EVALUATION OF SELECTED SAMPLES FROM THE TMI-2 CORE

by

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ABSTRACT

Core-bore samples from the K9 and N12 locations in the TMI-2 core were examined for microstructural and microchemical features. The purpose of the examinations was twofold; first to determine core temperatures at known elevations in the core, and second to obtain insight into materials interactions that lead to core degradation. The temperature at the ~50-cm elevation in the N12 location, a control rod position, was estimated to have been ~960°C and dropping sharply to less than 800°C a few centimeters below. These temperature estimates were based on the eutectic reaction between a control rod's Zircaloy guide tube and its stainless steel cladding, the β-phase transformation temperature in Zircaloy, and the melting temperature of the Ag-In-Cd control material. In the K9 location, local transient temperatures to ~900°C at the 37-cm elevation were estimated from the β-phase transformation in the Zircaloy cladding. Interactions of note were the guide tube/cladding eutectic interaction in the control rod, the apparent degradation of Zircaloy cladding by molten Cd and In, and the attack of stainless steel by Sn in a melt of Ag-In-Cd.

INTRODUCTION

Over the past five years, Argonne National Laboratory has been involved in the examination of core debris from a number of locations in the TMI-2 reactor. The principal purpose of these examinations has been to add to the body of knowledge being accumulated by a large number of laboratories in this country and abroad to understand the sequence of events that destroyed the reactor core. Understanding the accident sequence will help to validate core and material behavior codes for accident analysis as well as provide unique data to modify the code models if necessary. Such models are based on known materials' properties and interactions, the latter usually established in controlled-environment separate-effects tests in which specific interactions can be studied. These tests also provide the "known" background against which the TMI-2 specimen "unknowns" can be compared for the estimation of temperatures at a given core location.

This process is complicated, however, by the sheer extent of the accident and the multitude of materials interactions that occurred with a wide variety of core materials. Nevertheless, information on core temperatures during the accident can be gleaned to a first approximation by careful examination of the microstructure and microchemistry of core samples.

In this paper we will describe the examination of selected specimens taken from the TMI-2 core as "core bores" in a sample acquisition program conducted by the Idaho National Engineering Laboratory (INEL) [1]. A large number of core bore samples from this program are being examined by INEL and a lesser number by Argonne and the other participating laboratories. The twenty-odd core bore samples received at Argonne were classified variously as rod segments (from fuel, control, and poison rods), ceramic "rocks," and "agglomerates" of ceramic and metallic phases, all from seven different core radial locations. The rod segments came from the lower core elevations, the rocks from the molten region, and the agglomerates from the transition region below the molten region and from the crust above it. Because the rocks and the agglomerates generally tended to be rather similar within their grouping, after a general screening we chose to study in detail only those samples that contained striking features that either provided insight into the local temperatures or indicated the range of temperature or type of core damage over a larger axial distance. Our results, therefore, cannot be easily extrapolated to other core regions. Rather, this generalization can only be accomplished by combining our limited results with those of the other laboratories.

SAMPLE DESCRIPTION

In a previous paper [2], an overview was given of the Argonne examinations of some of our core bore samples. Since then more in-depth examinations have been done on (1) the Ag-In-Cd control rod segments from core position N12 and (2) the range of available samples from position K9. This range consists of fuel rod segments from near the bottom of the core and agglomerate samples from the transition region and the upper crust region.

The N12 control rod segment came from the 5-52 cm elevation. The top few centimeters of this segment was unique in that it provided insight into the reaction between the stainless steel cladding and the Zircaloy guide tube in the presence of essentially molten Ag-In-Cd.

The fuel rod segments from K9 came from between the 13- and 36-cm elevations. The transition agglomerate sample came from the

56-66 cm elevation, and the upper-crust agglomerate came from the 183-190 cm elevation.

Optical metallography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDX) were the analytical tools used to examine specimens from these larger samples.

RESULTS AND DISCUSSION

Control Rod Segment

The portion of the control rod segment of greatest interest was the molten tip at the 52 cm elevation and the portion of the rod just below the tip. This end of the rod segment is shown in Figure 1. The bent stainless-steel-clad rod is shown extending from the remnant of the Zircaloy guide tube. Over most of the length shown, the surface of the stainless steel cladding had apparently reacted with the missing section of the guide tube. Just below the semi-rounded top, shown in Figure 2, the stainless steel cladding was almost totally consumed in a eutectic reaction with the Zircaloy. The microstructure consists of a matrix of once-molten Ag-In-Cd, a stick-like phase apparently consisting of Zr_3Sn_2, (as determined from atomic ratios obtained by EDX analysis), and other Zr-rich particles. A single remnant of stainless steel cladding can be seen at 1 o'clock in the figure. This remnant was surrounded locally by a Zr-Fe-Cr-Ni matrix that contained Ag-In-Cd islands. It appears that the stainless steel is dissolving in a Zr-rich matrix and not into the molten Ag-In-Cd. This lack of interaction between the stainless steel and the Ag-In-Cd is consistent with the binary phase diagrams for Ag-Fe, Ag-Cr, and Ag-Ni, which show very limited mutual solubilities for these elements. The mutual solubilities of Ag and Zr are also negligibly small [3], explaining the existence of the Ag-In-Cd islands in a matrix of Zr-Fe-Cr-Ni.

The molten reaction product between the stainless steel and the Zircaloy apparently flowed downward on the outer surface of the rod, candling fashion, reacting with the surface as it went. Figure 3 shows this candling in a longitudinal section just below the transverse section shown in Figure 2. This section captured the upper extent of unreacted cladding on the inner surface while the outer surface was reacting with the candling material from above. The sharp change in the microstructure of the Ag-In-Cd from equiaxed to very elongated grains suggests a sharp temperature boundary where the elongated grains were apparently above the solidus temperature of ~800°C. Particles of the Zr_3Sn_2 phase were present in some of the long grains.

The termination of the candling, ~3.5 cm from the tip of the segment, is shown in Figure 4. Because of the thin reaction layer in this region, it was necessary to use scanning electron

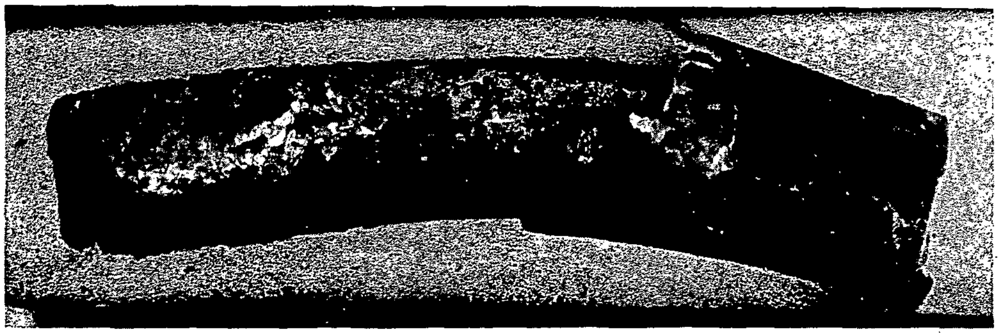

Figure 1. Segment of Ag-In-Cd control rod in guide tube remnant position N12, at the 47-52 cm elevation. Top is to the left where tip had melted.
MCT No. 243745 2X

Figure 2. Transverse section just below tip of control rod segment showing a single remnant of cladding (arrow) in a matrix of molten Zr-Fe-Ni-Cr. Particles in molten Ag-In-Cd are Zr_3Sn_2.
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(a) (b)

Figure 3. Longitudinal section of control rod 1.9 cm from tip, showing candling of reaction product. As-polished structure, (a), shows upper extent of cladding, while etched structure, (b), shows abrupt change in structure of Ag-In-Cd.
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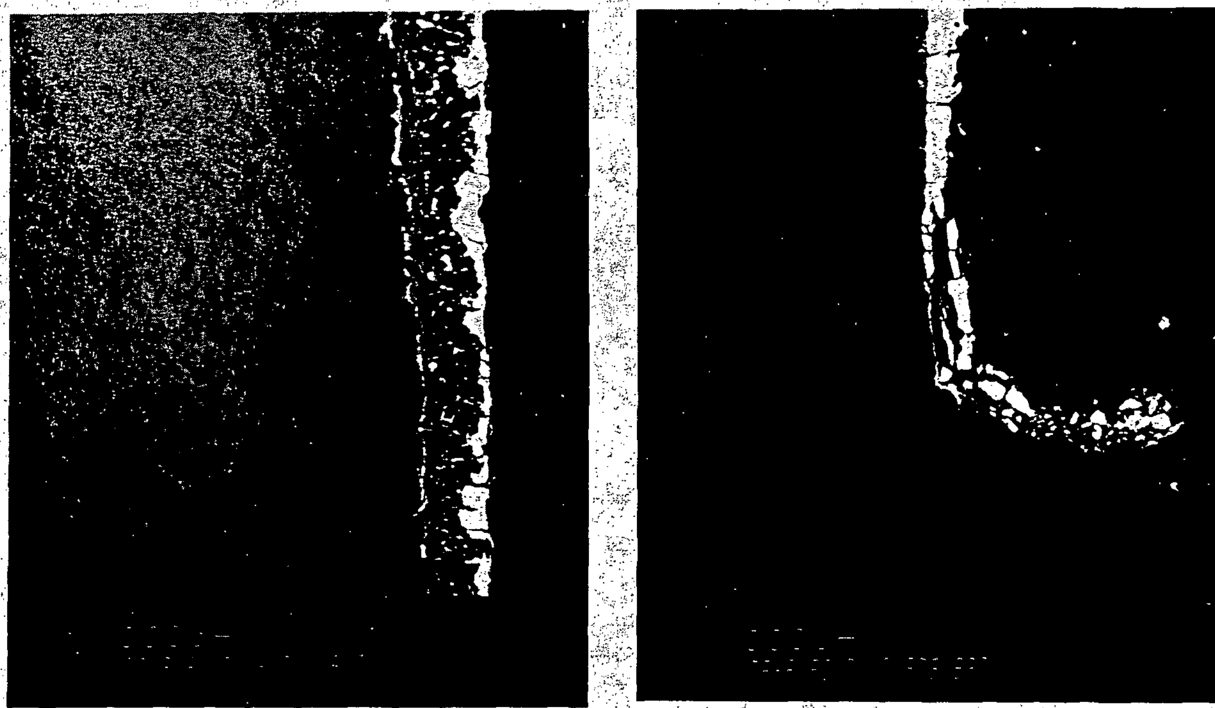

(a) (b)

Figure 4. SEM backscatter images showing duplex structure of candling reaction product, (a), and its termination ~3.5 cm from the tip end, (b).

microscopy to define the termination of the inner-layer part of the reaction. The inner layer is steel-rich, while the outer layer is Zr-rich. This structure is, in miniature, essentially the same structure found in a transverse section 1.9 cm from the tip [2].

The eutectic temperatures of the binary alloys Zr-Fe, Zr-Ni, and Zr-Ce are 934°C, 961°C, and 1300°C, respectively [4], which are considerably lower than the melting point (1450°C) of Type 304 stainless steel. That the reaction between the cladding and Zr-containing phase occurred adjacent to solid Ag-In-Cd (solidus temperature of ~800°C) suggests that temperatures were not significantly above the eutectic temperatures, and then for only a short period of time. Indeed, the lack of cladding on the left side of the rod adjacent to a free-standing structure of what is believed to have been molten Ag-In-Cd suggests that the events in this region took place very rapidly.

Below the 48.5-cm elevation where the eutectic reaction terminated, the control rod was intact with no obvious reactions between any of the components. The microstructure of the Zircaloy guide tube was fully transformed β-phase, indicating a temperature of greater than 900°C. At the 30-cm elevation, the microstructure of the Ag-In-Cd, shown in Figure 5, was recrystallized in an inner band. This pattern of recrystallization suggests that a second phase or additional element in the periphery of the rod is inhibiting recrystallization there. The identity of such a phase or element was not pursued, however. The Zircaloy guide tube at this elevation was only α-phase.

K9 Microstructures

Only the finding of some areas of transformation in the Zircaloy cladding of the fuel rod segments provided information on the temperature of these segments. Cladding structures at the 15-cm elevation showed no signs of elevated temperature. Only a few circumferentially oriented hydrides were present in the cladding. At the 37-cm elevation, there were occasional "sunburst" patterns of β-phase transformation from the outer surface inward. These areas penetrated about half the cladding thickness, as shown in Figure 6. The local character of these transformed areas suggests a very localized, transient thermal impact.

A specimen from an agglomerate sample taken at a lower transition region (56-66 cm elevation) captured two fuel rods in the process of disintegration, as shown in Figure 7. The composition of the various identified areas is given in Table 1. The matrix material between the two rods is predominantly Zr and Ag with lesser amounts of the other core constituents. Even what appear to be the "ghosts" of the cladding contain significant amounts of Ag. The area at "H," the thin grey line outlining the

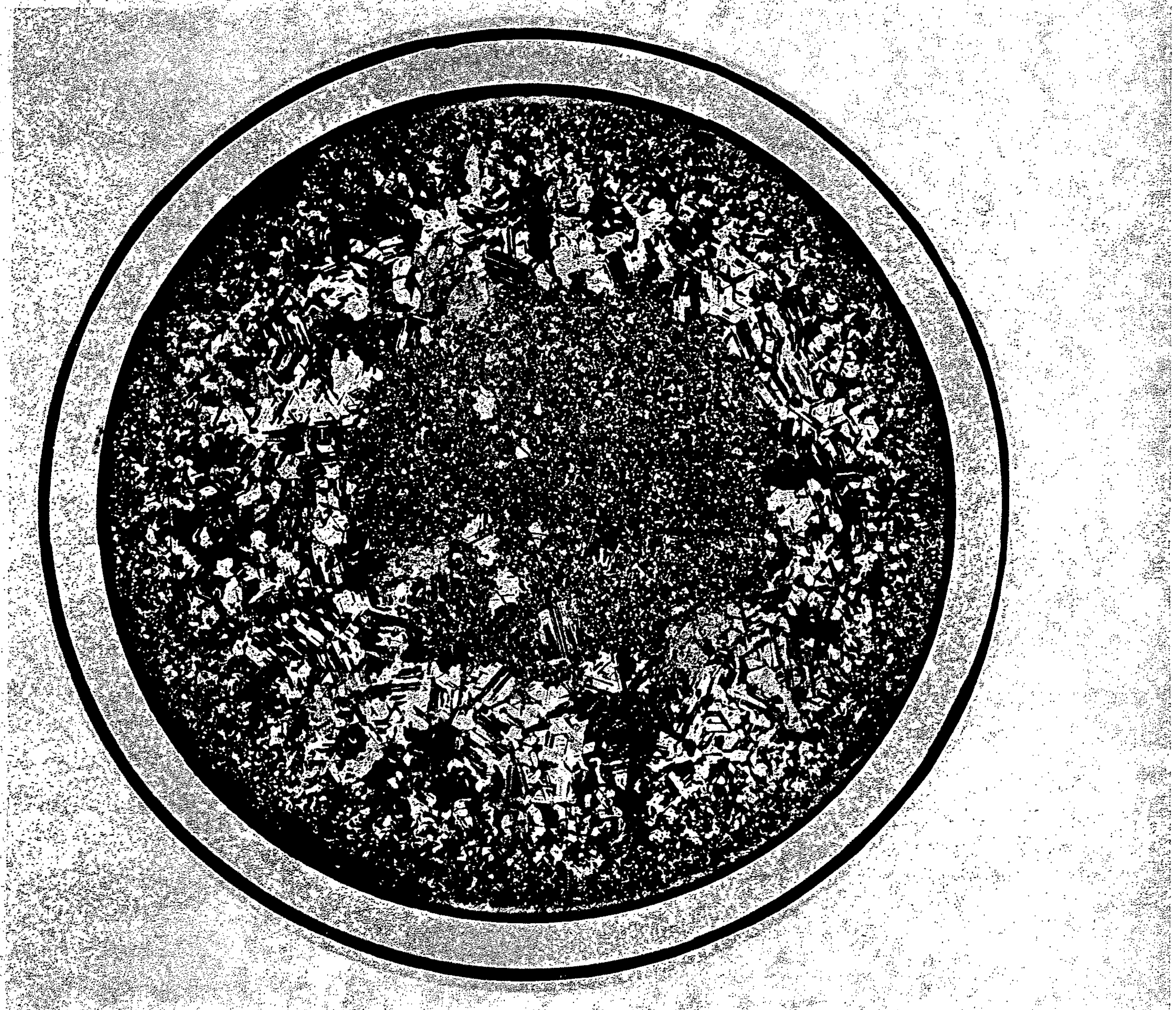

Figure 5. Recrystallized Ag-In-Cd at the 30-cm elevation in position N12.
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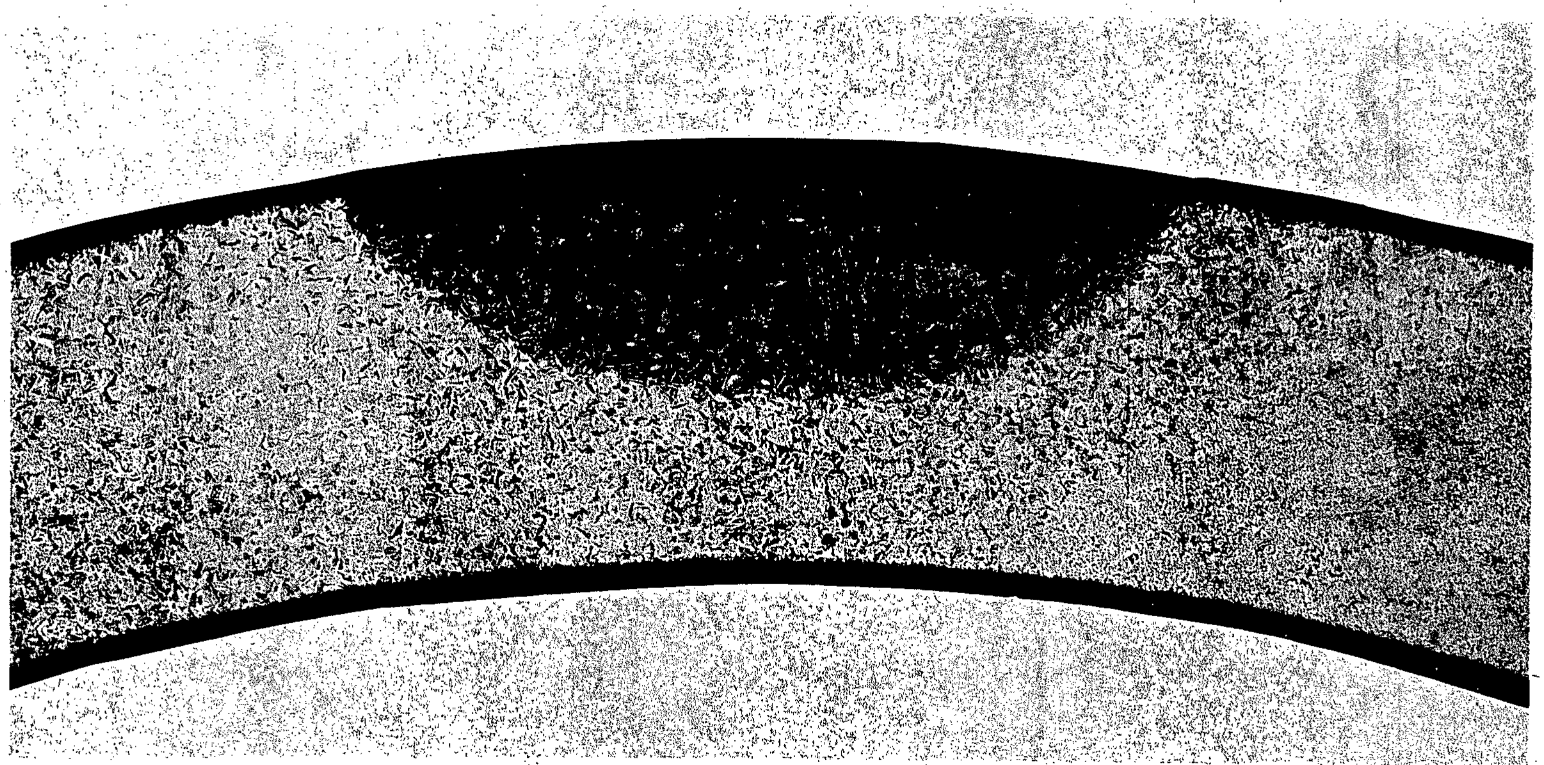

Figure 6. Local β-phase transformation of Zircaloy cladding at 37 cm in position K9.
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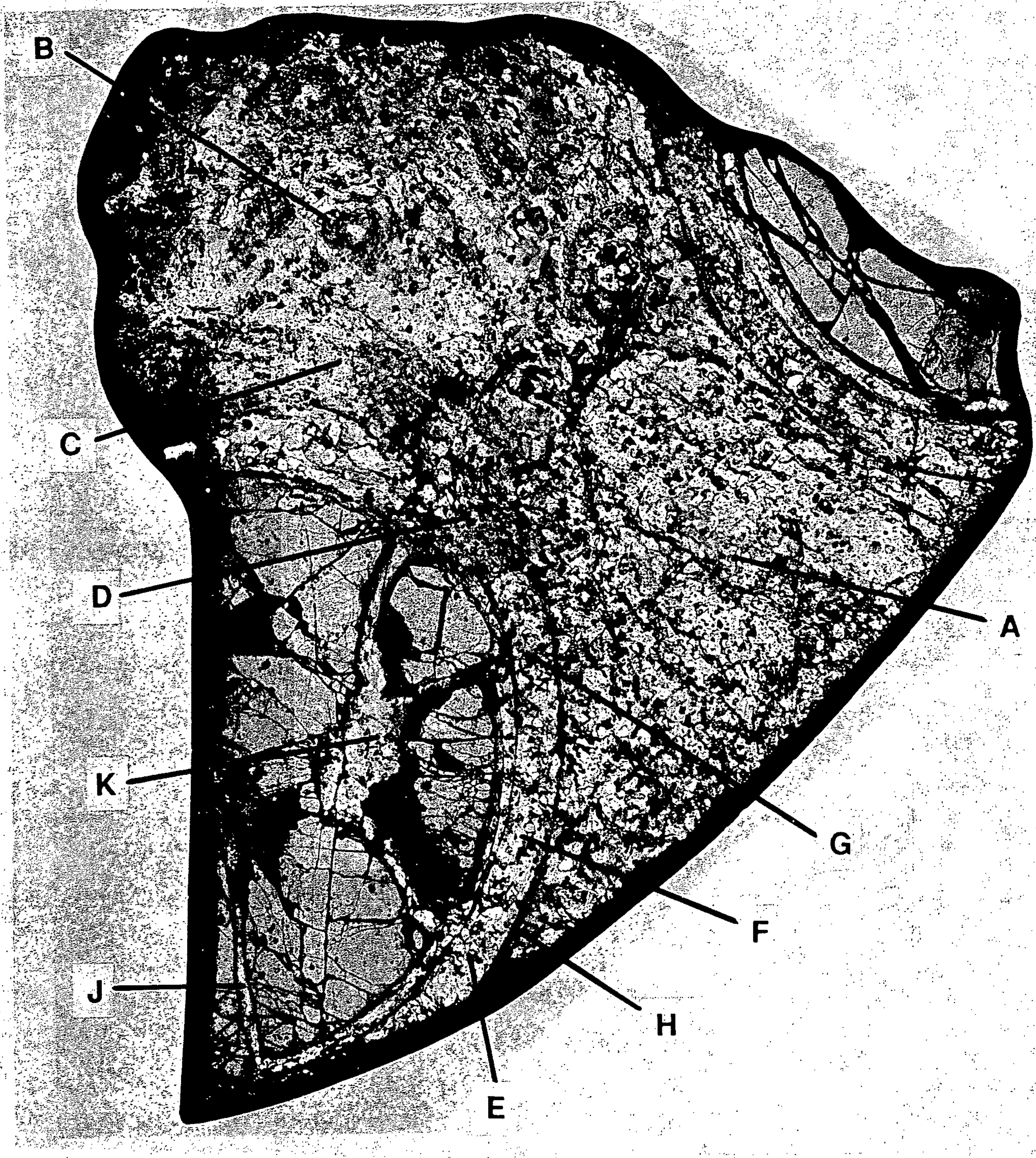

Figure 7. Transition region agglomerate from position K9 showing sections of two fuel rods being degraded.
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Table 1. EDX Composition Analysis (in wt.%) of Transition Region Agglomerate

Element	Matrix				"Cladding"				Dikes	
	A	B	C	D	E	F	G	H	J	K
Cr	0.9	0.6	0.3	0.2	0.8	1.3	0.9	--	1.5	1.4
Fe	5.2	3.5	2.2	2.1	5.3	5.8	4.8	--	7.4	6.4
Ni	2.8	2.2	2.0	2.0	2.4	2.6	2.1	--	3.8	3.5
Zr	59.3	68.5	75.5	62.9	64.3	58.3	57.9	83.3	67.1	64.5
Ag	21.5	15.5	13.1	22.7	18.5	24.7	24.7	--	*	18.0
Cd	1.5	2.3	0.0	1.5	0.0	1.3	1.0	8.9	*	0.0
In	3.0	3.0	3.0	3.5	0.0	2.6	2.4	7.9	*	0.8
U	5.8	4.4	4.0	5.2	3.5	3.4	2.5	0.0	20.2	5.5

*Not included to avoid biasing results in small sample volume.

"cladding," contained only Zr, Cd, and In as major constituents. This observation could suggest that molten Cd and In were the initiators in degrading the cladding. The cladding at "D" appears to have beem breached, allowing the matrix materials to form dikes in the cracked fuel. The reason for the high U composition of the dike at "J" is apparent from Figure 8, which shows particles of fuel from the walls of the crack being absorbed into the matrix of the dike. In general, this specimen shows a multiphase matrix material, heterogeneous in its appearance of flow zones, but homogeneous in overall composition.

The upper-crust agglomerate as it was received is shown in Figure 9 in a manner that highlights the contrast between the metallic (light) and ceramic (gray) phases. The metallic phase proved to be stainless steel with imbedded large particles of Ag-In-Cd. The ceramic matrix proved to be a generally homogeneous mixture of essentially pure U (presumed to be an oxide) and Zr-rich phases. The Zr-rich phase contained ~14 w/o Cd and 14 w/o In with the balance Zr. Interestingly, this same combination of elements made up the gray rim on the cladding ghosts in Figure 7.

Of note on the surface of the large stainless steel "masses" was a thin reaction zone. This zone, shown in Figure 10, was analyzed and was found to contain Ag, In, Cd, and fingers of stainless steel intimately involved with a Sn phase at the very surface. In areas where Sn was absent, the Ag-In-Cd was compatible with the stainless steel. It appears that the Sn promotes a dissolution of the stainless steel in the molten Ag-In-Cd.

SUMMARY AND CONCLUSIONS

Selected specimens from TMI-2 core bores were examined with the objective of establishing temperatures that likely existed during the accident at known elevations in the core. Given that only a relatively few specimens could be examined in any detail in this program, the results are limited in interpretation to very limited core locations. The examination of these specimens also indicated some materials interactions of note that provide some insight into the degradation mechanisms of the core materials involved.

Probable core temperatures deduced from the examination of fuel and control rod segments from positions K9 and N12, respectively, are as follows:

1) Incipient β-phase transformation in the Zircaloy cladding indicates at least transient temperatures to 900°C at the 37-cm elevation in K9.

Figure 8. SEM secondary electron image of dike of matrix material in UO_2 pellet of transition region agglomerate, showing dissolution of UO_2 along interfaces.

Figure 9. As-received section through upper crust agglomerate from position K9, highlighting metallic phase (bright) in a ceramic matrix of U-Zr-O and Cd-In.
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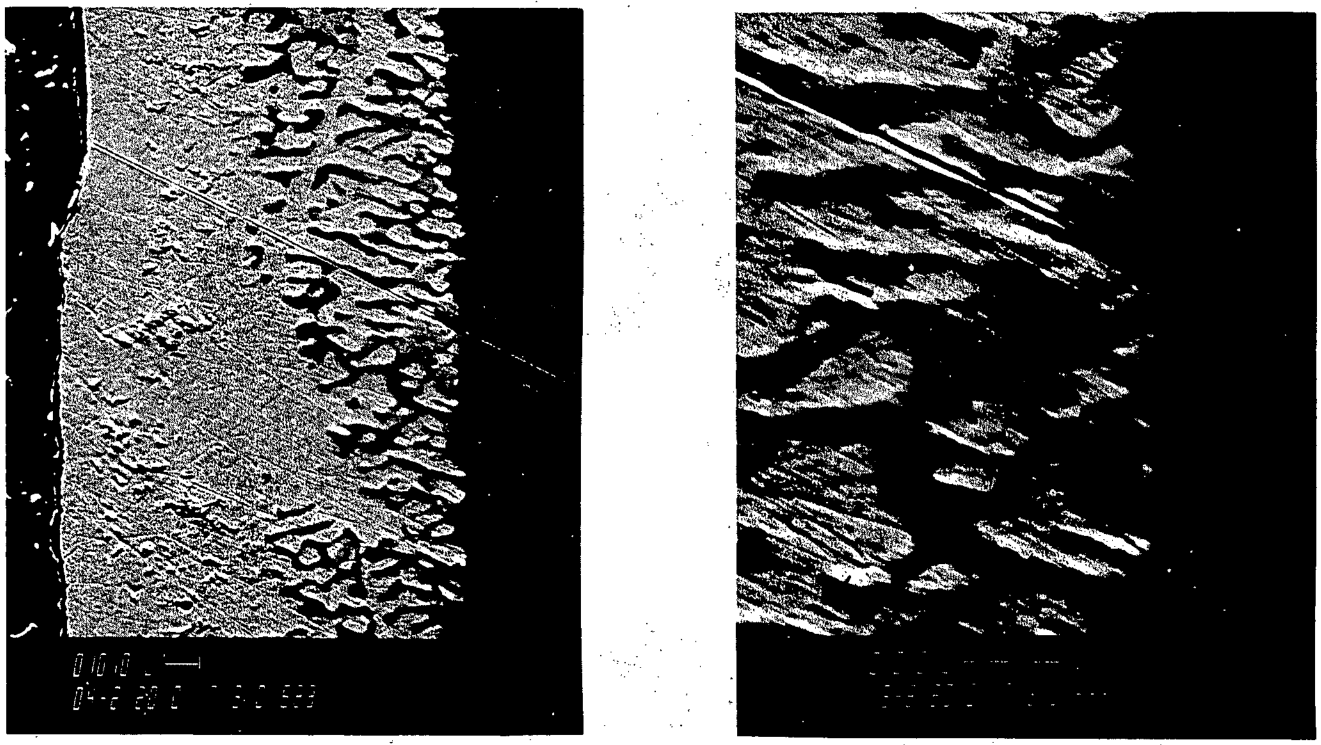

Figure 10. Surface dissolution of upper-crust stainless steel particle (dark gray) by Sn-containing phase (medium gray) in a Ag-In-Cd molten phase (light phase).

2) Complete β-phase transformation in the Zircaloy guide tube at the 48-cm elevation in N12 indicates temperatures >900°C.

3) Zircaloy/stainless steel eutectic reactions at the 52-cm elevation in N12 indicate temperatures in the 935-960°C range.

4) Lack of any β-phase transformation in the Zircaloy guide tube in N12 at the 30-cm elevation indicates temperatures <900°C.

Notable materials interactions were as follows:

1) Zircaloy guide tube/stainless steel cladding interaction at 935-960°C.

2) Molten Sn interaction with stainless steel in the presence of molten Ag-In-Cd, but compatibility between stainless steel and Ag-In-Cd where Sn was absent.

3) Possible degradation of Zircaloy by molten Cd and perhaps In.

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