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Secondary Phase Objects in As-cast U-10wt%Zr

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ACRONYMS

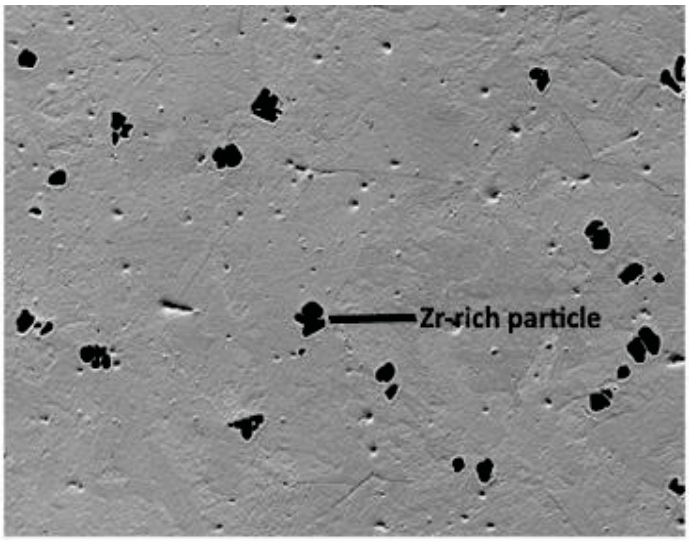
EDX	energy dispersive x-ray
EPMA	electron probe microanalyzer
FFTF	Fast Flux Test Facility
IMCL	Irradiated Materials Characterization Laboratory
SEM	scanning electron microscopy
WDX	wavelength dispersive x-ray spectroscopy

Precipitates or Undissolved Zirconium in As-cast U-10wt%Zr

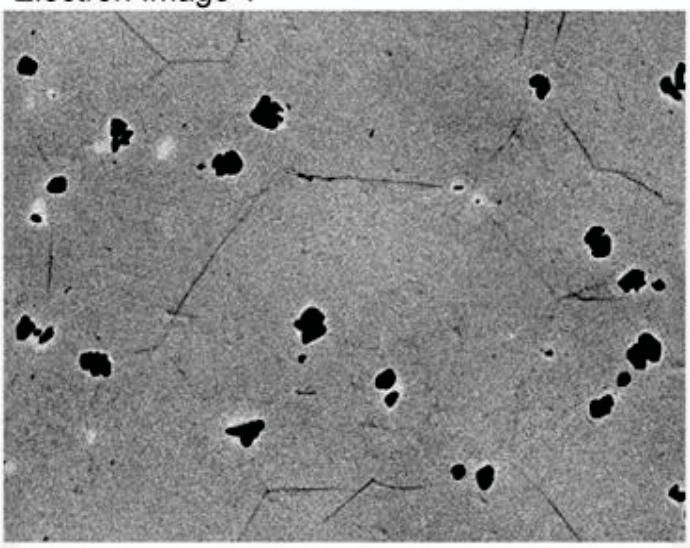
INTRODUCTION

Recent U-10Zr castings, namely billets for extrusion, have shown secondary phase objects when the as-cast material was examined using optical metallography and/or scanning electron microscopy (SEM).

Figure 1 shows an early SEM examination of a metallurgical mount produced from billet #1242 (U-10Zr). Note the dark objects in the electron image. Attempts to identify these objects indicated they were rich in zirconium, but not in uranium. EPMA examinations of other U-10Zr castings in the past had indicated that these were likely zirconium-carbides, but the SEM carbon scan here did not illuminate the objects. Because of potential interferences in EDS spectra for carbon and uranium, researchers expected to need to make a more detailed examination of this.



Electron Image 1



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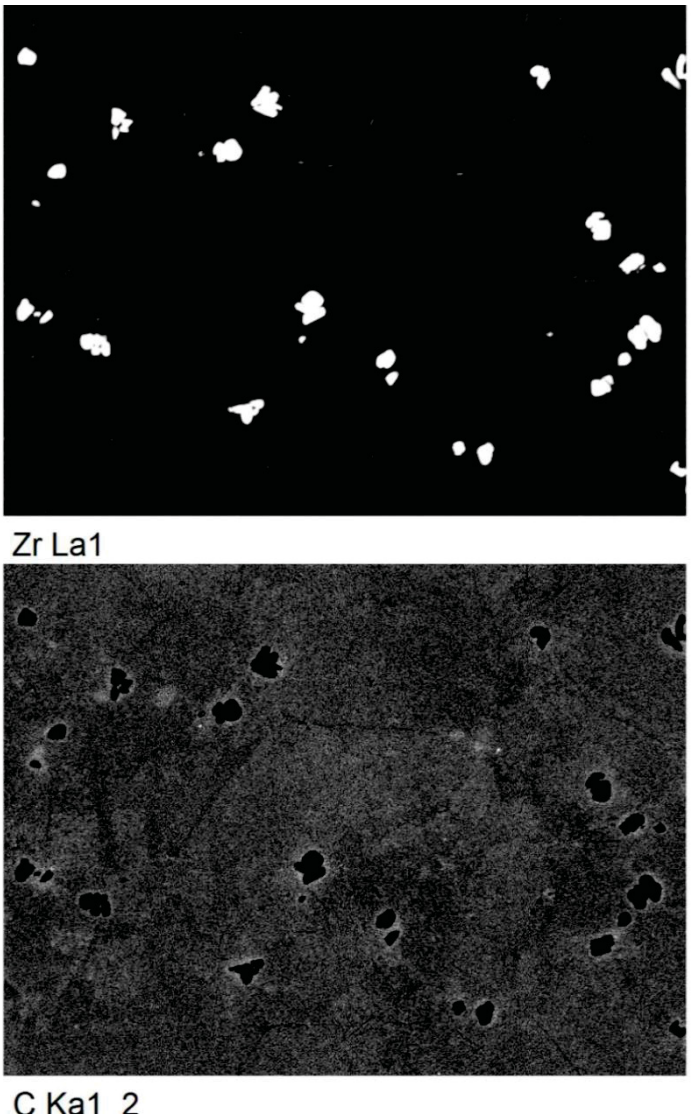

Figure 1. SEM images of a sample from billet #1242. The extra three images show images highlighted by characteristic x-ray generation representing uranium, zirconium, and carbon.

The question is whether these are different because they were performed using a scanning electron microscope instead of an electron probe microanalyzer (EPMA), or because they are from a larger, more slowly cooled casting and might be pure zirconium. Fuel microstructure is known to effect irradiation behavior and the historic EBR-II and FFTF injection cast U10Zr had acceptable in reactor performance. Thus, as different manufacturing techniques for new fuels are being considered, it is important to understand this process versus microstructure question.

To compare the images and analyses, previous EPMA work will first be reviewed.

EBR-II U-10ZR FUEL

In order to compare precipitate chemistries using EPMA analysis, researchers can study characterization of other U-10Zr fuel. Previous characterization studies were performed on U-10Zr fuel, which had been reclaimed from a stock EBR-II fuel pin, and another U-10Zr pin that could have been

used as a replacement in one of the MFF-series tests in the Fast Flux Test Facility (FFTF). The fuel had been injection cast (cooled quickly) and had also been subject to sodium bonding (one hour at 550˚C) subsequent to casting. These should have been representative of the U-10Zr fuel that had been used as standard driver fuel for EBR-II and partially qualification tested to be used in FFTF as well.

The important examinations to identify phases present were performed using the EPMA. In Figure 2, the angular precipitate in the lower middle area of the photo was identified as Zr_2Si; the silicides are always identifiable by their angular appearance, sometimes as needle-shaped and other times in other shapes such as the one shown below. The other large silicide particle on the right typifies another shape often seen.

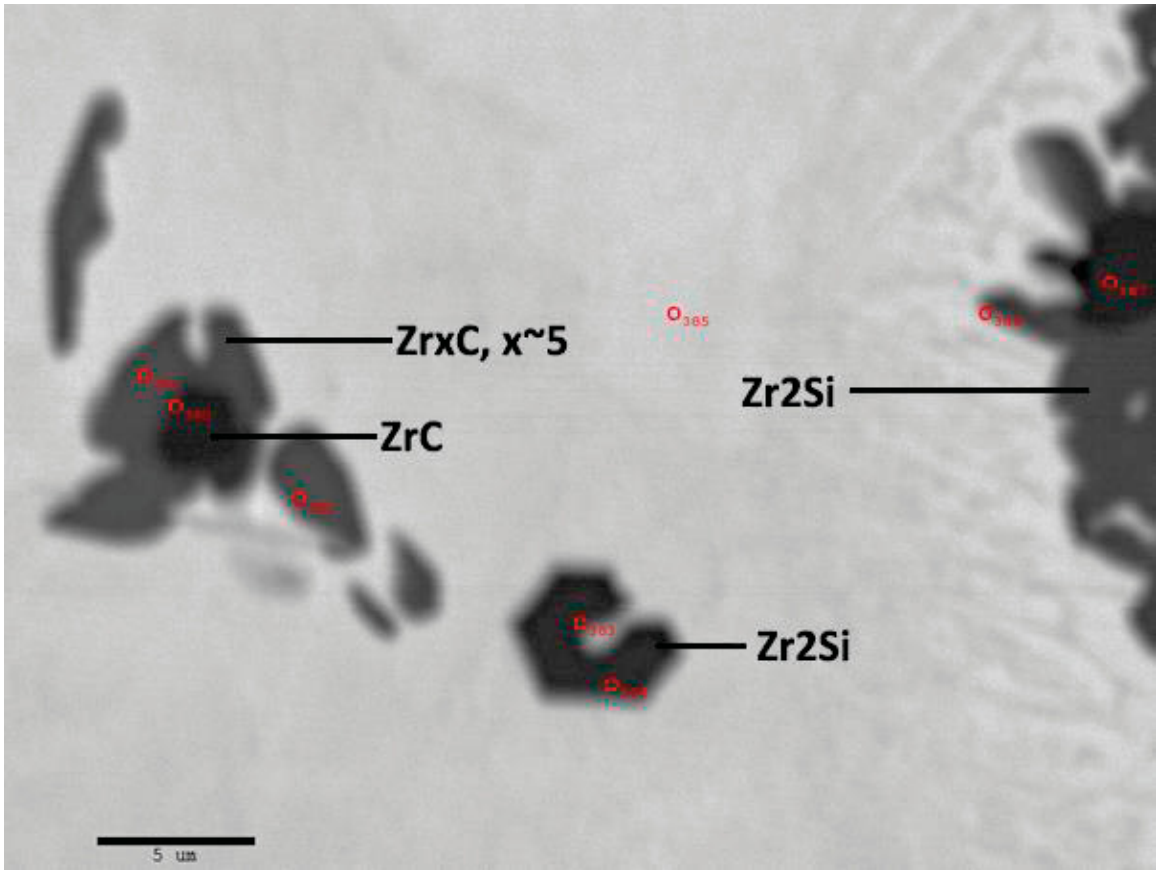

Figure 2. EPMA image of several types of precipitates formed in injection cast U-10Zr.

The other precipitates often had two colorations with a darker (heavier) center surrounded by a lighter gray. EPMA chemical information indicates the dark center is zirconium carbide (ZrC), while the lighter surrounding volume is composed of Z_xC with approximately x=2-7. Since this does not exist in the zirconium-carbon equilibrium phase diagram, it is assumed this is a metastable compound, or perhaps zirconium is stabilized by carbon. EPMA spot analyses are listed in Table 1.

Table 1. EPMA chemical analysis of location in Figure 2.

Spot	Si at.%	U at.%	C at.%	Zr at.%	Possible Phase ID
380	0.05	0.25	41.5	58.2	ZrC
381	0.00	0.59	16.5	82.9	
382	0.07	2.08	15.2	82.7	
383	29.2	2.81	11.8	56.1	Zr_2Si
384	32.0	0.39	10.0	57.6	Zr_2Si
385	0.06	87.5	0.00	12.5	
386	0.13	83.3	5.30	11.3	
387	33.8	0.14	8.77	57.3	Zr_2Si

Figure 3 shows other precipitates in the as-injection-cast sample that were identified as equilibrium zirconium carbide (ZrC).

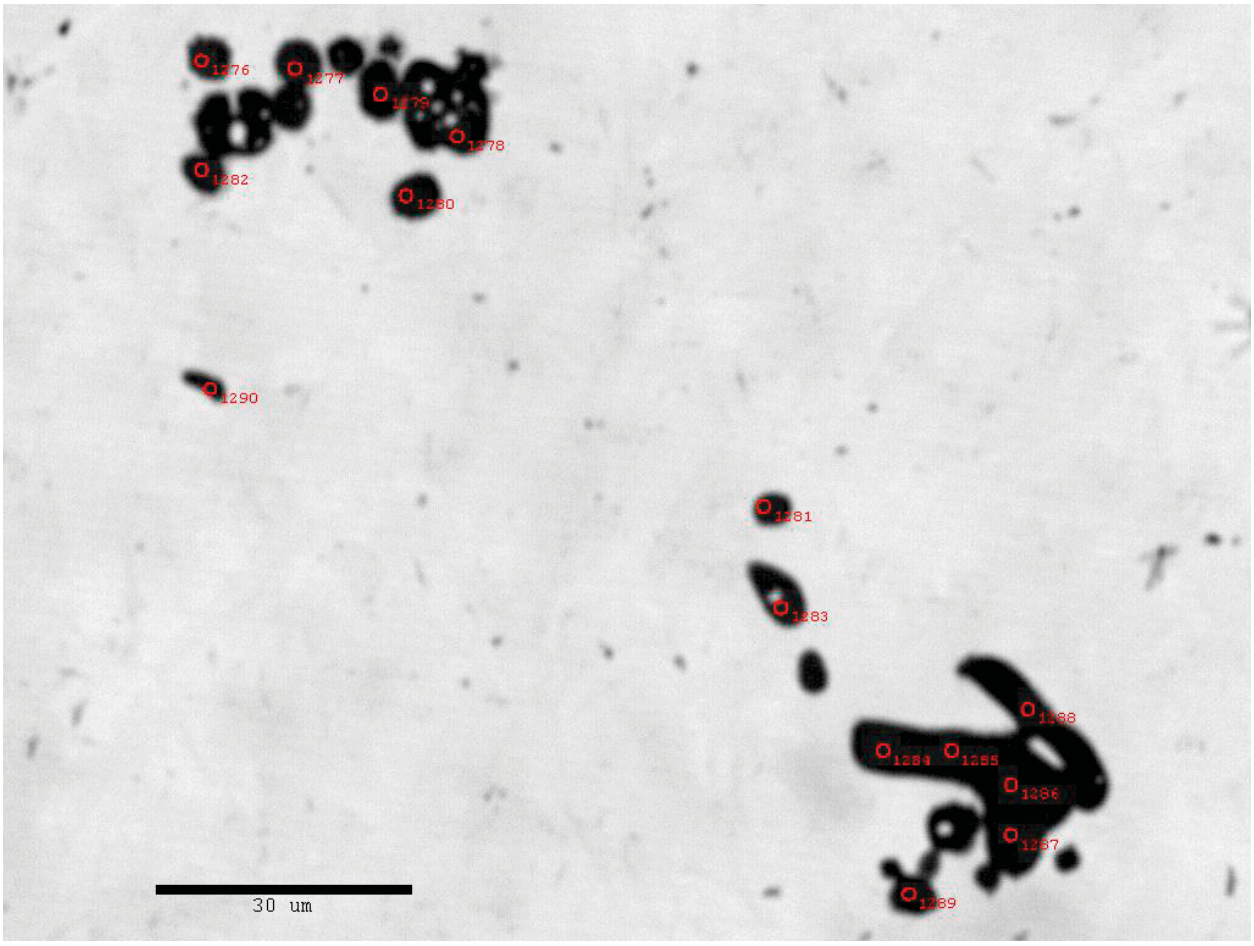

Figure 3. ZrC precipitates in an as-injection-cast U-10Zr fuel slug.

Table 2. EPMA chemical analysis of precipitates shown in Figure 3.

Spot	Si at%	U at%	Zr at%	C at%	Possible Phase ID
1276	0.08	69.8	22.6	7.5	
1277	0.20	6.81	47.0	46.0	ZrC
1278	0.02	0.36	52.3	47.3	ZrC
1279	0.03	0.12	52.7	47.2	ZrC
1280	0.03	0.93	50.9	48.1	ZrC
1281	0.14	2.53	52.2	45.1	ZrC
1282	0.03	0.43	51.2	48.3	ZrC
1283	0.00	0.37	51.7	47.9	ZrC
1284	0.01	0.07	52.4	47.5	ZrC
1285	0.00	0.05	52.6	47.4	ZrC
1286	0.01	0.08	52.1	47.8	ZrC
1287	0.01	0.05	52.1	47.8	ZrC
1288	0.02	0.20	51.7	48.1	ZrC
1289	0.00	0.35	52.7	47.0	ZrC
1290	0.09	52.5	30.0	17.4	

Figure 4 shows an area of the cross-section of the as-injection-cast U-10Zr fuel slug. The double layer to the right in the image is a "rind" that forms on the fuel slug at one end of the cast slug. (This is presumed to be the end that remains hot for a longer time as it is at the molten pool with the rest of the casting and quartz mold extending above it.) The rind is identified as having an inner layer of Zr_xC with x=2-3, either a metastable carbide or carbon-stabilized zirconium. The outer layer has a chemical composition of ZrSi, presumably forming by interaction with the quartz casting mold.

The other precipitates are the same as those identified in Figure 2, with a ZrC core surrounded by a Zr_xC (x~7) outer layer, except this time with some that have a nearly pure uranium center (white areas). EPMA spot analyses are listed in Table 3.

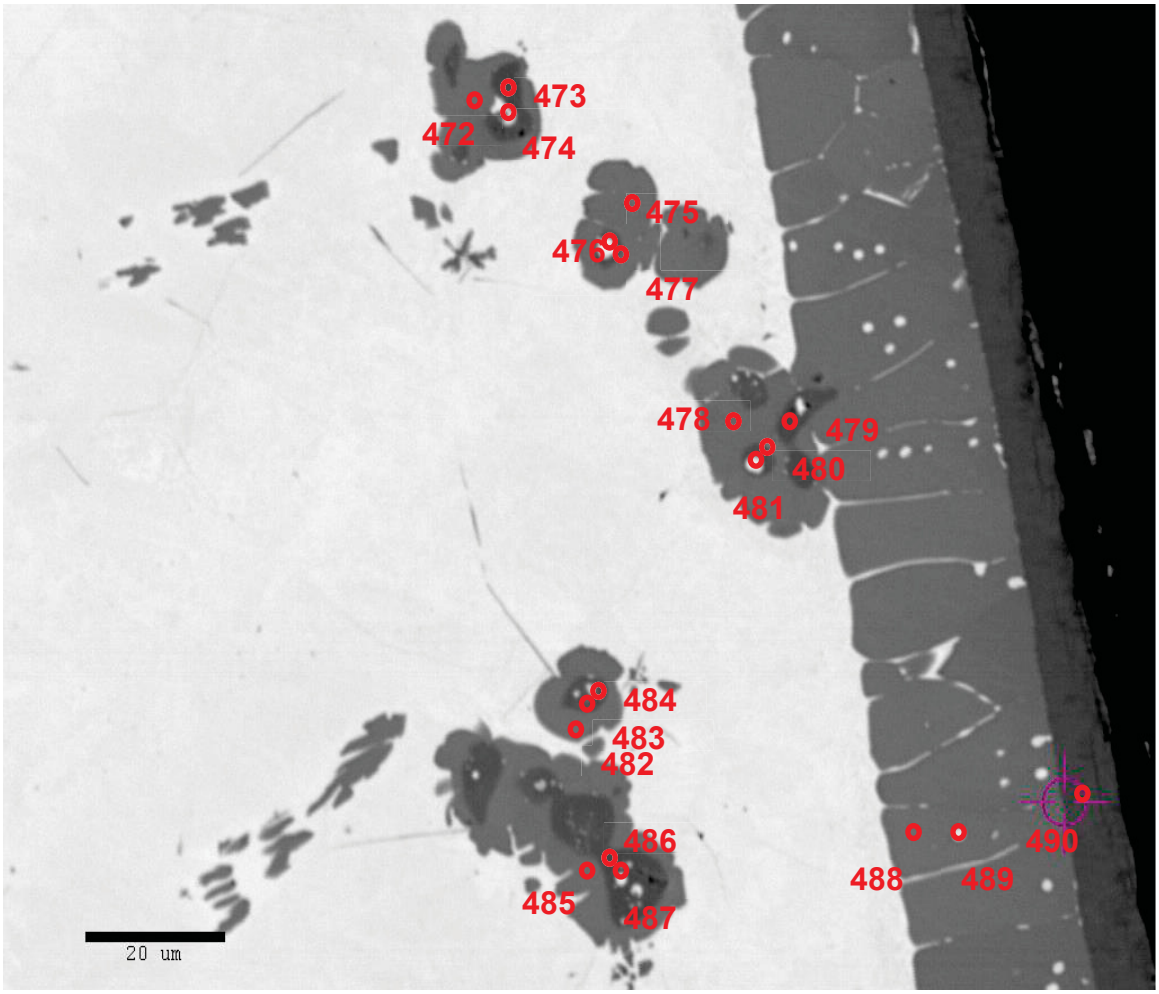

Figure 4. EPMA image of precipitates internal to as-injection-cast U-10Zr fuel and the “rind” (right), which forms on the outer surface of a portion of the fuel slug.

Table 3. EPMA chemical analysis of the precipitate and "rind" area in Figure 4.

Spot	Si at%	U at%	Zr at%	C at%	Possible Phase ID
472	0.03	1.13	86.0	12.8	
473	0.01	0.09	54.4	45.5	ZrC
474	0.11	65.3	15.5	19.1	
475	0.03	1.06	86.1	12.8	
476	0.03	0.89	59.0	40.1	ZrC
477	0.05	94.8	4.45	0.7	
478	0.01	1.17	85.6	13.2	
479	0.01	0.53	54.8	44.6	ZrC
480	0.00	0.13	55.4	44.5	ZrC
481	0.18	92.2	4.80	2.85	
482	0.03	1.19	85.2	13.6	
483	0.03	1.47	54.3	44.2	ZrC
484	0.06	0.26	55.5	44.2	ZrC
485	0.05	1.00	85.0	13.9	
486	0.00	0.09	53.6	46.3	ZrC
487	0.10	64.2	16.7	19.0	
488	0.02	1.32	85.4	13.2	
489	0.23	72.3	13.8	13.7	
490	46.9	0.40	45.8	6.91	ZrSi

SEM EXAMINATION OF BILLET MATERIALS

Since the EPMA is in the process of being set up in the Irradiated Materials Characterization Laboratory (IMCL), the challenge was to make the best attempt to use existing SEM examination capabilities to assess whether the particles or precipitates in the billet material have the carbon levels seen in the EBR-II injection-cast fuel. In other words, the question is whether particles/precipitates formed by precipitation because of zirconium reaction with available carbon, or whether they represent undissolved zirconium feed material. The size and uniformity tend to suggest the latter is not likely. Proof of precipitation of zirconium with carbon is, therefore, required, without use of an EPMA.

Using SEM and energy dispersive x-ray (EDX) to evaluate light elements is complex and is usually discouraged because high uncertainties in the low-energy x-ray spectra can be related to background interference. However, experiments were done using EDX as a quick tool to look at the billet castings. Two U90-Zr10 samples were analyzed, one from a recently cast billet (#1242), the same one examined previously by both optical metallography and by SEM (see Figure 1). The other sample, #1357, is from an EBR-II fuel slug, while #1242 is taken from a recently cast extrusion billet, #1242. Sample #1357 was akin to the samples previously discussed in this report that were reclaimed from an EBR-II driver fuel pin. In the earlier work, EPMA identified two types of carbide deposits ($Zr_{3\text{-}7}C$ and ZrC) that could be the same kind of precipitate as seen in #1242.

Using EDX and an SEM instead of EPMA, the presence of uranium indicates some interference in the x-ray spectra and thus, areas rich in uranium (i.e., matrix) seem erroneously rich in carbon. This is a result of the peak overlaps and the way in which the built-in software handles this overlap. This makes it

difficult to detect the presence of carbon using these methods and virtually impossible to do any quantitative analysis.

To illustrate an example of this, Figure 5 shows a backscatter image of the #1242 sample from a U-10Zr billet. Also shown are dot maps highlighting areas that should have enhanced concentrations of whichever element is selected. The more intensely colorized the area is, the higher the concentration is supposed to be. However, while the zirconium map does indicate zirconium in the particles, and uranium in the matrix, it indicates that carbon is most concentrated in the matrix also. This is caused by the interference the uranium makes with the carbon peak at low energy.

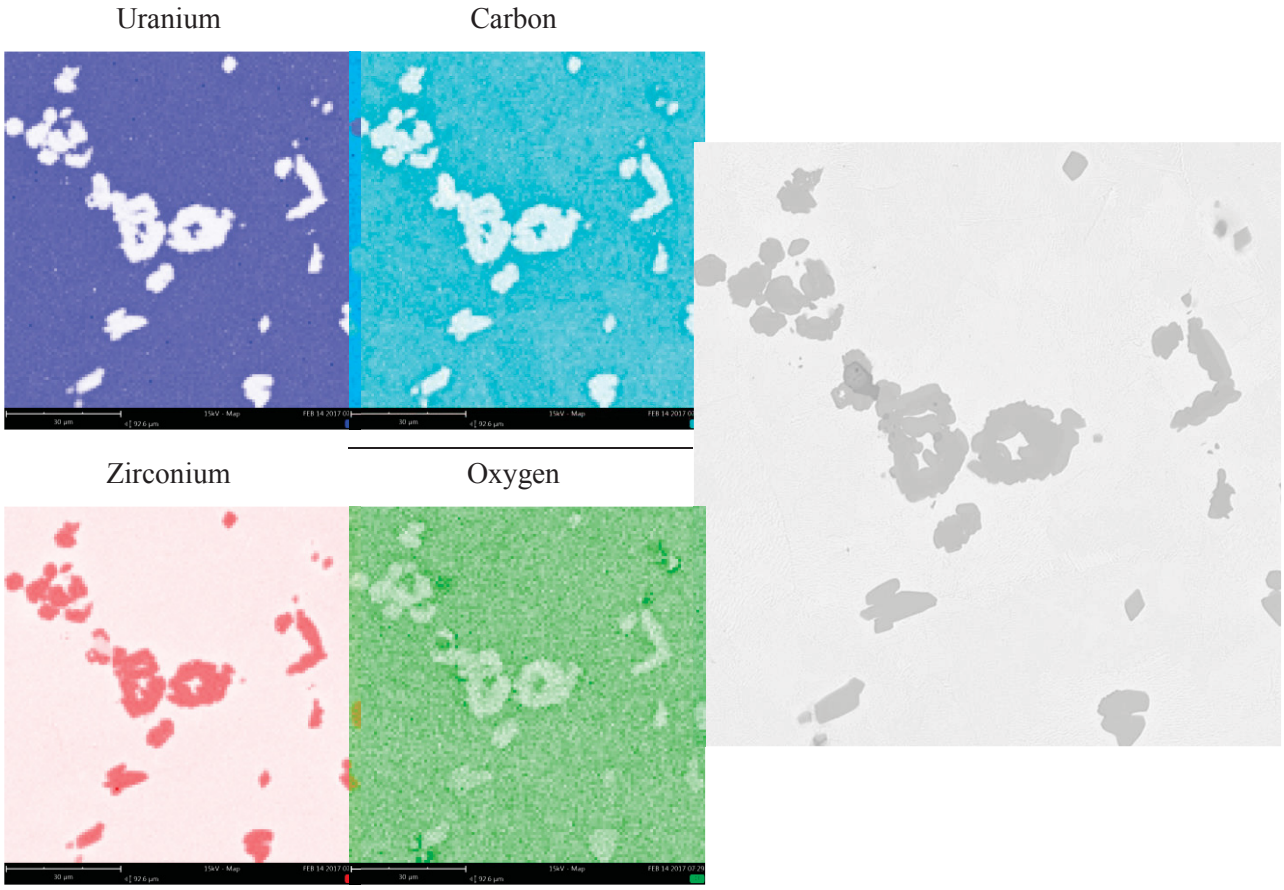

Figure 5. EDX results showing an erroneous carbon signal in the matrix.

However, the following approach can be used, which can yield a qualitative answer to identify the presence of carbon in the precipitates, or indicate that it is not likely present to any significant fraction.

There is interference from a uranium peak with the carbon peak at low energy (the K-line). The task is to separate the uranium-induced counts at that energy from those of the carbon. To do that without relying on the built-in software (which is sensitive to errors from many sources), five spectra are taken from spots clearly in the matrix areas of the sample. These spectra are taken during the same SEM operating session to minimize any differences in the conditions (e.g., accelerating voltage, atmosphere, and working distance). They provide a source of uranium information from which the uranium interference at the carbon K-line can be estimated.

In the uranium-rich area, the counts of uranium in the M-line (the first large and relatively independent uranium peak) are taken, as well as the counts attributed to uranium at the energy where the

carbon K-line occurs. This ratio is assumed to be the same in the spectra taken at the particle location, so using the counts at the uranium M-line location, the uranium counts interfering with the carbon K-line peak can be estimated and subtracted from the peak at the carbon K-line location. These counts are therefore assigned as the carbon peak intensity.

To follow this process, take these steps:

1. Take five spectra in areas expected to be pure uranium.
2. Measure the ratio of counts between the large uranium M-line and the uranium peak plus background at the carbon K-line location.
3. Take a spectrum at one of the particles/precipitates.
4. Use the average ratio determined in Step 2 to estimate the uranium plus background interference (number of counts) at the carbon K-line location. Call that count Ip, the interference count for the precipitate spectrum.

The equation describing this final step is:

$$\mathbf{I_p} \text{ at carbon K-line} = (C/U)_M * U_P, \quad (1)$$

where **Ip** is the interference count in the precipitate/particle spectrum at the carbon K-line, $\mathbf{(C/U)_M}$ is the average ratio measured in Step 2 above using matrix spectra, and **Up** is the count in the precipitate spectra at the uranium M-line location. The spectra in Figures 6 and 7 illustrate which peaks are discussed here.

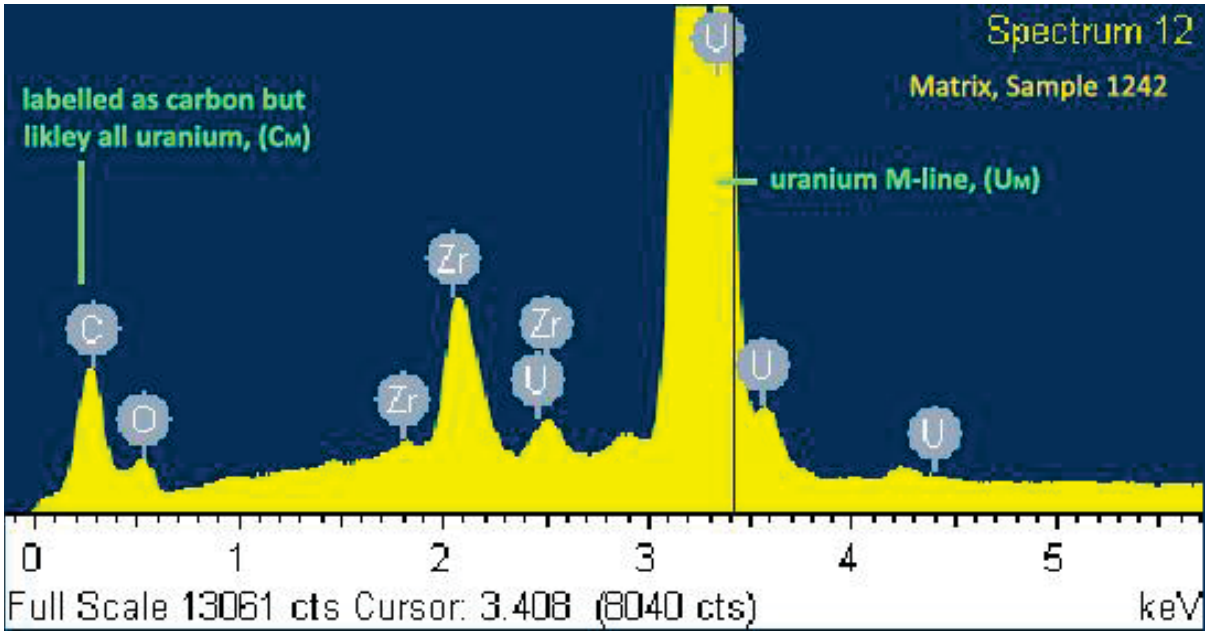

Figure 6. X-ray spectrum created in a spot SEM analysis of the uranium-zirconium matrix in sample #1242.

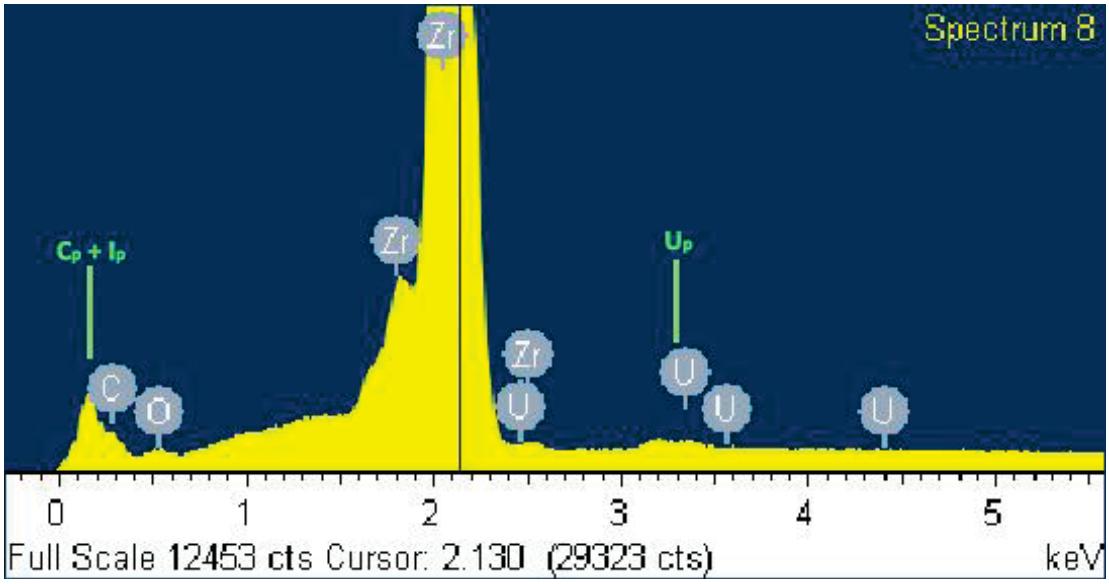

Figure 7. X-ray spectrum created in a spot SEM analysis of a precipitate in sample #1242.

The $\mathbf{I_p}$'s are subtracted from the counts at the carbon K-line and have to be compared to the interference counts on the carbon K-line to produce the counts attributable to carbon. When analyzing the precipitates, this ratio has been used to evaluate the interference of the surrounding matrix (or small amount of uranium in the precipitates) on the carbon identification.

If the precipitate count is higher than the interference in that location, then researchers can affirm that carbon is present. Table 4 and Table 5 show the results of some of these analyses for the #1242 billet sample in the matrix and in the precipitates, respectively. Note that, comparatively, the uranium matrix contains little carbon, while the precipitates do contain a significant amount of carbon. Unfortunately, the amount cannot be measured using SEM and this technique.

Table 4. Uranium and carbon in the matrix .

Sample #1242	Matrix		
U Counts (3.165)	C Counts (0.277)	Ratio C/U	
92,952	10,825	0.116	
94,417	11,074	0.117	
92,999	8,905	0.096	
93,047	10,422	0.112	Average = 0.110,

Table 5. Calculation of carbon presence in the precipitates.

Sample #1242, precipitates					
U Counts	***C Counts***	***C Interference***	***C Not Related to U***	***Is it Carbide?***	***C/U***
4,289	2,939	473.4	2,465.6 (85% of total C count)	C	0.57
7,319	2,405	807.8	1,597.2 (66%)	C?	0.22
6,026	2,283	665.1	1,617.9 (71%)	C	0.27
3,991	18,375	440.5	17,934.5	C	4.5
5,543	2,124	611.8	1,512.2	C	0.27

Wavelength dispersive x-ray spectroscopy (WDX) was also used to try to identify the presence of carbon; however, the results were not consistent, probably due to the presence of the different precipitates. The WDX technique works on a principal similar to that of the EPMA, but can only look for one element at a time and requires standards. The small amount of carbon in Zr6C (as was observed by the EPMA on sample #1357) may be not identifiable, while the carbon in the ZrC will yield its presence.

The #1357 EBR-II fuel sample was also analyzed in this same way. Figure 8 shows an SEM image of the precipitates in the #1357 sample. Table 5 shows the analyses of the x-ray data collected from the spots (Spectrum 1, etc.) in Figure 8. Perhaps the easiest way to see why certain data indicated the presence of carbon and others did not is to look at the uranium/carbon ratio information, although Spectrums 4 and 8 show equivalent uranium/carbon ratios.

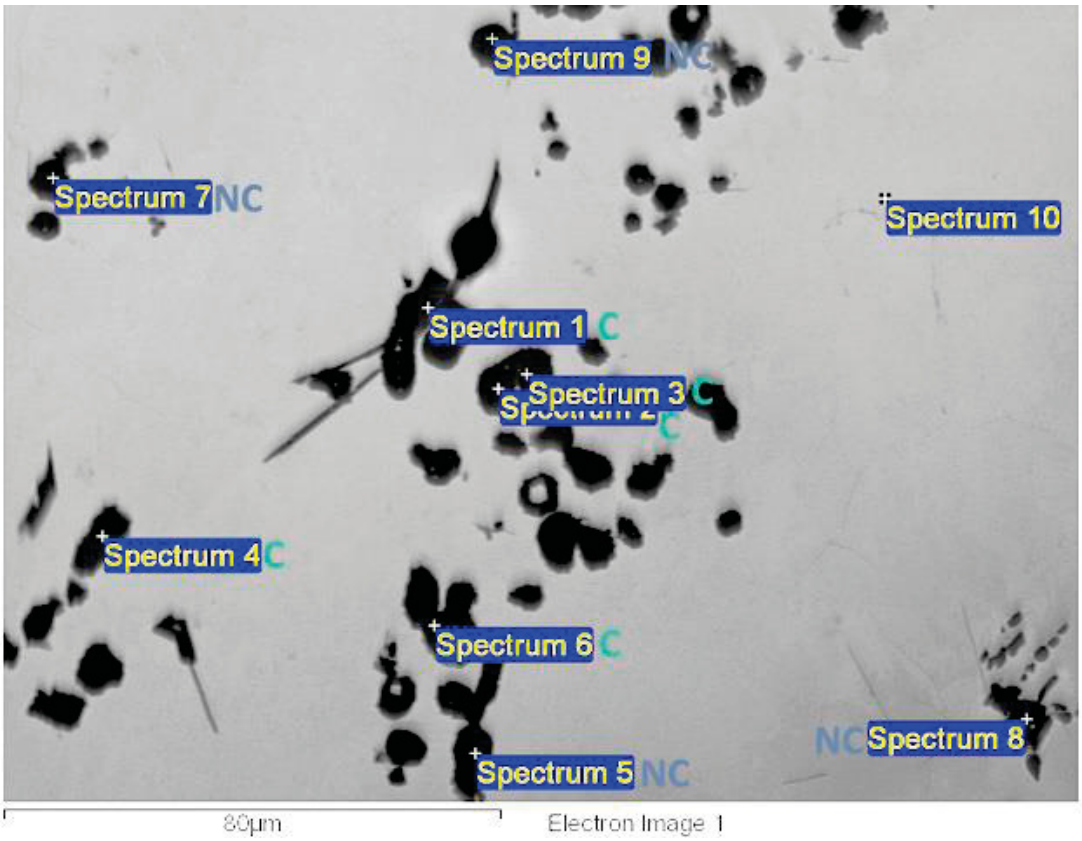

Figure 8. Section of EBR-II fuel sample #1357 showing precipitates and the spot analyses done for the presence of carbon.

Table 6. Analyses for carbon despite interference with uranium x-ray energies.

	U Counts	*C Counts*	*C Related to U*	*C Not Related to U*	*Is it C Considering Error?*	*C/U*
Spec1	1906	1198	324.85	873.15	C	0.46
Spec2	1905	1338	324.68	1013.32	C	0.53
Spec3	1399	1444	238.44	1205.56	C	0.86
Spec4	4091	1495	697.25	797.752	C ?	0.20
Spec5	17239	3120	2938.13	181.87	No C	0.01
Spec6	981	1539	167.20	1371.80	C	1.40
Spec7	14011	2431	2387.97	43.03	No C	0.00
Spec8	12081	3997	2059.03	1937.97	No C ?	0.16
Spec9	18679	4526	3183.56	1342.44	No C	0.07
Spec10	2529	523	431.03	91.97	No C	0.46

The matrix locations, like Spectrum 10 in Figure 8, were also analyzed, and the results are shown in Table 7. The table highlights the difference to the analyses of the precipitates (Table 6) in terms of the uranium/carbon ratio, except for Spectrum 7.

Table 7. Analysis of x-ray data taken from matrix (uranium) areas in Sample #1357.

U Counts (3.165)	C Counts (0.277)	C/U
34088	6352	0.186
32912	6166	0.187
29576	4528	0.153
29130	4332	0.149
		0.150
29783	5304	0.178
34039	6449	0.189

CONCLUSIONS

When samples of U-10Zr metallic fuel that would have been used as driver fuel in EBR-II or FFTF was examined previously using EPMA, it was found that most of the secondary phase in the expected α-uranium and δ-phase UZr_2 matrix was some form of zirconium-carbon compound, sometimes having a Zr:C atomic ratio of 1:1 denoting the stable zirconium carbide, ZrC. Others had excess zirconium showing Zr:C of ~5. This may me Zr stabilized by carbon. There were also zirconium silicide precipitates, but these would have formed because the duel slugs were cast into quartz molds and the fuel could have interacted with the mold.

Recently, cast U-10Zr billets used for extrusion, were examined using optical metallography by an independent laboratory and particles resembling the ones observed in the old injection cast fuel were noted in the fuel microstructure. It was postulated that this might be undissolved zirconium feed material, although the size and number distribution of the particles (uniform in both cases) suggested they were precipitated.

The EPMA would not be available again for several many months so SEM was used in and attempt to prove whether the particles were indeed undissolved zirconium or were the same precipitates observed in the injection cast material. Although experimentally a difficult task to prove the existence of carbon in the particles using SEM because of the interference of uranium x-ray peaks at the same energies, it is believed that statistically the scans done at positions of the particles indicated significantly more carbon than did scans on the uranium matrix. We are relatively confident that these are precipitates and not remnants of zirconium feedstock. They can be re-examined when the EPMA becomes available if more certainty is required.