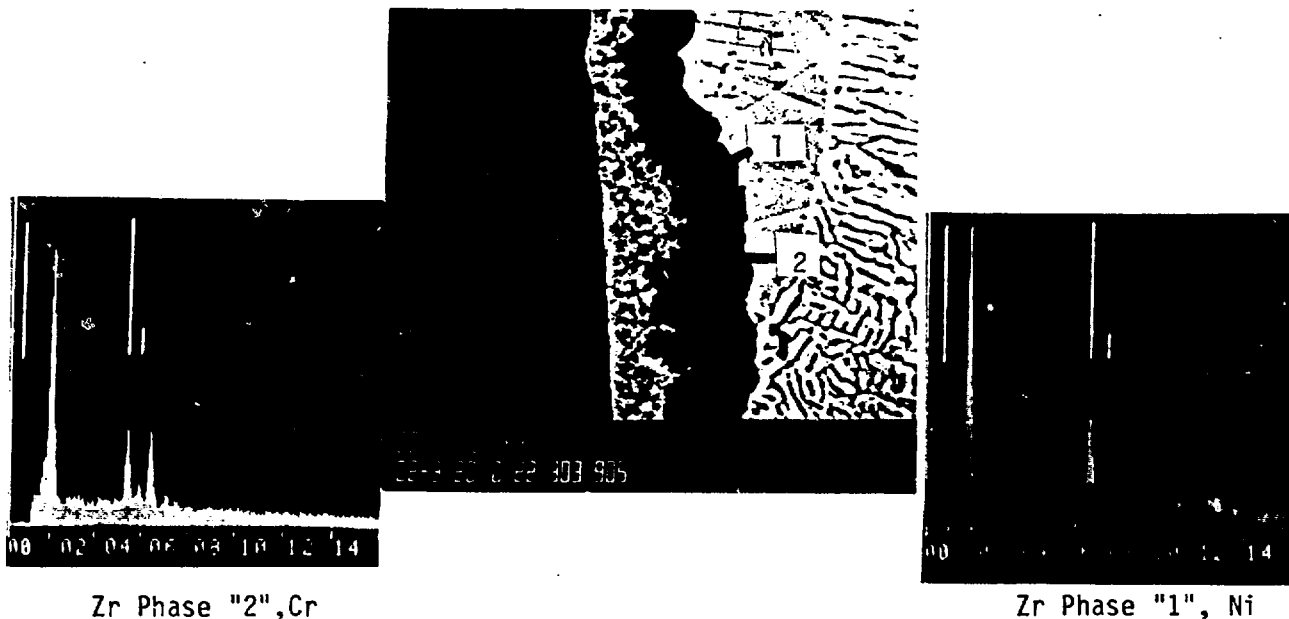@ 700°C, Using X-ray and Auger Electron Analysis

- 4 -

Zr Phase "2",Cr   Zr Phase "1", Ni

Fig. 2.   Interface Between U-19Pu-10Zr and
          D-9 after 300 h at 730°C

of the interface that contains N up to the solubility limit in the α Zr
phase. Between this layer and the steel exists a thin, 0.5-2 μ, layer of fuel
that is markedly enriched in Pu and, in the case of U-Pu-Zr fuel, contains
some Fe, Cr and Zr as well as a few percent N, O, and C. The situation with
fuel-austenitic steel combinations is essentially similar except that Ni and
Cr are segregated in the Zr layer as shown in Fig. 2. The evidently more
rapid diffusion of Ni results in a depletion of Ni in the steel to a depth of
a few microns, in effect forming a ferritic layer at the steel-fuel interface.

At temperatures above 725°C, several degrees of interaction were observed
ranging from incipient molten phase formation to complete melting of fuel and
part of the steel in some diffusion couples at temperatures above 800°C. A
schematic presentation of the test results in simple terms of observed molten
phase formation is given in Fig. 3. Little can be said about the samples that
experience gross melting during 300 h anneals to ellucidate the interdiffusion
other than that severe intermixing of steel and fuel components at these high
temperatures, and the attendant formation of low melting eutectic compos-
itions, obliterated the original diffusion couples. We will therefore con-
centrate on the temperature range of approximately 725°C to 775°C where
various stages of incipient molten phase formations were observed.

TEMPERATURE DEGREES C.

825
800
775
750
725
700
675
650

LEGEND

[NO MELTING]
[INIT. MELT]
[GROSS MELT]

U-8PU-10ZR
D-9 CLADDING

U-19PU-10ZR
D-9 CLADDING

U-8PU-10ZR
HT-9 CLADDING

U-19PU-10ZR
HT-9 CLADDING
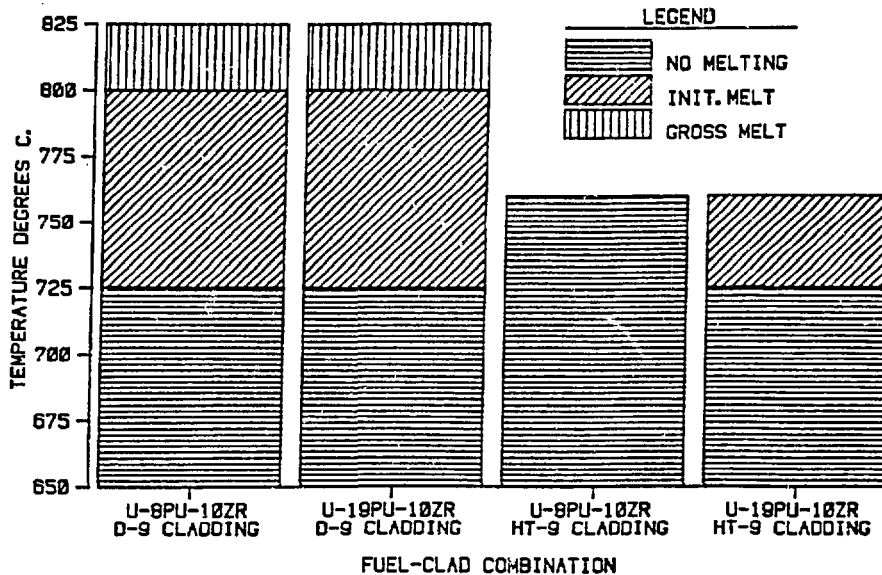
FUEL-CLAD COMBINATION

Fig. 3. Schematic Presentation of Fuel-Cladding
Compatibility Test Results

Some examples of early stages of molten phase formation are shown in
Fig. 4. The example shows a U-Pu-Zr/D9 couple annealed for 700 h at 750°C.
Figure 4-A shows the transition of the zone of incipient molten phase for-
mation and the Zr fuel band structure similar to that found at lower tem-
peratures. This molten phase formation always starts at the center of the dif-
fusion couple and appears to spread outward to the periphery of the sample
(downward in Fig. 4-A). Figure 4-B represents the microstructure of the
interaction zone. Most of the Zr layer has fallen out during grinding of the
sample but it consisted of a two-phase structure as shown preserved in
Fig. 4-A. This two phase structure is similar to that found in lower tem-
perature samples and is a result of Ni segregation. The light grey dendritic
phase (labeled 1), is high in Cr and Fe and is probably the equivalent of
U_2Fe. These dendrites reach to the boundary of the Ni depleted zone that was
mentioned in a preceding paragraph. The light phase (labeled 2) was judged,
from its composition and morphology, to have been molten at the test
temperature. The phase (labeled 3), contains a large amount of Zr as does the
mixture between phases (2) and (3). It seems that the liquid (U-Pu-Fe) phase
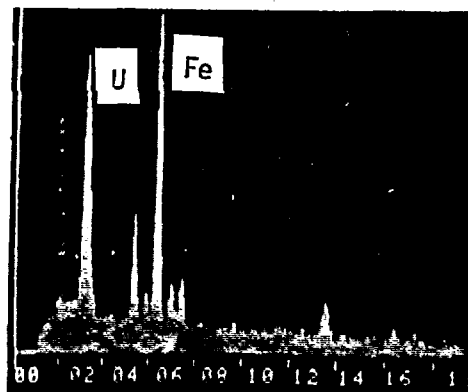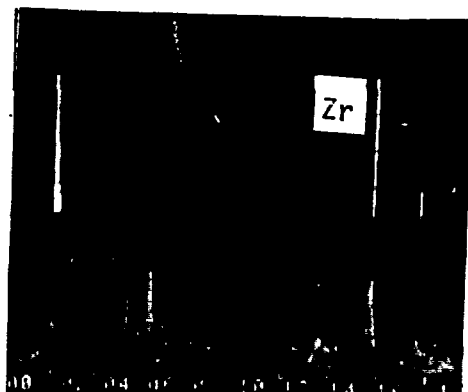is dissolving Zr and thereby solidifying on the Zr side of the band.
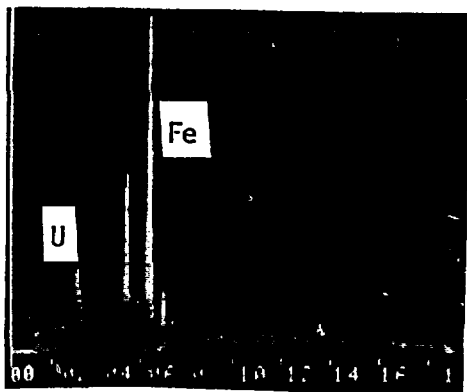
Fig. 4. Interaction Between U-19Pu-10Zr Fuel and
Austenitic Cladding (D-9) 700 h @ 750°C

The example of a U-Pu-Zr/HT-9 couple, annealed at 725°C for 300 h, in Fig. 5 serves to point out similarities as well as the difference between the interaction of U-Pu-Zr and austenitic and ferritic steel As in the case of D-9, the enhanced interaction associated with the formation of molten phases starts at the center of the sample and progresses outward to the periphery (see Fig. 5-A). The microstructure of the interaction zone shows some very unique features, in particular the distinct band structure and the grain growth in the steel. The tip of the meltfront shown enlarged in Fig. 5 is essentially U-Pu-Fe.

Increasing amounts of Zr and Fe are present behind the meltfront (see Fig. 6) resulting in solidification and band formation. The narrow layer of blocky precipitates separating two fuel-rich bands contains primarily Cr, Fe and C and N. The dark intergranular phase in the fuel-rich zones is high in Zr. Both features are shown in detail in Fig. 5.

III. DISCUSSION

In the present tests of D9 and HT9 stainless steel and U-Pu-Zr fuel combinations, no evidence of molten phase formation was found up to a temperature of 725°C. This is approximately the same temperature limit found in previous experiments with 304 and 316 Type stainless steel and U-5Fs fuel [2]. The previous work also reported molten phase formation at approximately 800°C for several combinations of 304 and 316 Type stainless steel and U-Pu-Zr fuel, with one combination, i.e., 304 SST + U-17-Pu-6Zr fuel showing melting at 725°C after an 168 h anneal. These results taken together point out that the initial formation of molten phases between stainless steel and U-Pu-Zr fuel probably occurs in the 725°C-800°C temperature range depending on minor differences in chemistry and local conditions at the fuel-steel interface.

The role of Zr in raising the molten phase temperatures well above those of the U-Pu-Fe (Ni) eutectic compositions is clear, but it is the minor compositional differences and local conditions at the diffusion interface that determine the efficacy of Zr. Diffusion of Fe and Ni into the fuel does not present a problem because the presence of Zr in the fuel prevents the formation of low melting eutectic compositions. The extent of diffusion of Pu and U into the steel without accompanying diffusion of Zr is the key problem in fuel-cladding capability. This process appears to be controlled by Zr as well, but in a more complex manner involving the formation of a Zr compound layer at the fuel-steel interface. Previous annealing experiments with U-Pu-Zr alloys in NaK and He filled stainless steel capsules also showed formation of Zr and Pu rich bands at surfaces that were not in contact with steel [4]. As was suggested in [1,4] and is clearly confirmed by the present results, the efficiency of this layer formation depends on the availability of interstitial elements. The main source of interstitial elments in the fuel element is the cladding, but in the present diffusion tests the atmosphere in the test capsule may have contributed.
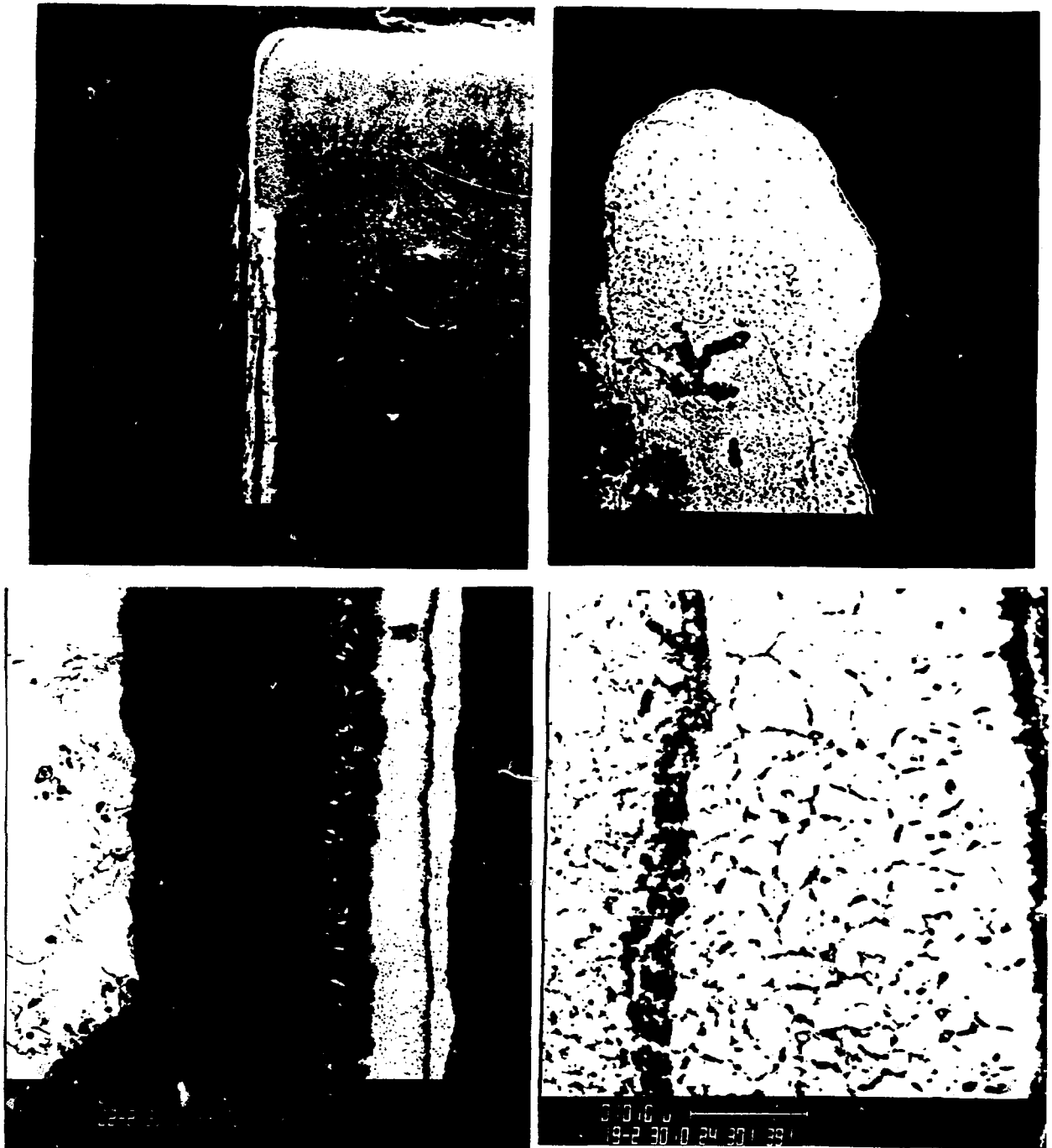
Fig. 5. Interaction Between Fuel and Ferritic Cladding HT-9
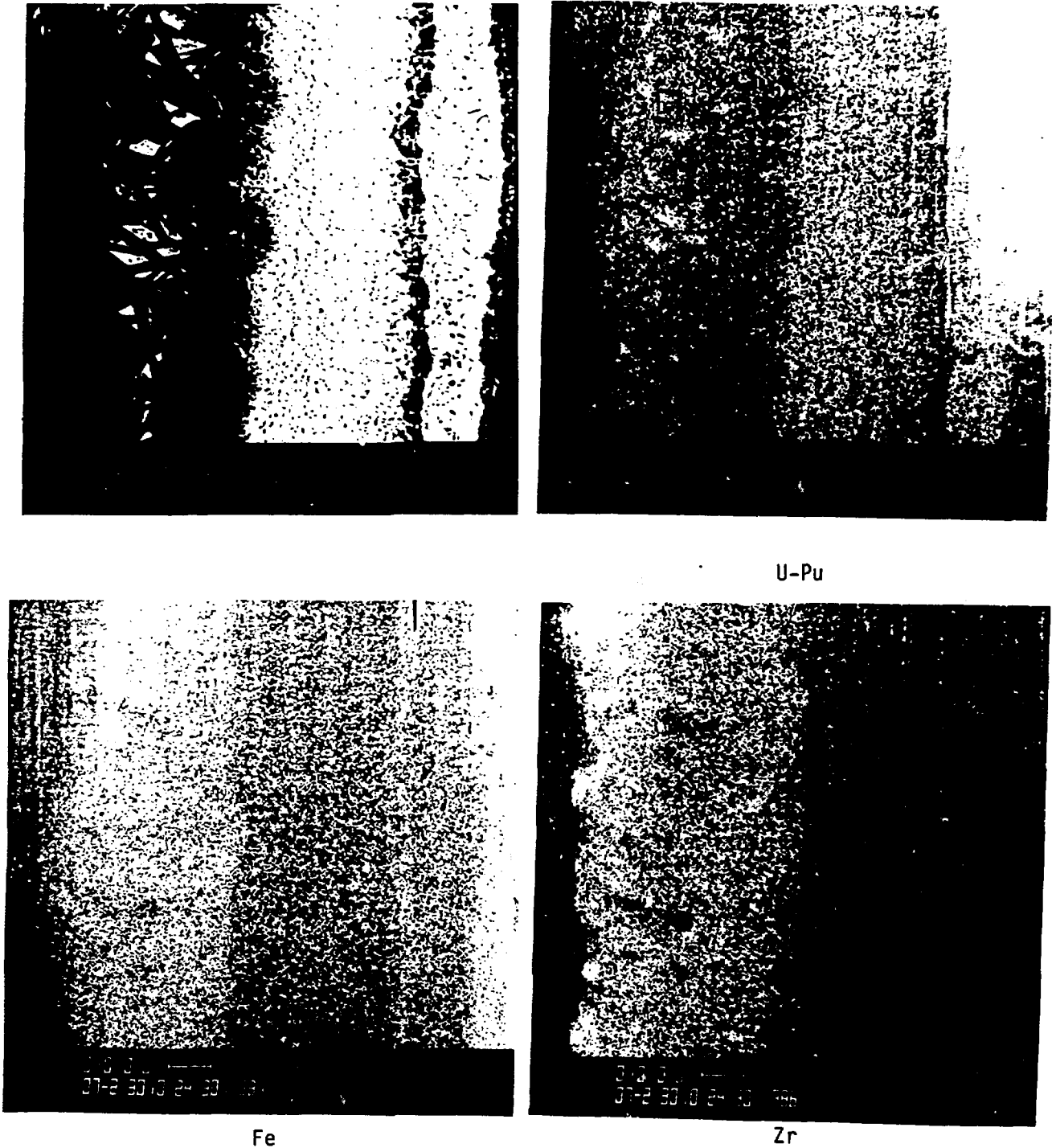300 h @ 725°C

U-Pu

Fe

Zr

Fig. 6. X-ray Dot-Map Showing Distribution of
Fe, Zr and U-Pu in HT-9/Fuel Interaction Zone

The thickness of the Zr layer at the diffusion interface is determined by the available Zr and N in its vicinity. Fe and Ni appear to diffuse readily into the Zr layer with the Ni diffusing faster as expected [3]. The rapid diffusion of Ni results in the formation of two phases in the Zr layer, as well as the formation of a ferritic layer in the adjacent D9 steel. This feature and the difference in available N explains the difference in structure of the fuel-steel interaction bands between D9 and HT9.

The extent of initial interdiffusion of Pu and U with cladding elements. or the diffusion of U and Pu through the Zr layer determines the eventual formation of a U-Pu-Fe molten phase. At very high temperatures this occurs in a short time, but in the range of 725°C-800°C, The thickness, uniformity, and rate of formation of the Zr layer appears to be the controlling factor. Almost all diffusion interfaces had a dish-shaped Zr layer, i.e., the Zr layer was thicker toward the periphery of the sample and indeed molten phase formation always started at the sample center where the Zr layer formation was least. Note that in fuel elements, the Zr layer on the fuel surface is substantial because reaction with the ZrO_2 mold wash establishes a high Zr concentration on the surface of the fuel pin even vefore irradiation [5].

It is not clear at this time whether sample preparation or capsule atmosphere is the cause for the dish shaped Zr layer. Upon initial formation of a U-Pu-Fe molten phase, diffusivities of all species involved is enhanced. The molten phase appears to dissolve Zr and solidify. This results in a rapid lateral motion of the meltfront while the overall penetration into the steel is slowed down. The great affinity of Zr for N results in a decomposition of precipitates in HT9 and pronounced recrystalization of the steel. This also occurs before a molten phase is formed but on a much smaller scale.

It seems that a thick and uniform Zr layer retards the formation of molten phases, and that the ample availability of Zr, and N in particular, can assure such a layer.

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