NOTICE

This report contains information of a preliminary nature and was prepared primarily for internal use at the originating installation. It is subject to revision or correction and therefore does not represent a final report. It is passed to the recipient in confidence and should not be abstracted or further disclosed without the approval of the originating installation or USDOE Office of Scientific and Technical Information, Oak Ridge, TN 37830.

ANL-IFR--35

TI86 025970

February 1986

METALLOGRAPHIC CHARACTERIZATION OF UNIRRADIATED U-Pu-Zr FUEL

by

R. V. Strain and J. E. Sanecki

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

APPLIED TECHNOLOGY

Any Further Distribution by any Holder of this Document or of the Data Therein to Third Parties Representing Foreign Interests, Foreign Governments, Foreign Companies and Foreign Subsidiaries or Foreign Divisions of U.S. Companies Should Be Coordinated with the Deputy Assistant Secretary for Reactor Systems, Development and Technology, Department of Energy

IFR TECHNICAL MEMORANDUM NO. 35

~~Results reported in the IFR-TM series of memoranda frequently are preliminary and subject to revision. Consequently they should not be quoted or referenced without the author's permission.~~

NO ACCESS RESTRICTIONS

This document is not considered OUO-Applied Technology. It was reviewed for Export Controlled Information and found to be suitable for unlimited access and reproduction.

This label reflects Applied Technology instructions issued April 13, 2006, by the the Department of Energy Office of Nuclear Energy. Additional guidance has also been provided by DOE in 2016 and 2018 memos, as well as from NNSA.

Any
there
foreign
comp
Breed

Paul Betten, ANL

7/24/2019

Date

data
ents,
J. S.
y for

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

~~Released for announcement
in ATP. Distribution limited to
participants in the LMFB
program. Others request from
ASST. DOE.~~

JSW

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iv
I. INTRODUCTION	1
II. SAMPLE DESCRIPTION	2
III. GENERAL FEATURES OF THE SAMPLES	3
A. Globular Phase Distribution	5
B. Surface Layers	12
C. Grain Boundaries and Other Features	17
IV. MICRO-CHEMISTRY OF THE SAMPLES	23
A. SEM-EDX	23
B. SAM Analysis of the Surface Layer	26
C. SAM Analysis of the Globular Phase	26
D. SAM Analysis of the Matrix	31
V. DISCUSSION	31
VI. CONCLUSIONS	33
REFERENCES	35

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Typical Casting Defects in the Current U-Pu-Zr Fuel Pin	7
2.	Typical Examples of the Globular Phase: Top of the Pin from Casting Batch EFL-029	8
3.	Typical Examples of the Globular Phase: Bottom of the Pin from Casting Batch EFL-029	9
4.	Strips Across Selected Samples at Approximated 100X	10
5.	Microstructure of the Fuel Near the Edge of the Sample and the Layer on the Surface Near the Top of the Pin from Batch EFL-029	13
6.	Microstructure of the Fuel Near the Edge of the Sample and the Layer on the Surface Near the Bottom of the Pin from Batch EFL-029	14
7.	Surface Layer on Bottom Samples from Casting Batch EFL-031 ...	15
8.	Surface Layer on Bottom Samples from Casting Batch EFL-036 ...	16
9.	Thick Surface Layer on a Sample from Batch EFL-031	18
10.	Surface Layer on Fuel Pin VC-1-2	19
11.	Typical As-Cast Microstructure of Batch EFL-029	20
12.	Typical Microstructure of Fuel Pin VC-1-2	21
13.	Typical As-Cast Microstructure of Batch EFL-036	22
14.	Typical X-ray Spectra from the Globular Phase and Matrix of the Ternary Fuel; Near the Centerline of a Pin from Batch EFL-029	24
15.	SEM EDX for the Surface Layer on a Sample from Batch EFL-029	25
16.	SAM Data for the Surface Layer on a Bottom Sample from Batch EFL-029	27

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
17.	SAM Data for Inclusions in a Bottom Sample from Batch EFL 029	28
18.	SAM Data for Inclusions in a Bottom Sample from Pin VC-1-2	30

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Chemical Analysis of Pin, VC-1-2, Batch R450	4
2.	Chemical Analyses of Current Casting Batches	4
3.	Results of Quantitative Metallography to Determine the Areal % of the Gobular Phase	11

METALLOGRAPHIC CHARACTERIZATION OF UNIRRADIATED U-Pu-Zr FUEL

by

R. V. Strain and J. E. Sanecki

ABSTRACT

A microstructural and micro-chemical characterization was performed on samples of U-Pu-Zr metal fuel from three recent casting batches and from a fuel pin that was fabricated in the 1960's. The purpose of the characterization was to determine if features were present in the new castings that might indicate the irradiation performance of the newly fabricated pins could be expected to be different than the "old" fuel. Most of the effort was directed at samples from as-cast pins, but samples from bonded pins and segments of pins that had been heat-treated for 300 h at 750°C were also examined. The examinations revealed that a globular second phase was present in all of the fuel pins. Quantitative metallography indicated that the area fraction of this second phase ranged from about 0.02 to 0.055 and that the bonding operation or heat-treatment did not change the amount of the phase that was present. Scanning Auger spectroscopy indicated that this phase consisted of zirconium with several wt.% of oxygen, carbon, and nitrogen present. A surface layer that also was high in zirconium was present on all of the samples. This layer tended to be thicker on samples from the bottom of the castings (10 to 50 microns) and thinner at the top (2 to 10 microns). The examinations found no significant differences between the current castings and the "old" fuel pins.

I. INTRODUCTION

The irradiation performance of U-Pu-Zr fuel system was studied in the late 1960's and the results of tests irradiated to a burnup of about 4.5 at. % indicated no problems under those irradiation conditions(1). The general method of fabricating the fuel pins for the current irradiation tests and those performed in the 1960's are similar. The pins are cast by melting the alloy in a crucible under a vacuum, plunging silica molds into the melt, and pressurizing the furnace to drive the melt up into the molds. This process of "injection casting" is described more completely in reference (2). Although the general technique of injection casting has not changed, some of the details of the process such as the techniques used to assure a homogenous composition in the melt have been altered in the current casting process.

This report describes the metallographic characterization of samples of fuel pins from three casting batches that are representative of the current casting process and characterization of a pin representative of the fuel fabricated in the 1960's. The purpose of this work was to determine if there were any microstructural or micro-chemical features that indicate differences between the current pins and the old pin that could influence their irradiation performance.

The microstructure of samples of the fuel pins from these casting batches have been studied using optical metallography and scanning electron microscopy (SEM). The micro-chemistry of these

samples was determined using energy dispersive X-ray spectroscopy (EDX) on the SEM and Auger electron spectroscopy on the scanning Auger microprobe (SAM). The results from micro-chemical analyses using these instruments have large uncertainties in the values for Pu. Future examinations are expected to eliminate this deficiency in the current data.

II. SAMPLE DESCRIPTION

The samples examined in this study were obtained from the upper and lower ends of a single fuel pin from each casting batch. Samples from casting batches EFL-029, EFL-031, and EFL-036 as well as samples from the "old" fuel pin VC-1-2 (casting batch R450) have been characterized in this study. The nominal composition of these batches were:

EFL-029	U-8%Pu-10%Zr
EFL-031	U-8%Pu-10%Zr
EFL-036	U-19%Pu-10%Zr
VC-1-2	U-15%Pu-11%Zr

In addition to examining samples of pins in the as-cast condition some samples were examined after fuel pin bonding (about 2 h at 500 C) and some after a heat treatment of 300 h at 750 C. Samples from batch EFL-029 were examined after all three treatments (as-cast, bonded, and heat-treated), while samples from batch EFL-036 were examined in the as-cast and heat treated condition. Casting batch EFL-031 was examined in only the as-cast condition and the VC-1-2 pin was examined in the bonded condition only.

The actual chemical analysis for VC-1-2 (batch R450, including impurities is given in Table 1. Chemical analyses for the major constituents of the current batches are given in Table 2. Data on the impurity content of the current batches are unavailable at this time.

III. GENERAL FEATURES OF THE SAMPLES

Samples were prepared for examination by cutting the pieces of the pins to provide samples that were about 0.2-in. long. The samples were placed in brass mounts using a low melting Pb-Bi alloy so that transverse cross-section could be examined. The all-metal mounts were used to avoid problems in achieving the ultra-high vacuum required for the SAM. Resin mounts are too volatile to provide these high vacuums and clean surface conditions that are required for the SAM to be obtained. The samples were ground using SiC papers and polished using diamond pastes. The hot cell and glove boxes used in preparing and examining

**Table 1. Chemical Analysis of Archive Pin,
VC-1-2, Batch R45**

<u>Element</u>	<u>Wt. %</u>
Zr	11.2
Pu	15.3
U	Balance

<u>Impurities</u>	<u>ppm</u>
O ₂	500
N ₂	490
H ₂	3
Si	150
Fe	200
Al	50
C	50
Ni	100
Y	50

Density, g/cc	15.3
---------------	------

Table 2. Chemical Analysis of Current Casting Batches

<u>Batch</u>	<u>Zr, wt. %</u>	<u>Pu, wt. %</u>	<u>U, wt. %</u>	<u>Density g/cc</u>
EFL-029	10.0	8.0	82.2	15.7
EFL-031	10.4	7.8	82.1	14.7
EFL-036	10.4	18.8	71.4	15.7

these samples had nitrogen atmosphere with oxygen and moisture contents of about 100 and 500 ppm respectively. Even in this relatively good atmosphere the surface of these samples oxidized fairly rapidly. As a result, these samples were repolished using 1 micron diamond paste just prior (within 5 to 10 minutes) to placing them in the electron beam instruments.

Nearly all of the microstructural characterization of the samples was performed on the SEM. Optical microscopy of samples in the as-polished condition revealed very little structure. A globular phase was discernible, but was difficult to photograph as it appeared to be in relief, slightly above the surface of the matrix. The samples were not etched to bring out the microstructure for optical microscopy for several reasons. The etching process might interfere with the micro-chemical analyses that were to be performed on the samples. Initial attempts to etch the samples were unsuccessful in producing observable microstructures (probably because no structure existed in the samples tried). And finally, the SEM was capable of revealing the microstructures without etching the samples, so there was no real need for the optical microscopy.

A. Globular Phase Distribution

The SEM examinations showed two prominent features in the as-polished samples. The first feature was that castings contained small amounts of porosity that were assumed to be shrinkage voids or bubbles in the castings. An example of voids that may be

shrinkage voids because of their relatively small size and their apparent formation along grain boundaries is shown in the micrograph on the left side of Figure 1. An example of a larger, round void that has been categorized as a gas bubble because of its spherical shape is shown in the micrograph on the right side of Figure 1. Casting defects of these types were found in nearly all of the cross-sections that were examined during this study. The casting defects generally represented an extremely small area fraction of the samples, but no effort to quantify them was made as the amount of porosity in the castings is probably more accurately reflected in its density.

The other prominent feature in these cross-sections was the presence of a globular second phase. Typical examples of this globular phase are shown in Figures 2 and 3. The distribution of the globular phase is shown in the diametral strips across some of the samples that are shown in Fig. 4. These micrographs were intentionally made with high contrast so that the volume percent occupied by the globular phase could be determined using a Quantimet image analyzer. The globular phase is randomly distributed in the samples with some areas having relatively high concentrations of the phase and other areas being relatively devoid of it. Results of the determination of the volume fraction of the globular phase are given in Table 3. The values reported in this table include small voids in the castings in addition to the globular phase. Including these voids in the

SHRINKAGE VOIDS

GAS BUBBLE

Fig. 1. Typical Casting Defects in the Current U-Pu-Zr Fuel Pin

B.S.E. IMAGE, 100X

B.S.E. IMAGE 500X

B.S.E. IMAGE, 2000X

Fig. 2. Typical Examples of the Globular Phase: Top of the Pin from Casting Batch EFL-029

B.S.E. IMAGE, 100X

B.S.E. IMAGE 500X

B.S.E. IMAGE, 2000X

Fig. 3. Typical Examples of the Globular Phase: Bottom of the Pin from Casting Batch EFL-029

EFL-029: AS-CAST

EFL-031: AS-CAST

EFL-036: AS-CAST

EFL-029: BONDED

VC-1-2: BONDED

EFL-029: HEAT TREATED

EFL-036: HEAT TREATED

Fig. 4. Strips Across Selected Samples at Approximately 30X

**Table 3. Results of Quantitative Metallography to
Determine the Areal % of the Globular Phase**

Sample No.	Casting Batch	Location	A	B	C	D	E	F	G	H	AVG	
286B-16	VC-1-2	Bottom	2.50	2.70	2.83	2.05	1.04	.57	2.67	1.10	1.93	
290B-2	EFL-029	Bottom	3.33	3.21	3.65	4.08	4.31	4.10	2.12	2.16	3.37	
290B-3	EFL-029	Bottom	3.28	5.70	2.98	2.36	1.68	3.30	0.98		2.90	
293A-3	EFL-036	Top	2.64	5.23	2.38	.70	.77				2.34	
293A-4	EFL-036	Top	.90	.91	.74	1.45	3.37	2.20	.89	1.66	1.52	
293B-4	EFL-036	Bottom	2.19	3.35	2.82	2.41	2.91	1.52	2.07	1.89	2.40	
295A-2	EFL-031	Bottom	2.65	7.12	9.11	5.77	4.82	4.51			5.66	
295A-3	EFL-031	Bottom	7.11	5.27	2.82	4.71	3.95	4.72	9.71		5.47	二
309A-1	EFL-029	Bonded	3.57	3.74	1.72	1.25	1.68	.43	1.49		1.98	
309A-2	EFL-029	Bonded	3.48	1.54	2.67	2.48	3.51	3.50	1.47	1.95	2.58	
DC-4-1	EFL-029	Compat	2.04	2.55	2.51	2.57	1.10	1.61			2.06	
DC-4-1	EFL-036	Compat	2.67	1.79	1.36	1.03	3.05	2.52	1.16	1.63	1.90	

globular phase tends to over estimate the volume fraction of the phase. However, the large voids were not included and the instrument was not capable of detecting the smaller inclusions so the error may have actually been on the low side rather than the high side of these values. Estimates based on manual point counting to determine the amount of the globular phase were about twice those obtained from the Quantimet. The Quantimet measurements showed that all of these samples except those from batch EFL-031 contained between 1.5 and 3.4 volume % of the globular phase. Both of the samples from EFL-031 that were examined contained higher amounts (about 5.5 volume %) of the globular phase. These data also indicate that there is no tendency for the amount of the globular phase to increase during bonding or 300h heat treatment at 750 C.

B. Surface Layers

Initial SEM examination of the samples from batch EFL-029 revealed that this casting has a layer on its outer surface. This layer was thicker on the sample from the bottom of the fuel pin than it was on the sample from the top of the fuel pin as shown in Figs. 5 and 6. The examination of additional samples of the U-Pu-Zr fuel confirmed this initial finding. Typical areas of the surface layer are shown in Figs. 7 and 8. These results indicate that the layers were thicker on the samples from the bottom of the fuel pins (varied from 10 to 50 microns) and thin-

S.E. IMAGE, 500X

B.S.E. IMAGE 500X

B.S.E. IMAGE, 2000X

**Fig. 5. Microstructure of the Fuel Near the Edge of the Sample
and the Layer on the Surface Near the Top of the Pin
from Batch EFL-029**

B.S.E. IMAGE, 100X

B.S.E. IMAGE 500X

B.S.E. IMAGE, 2000X

Fig. 6. Microstructure of the Fuel Near the Edge of the Sample
and the Layer on the Surface Near the Bottom of the Pin
from Batch EFL-029

FUEL

LAYER

S.E. IMAGE, 500X

FUEL

LAYER

B.S.E. IMAGE, 1000X

Fig. 7. Surface Layer on Bottom Samples from Casting Batch EFL-031

LAYER

FUEL

HIGH CONTRAST, 1000X

FUEL

LAYER

LOW CONTRAST, 2000X

Fig. 8. Surface Layer on Bottom Samples from Casting Batch EFL-036

ner on samples from the top of the fuel pins (2 to 10 microns). At several locations on the perimeter of the bottom sample from EFL-031, a very thick (50 microns) layer was present as shown in Fig. 9. In some locations on some of the samples (EFL-029 bonded, EFL-031, and EFL-036), the surface material appeared to consist of a dense inner layer and a less dense outer layer. It may be that this less dense outer layer was missed during the initial examination of these samples. At high contrast in the BSE mode the less dense outer layer does not appear in the images as is indicated in Fig. 8. The outer layer is apparent only in the SE mode or at low contrast in the BSE mode. A thin intermittent surface layer was found on a sample from the VC-1-2 pin during a reexamination of this sample as shown in Fig. 10. This surface layer had been missed during early examinations of this pin.

C. Grain Boundaries and Other Features

Although few microstructural features were present in the matrix of the as-polished samples, some typical micrographs at a magnification of about 500X are shown in Figs. 11, 12, and 13. The micrographs of samples from EFL-029 and the VC-1-2 pin show that in addition to the globular phase, dendrites (leafy or flowery structures) and rod-shaped inclusions were present. Using very high contrast in the BSE mode, the grain boundaries in samples from the EFL-036 batch were apparent as shown in Fig. 13. Close examination of the SE images of the VC-1-2 pin also show faint traces of the grain boundaries. Efforts to bring out the

200X, B.S.E. IMAGE

1000XM B.S.E. IMAGE

Fig. 9. Thick Surface Layer on a Sample from Batch EFL-031

Fig. 10. Surface Layer on Fuel Pin VC-1-2

BOTTOM SAMPLE

TOP SAMPLE

Fig. 11. Typical As-Cast Microstructure of Batch EFL-029

S.E. IMAGE, 500X

S.E. IMAGE, 500X

Fig. 12. Typical Microstructure of Fuel Pin VC-1-2

S.E. IMAGE, 500X

B.S.E. IMAGE, 500X

Fig. 13. Typical As-Cast Microstructure of Batch EFL-036

grain boundaries using high contrast in the BSE mode were not successful for batches EFL-029 and EFL-031.

IV. MICRO-CHEMISTRY OF THE SAMPLES

A. SEM-EDX

Energy dispersive X-ray spectroscopy (EDX) was performed on several of the samples using the SEM. Typical spectra from the globular phase and from the base material (or matrix) are shown in Fig. 14. These data show that the globular phase consisted primarily of Zr and that the matrix also contained a significant amount of Zr. However, the largest peaks for U and Pu were at 3.16 and 3.35 keV and were too close together to separate without computer based deconvolution techniques that were not available for the shielded SEM. In EDX of random examples of the globular phase, a significant amount of Si was found in the phase in a few cases. Although low atomic number elements (< atomic no. 10) can not be detected directly with EDX, variation in the X-ray intensity for Zr in the globular phase at various locations indicated that low atomic number elements were also present in the phase.

The layer on the surface of the sample from the bottom of the EFL-029 pin was also analyzed with the EDX. These data indicated that there were two dark gray phases present, which were high in Zr, and a lighter gray phase with a Zr to U and Pu ratio similar to that of the matrix material as shown in Fig. 15. X-ray data

**X-RAY SPECTRUM
GLOBULAR PHASE**

**X-RAY SPECTRUM
BASE MATERIAL**

Fig. 14. Typical X-ray Spectra from the Globular Phase and Matrix of the Ternary Fuel; Near the Centerline of a Pin from Batch EFL-029

<u>Location in Micrograph</u>	<u>Description</u>	<u>X-Ray Intensity, Counts/s</u>		
		<u>U</u>	<u>Zr</u>	<u>Si</u>
A	Medium Gray	0.4	12.0	5.0
B	Dark Gray	1.4	16.0	5.5
C	Light Gray	12.0	2.2	1.1
D	Medium Gray	6.0	4.0	3.0
E	Light Gray	12.0	0.4	--

Fig. 15. SEM EDX Data for the Surface Layer on a Sample from Batch EFL-029

from a band about 15 microns wide in the matrix at the edge of the pin indicated Zr was depleted in this area.

B. SAM Analysis of the Surface Layer

The scanning Auger microprobe (SAM) was used to analyze the composition of the outer layer on the bottom sample from batch EFL-029. The SAM interrogates the surface of a sample by detecting low energy electrons (Auger electrons) that are emitted as a result of excitation of the sample by the electron beam. The SAM is capable of detecting elements with atomic numbers as low as 3 (Lithium). Each area that was examined was sputtered so that a clean surface was examined.

The results of analysis of the surface layer on the bottom sample from batch EFL-029 is shown in Fig. 16. These data show that the darker material adjacent of the fuel is Zr that contains between 12 and 18 wt % O and 4 to 6 wt % C. The light gray phases contain Zr and Si as well as oxygen and carbon. The medium gray phase on the outer edge of the layer has a composition similar to the fuel but contains a greater amount of oxygen (about 2 wt %) than the fuel.

C. SAM Analysis of the Globular Phase

The SAM was used to examine inclusions in the bottom samples from batch EFL-029 and a bottom sample from pin VC-1-2. The data on inclusions from near the centerline and edge of the EFL-029 sample are given in Fig. 17. These results indicate the inclu-

<u>Location in Micrograph</u>	<u>Description</u>	<u>U, wt%</u>	<u>Pu, wt%</u>	<u>Zr, wt%</u>	<u>Si, wt%</u>	<u>O, wt%</u>	<u>C, wt%</u>	<u>N, wt%</u>
A	Dark	0	0	82	0	12	6	0
B	Dark	0	0	87	0	10	3	0
C	Light	0	0	61	17	18	4	0
D	Light	0	0	41	40	9	10	0
E	Medium	86	0	12	0	2	0	0

Fig. 16. SAM Data for the Surface Layer on a Bottom Sample from Batch EFL-029

EDGE

CENTER

<u>Location in Micrograph</u>	<u>Description</u>	<u>U, wt%</u>	<u>Pu, wt%</u>	<u>Zr, wt%</u>	<u>Si, wt%</u>	<u>O, wt%</u>	<u>C, wt%</u>	<u>N, wt%</u>
A	Dark	0	0	78	0	5	16	1
B	Dark	0	0	72	0	4	15	0
C	Dark	0	0	80	0	4	16	0
D	Dark	0	0	77	0	4	18	1

Fig. 17. SAM Data for Inclusions in a Bottom Sample from Batch EFL-029

sions consisted of Zr with small concentrations of O and N, but relatively large amounts of C. These high C concentrations are considered suspect as it is unlikely that the atom ratio of C to Zr would be greater than 1 (about 12 wt % C). An inclusion near the OD of this sample had a darker center in the BSE image, indicating a change in composition. The SAM data indicated that the center of the inclusion contained a relatively high concentration of Pu (26 wt %) as well as high O (5 wt %) and C (10 wt %). The outer ring of the inclusion had a composition similar to the inclusions near the center of the sample (Zr 78 wt %, O 5 wt %, N 1 wt %, and C 16 wt %).

Results of SAM analyses of inclusions in a sample from the bottom of the VC-1-2 pin are given in Fig. 18. These data indicate that the inclusions near the center of the sample contained about 94 wt % Zr, 3 to 4 wt % O, 1 wt % C and 1 wt % N. The inclusion near the OD of the sample contained slightly less Zr and had higher concentrations of the interstitials. The needle-like inclusions in this sample contained U and Pu, but also had higher concentrations of Zr and O than the matrix (Zr 25 wt % and O 1 wt %). Analyses of the needle-like phase were not accurate because the needles were so narrow that the beam spilled over onto the matrix. The data do indicate the needles were a separate phase that was high in Pu and Zr.

Near Edge

Center

<u>Location in Micrography</u>	<u>Description</u>	<u>U, wt%</u>	<u>Pu, wt%</u>	<u>Zr, wt%</u>	<u>Si, wt%</u>	<u>O, wt%</u>	<u>C, wt%</u>	<u>N, wt%</u>
A	Near Edge	0	0	92	0	5	2	1
B	Near Edge	0	0	88	0	4	7	1
C	Near Edge	0	0	92	0	5	2	1
D	Near Edge	0	0	90	0	4	4	2
E	Near Edge	0	0	84	0	5	8	3
F	Center	0	0	95	0	3	1	1
G	Center	0	0	94	0	4	1	1
H	Center	0	0	95	0	3	1	1
J	Center	0	0	92	0	4	3	1
K	Needle	66	9	24	0	1	0	0
M	Needle	59	13	27	0	1	0	0

Fig. 18. SAM Data for Inclusions in a Bottom
Sample from Pin VC-1-2

D. SAM Analysis of the Matrix

The SAM was also used to analyze the matrix of a bottom sample from EFL-029 and VC-1-2. However, these results showed that the SAM has relatively poor sensitivity for Pu, which resulted in very small peaks with relatively large errors possible for the Pu analysis. The results of the SAM analysis are normalized to 100%, so errors in the Pu data could also influence the results for the other constituents. The average of all analysis on the matrix of the VC-1-2 sample was: Zr 10.1 wt %, U 79.0 wt %, and Pu 10.8 wt %. The average of all analyses on the matrix of the EFL-029 sample was: Zr 6.6 wt %, U 86.0 wt %, and Pu 7.5 wt %. The data from the EFL-029 sample also showed a trend of lower Zr content near the edge of the sample as compared to its center. The lack of agreement in the average values for both of the samples for Pu and the low average value for Zr for the EFL-029 sample indicate that the SAM does not provide reliable micro-chemical data for the matrix of these samples.

V. DISCUSSION

The microstructural and micro-chemical characterization of samples of U-Pu-Zr fuel has shown several features that were common to all of the samples. These features include a globular phase that has a high Zr content, a generally featureless matrix (except at higher Pu contents), and a surface layer that is higher in interstitial impurities than the matrix.

Micro-chemical analysis of the high Zr globular phase has

shown that it contains varying amounts of oxygen, carbon, and nitrogen. In general, the amount of oxygen and carbon present in the globular phase corresponds to oxygen stabilized alpha zirconium $Zr(O)$ and ZrC . These Zr-compounds are very stable chemically, and therefore, the amount of the material would not be expected to change significantly as a result of heat treatment unless additional sources of the interstitial elements were present. This behavior is supported by the fact that the Zr-rich phase did not change significantly during the bonding or heat-treating of these samples. It appears that the second phase was formed during and before the casting operation. It is likely that any interstitial impurities that were present in the feed materials would be gettered by the Zr during the casting operation. In addition, during the heating of the charge to the casting temperature some additional carbon would be picked-up from the graphite crucible. The Si in some of the inclusions and in the surface layer on the samples indicates that additional oxygen was picked-up from the Vycor molds and from the zirconia wash on the molds during the casting operation. The greater amount of the Zr-rich phase and a relatively high Si content in the EFL-031 batch correlates with a greater amount of reaction during the casting operation as a result of a higher casting temperature for that casting batch.

The fact that grain boundaries were discernible in the EFL-036 and VC-1-2 samples and not in the EFL-029 and -031 samples indicates that the Pu content of the alloy has an influence on the as-cast structure of the matrix. The structures of the EFL-029 and the EFL-036 samples that were heat treated during a compatibility test were significantly different than the as-cast structures as shown in Fig. 4. However, a discussion of the microstructure of the heat treated samples is beyond the scope of this characterization.

This characterization showed that the SAM was useful in analyzing for the low atomic number elements that were present in the globular phase and in the surface layer. The low sensitivity of the instrument for Pu results in questionable results for analysis of the fuel matrix. Either electron microprobe analysis (X-ray wavelength dispersive analysis) or analysis with a SEM with computer capability to deconvolute the energy dispersive results should be capable of providing micro-chemical analysis of the matrix. Electron microprobe analysis will be performed on these samples and reported at a later date.

VI. CONCLUSIONS

The characterization of the current casting batches of the U-Pu-Zr fuel as well as samples from an "old" pin has shown that second phase in the as-cast structure is Zr that is probably stabilized in the alpha phase with the interstitial elements O, C, and N. The amount of this phase appears to be stable during

bonding (about 2 h at 500 C) and during heat treating for up to 300 h at 750 C. The amount of this phase that is present appears to depend on the casting parameters as the higher temperature during the casting of EFL-031 appears to have resulted in a greater amount of the Zr-rich phase. Based on the apparent stability of the Zr-rich phase, no change in the irradiation performance of the fuel from these casting batches would be expected. However, it may be prudent to monitor the irradiation performance of fuel pins from these batches separately rather than lumping them into a single category of 8 wt % Pu pins.

All of the samples, including those for the VC-1-2 pin, exhibited a surface layer. This layer consisted mainly of Zr that contained relatively high amounts of O and a lesser amount of C. In most cases material with a composition similar to the fuel matrix, but with higher O content was also present in the outer band of the layer. The surface layers were thicker on samples from the bottom of the castings than those from the top. The surface layers appear to result from interaction between the melt and the mold (and the mold wash) during the casting operation. The bottom of the casting remains hot for a longer time than the top during the casting operation so has a longer time to react with the mold.

Micro-chemical data on the composition of the matrix has not been accurate as a result of the instruments being insensitive to Pu. Future examinations should correct this deficiency.

This examination found no differences in the current castings and the "old" fuel pin that would be expected to result in differences in the irradiation performance of the fuel.

REFERENCES

1. W. F. Murphy, et. al., "Postirradiation Examination of U-PU-Zr Fuel Elements Irradiated in EBR-II to 4.5 Atomic Percent Burnup, "ANL-7602, November 1969.
2. A. B. Shuck, et. al., "Fabrication of EBR-II Core I Fuel Rods," ANL-6274, 1967.