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Identification and Quantification of Carbon Phases in Conversion Fuel for the Transient Reactor Test Facility

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INTRODUCTION

As part of an overall effort to convert US research reactors to low-enriched uranium (LEU) fuel, a LEU conversion fuel is being designed for the Transient Reactor Test Facility (TREAT) at the Idaho National Laboratory. TREAT fuel compacts are comprised of UO₂ fuel particles in a graphitic matrix material. In order to refine heat transfer modeling, as well as determine other physical and nuclear characteristics of the fuel, the amount and type of graphite and non-graphite phases within the fuel matrix must be known.

In this study, we performed a series of complementary analyses, designed to allow detailed characterization of the graphite and phenolic resin based fuel matrix. Methods included Scanning Electron Microscopy, Raman spectroscopy, and X-ray Diffraction.

Our results indicate that no single characterization technique will yield all of the desired information; however, through the use of statistical and empirical data analysis, such as curve fitting, partial least squares regression, volume extrapolation and spectra peak ratios, a degree of certainty for the quantity of each phase can potentially be obtained.

DESCRIPTION OF THE EXPERIMENTAL WORK

For this work, developmental LEU conversion compacts were analyzed using a complementary set of analyses, to describe and quantify the carbon phases present within the fuel matrix. The compacts themselves were produced using zirconia (as a uranium oxide substitute) mixed with matrix material comprised of natural and synthetic graphite, novolac phenolic resin, hexamethylenetetramine (HMTA) and other carbon based additives. The mixture was compacted and heat treated to create the final fuel form [1]. It was expected that the resin, HMTA and other carbonaceous additives would form an amorphous carbon structure upon heating and thermal decomposition. Based on the relatively low final heat treatment temperature (950C), large scale graphitization of the non-graphite additives was not expected; however, the goal of the project was to identify any small-scale graphite nucleation that may occur [2].

Scanning Electron Microscopy (SEM)

Various methods of SEM analysis were deployed, including standard secondary electron microscopy, Back-Scatter Electron (BSE) analysis and Energy Dispersive X-ray Spectroscopy (EDS). SEM was used to image the matrix to distinguish between the graphite and non-graphitic carbon for potential image analysis quantification methods, as well as to identify areas of significance for further analysis [3].

Initial analysis performed using secondary electron SEM and EDS did not show an obvious distinction between the different carbon morphological phases. Figures 1 and 2 are images of the compact taken using SEM taken at the Center for Advanced Energy Studies (CAES) at Idaho National Laboratory (INL) demonstrating the lack of contrast between phases using secondary electron. The bright white portions of the image were identified as zirconia using EDS, with the rest of the image identified as carbonaceous.

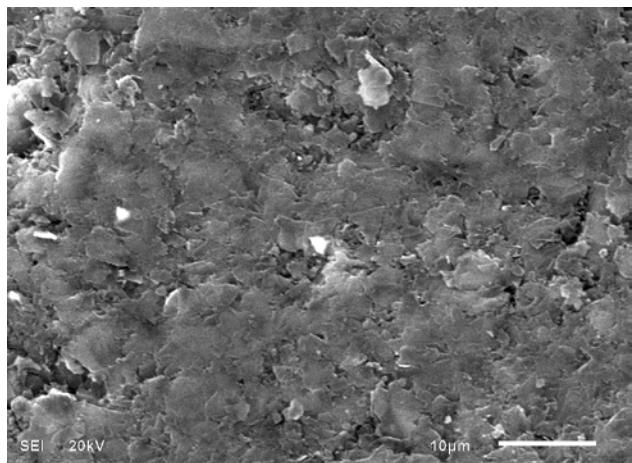


Fig. 1. SEM image of a TREAT LEU conversion development compact (2000x Magnification).

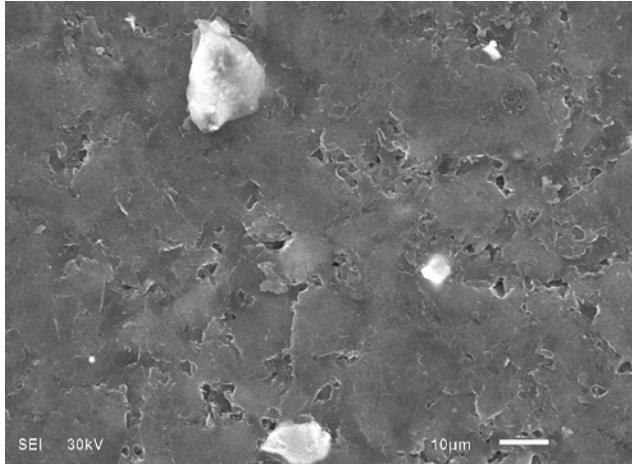


Fig. 2. SEM image of a TREAT LEU conversion development compact showing Zirconia particles (white) identified with EDS (1000x Magnification).

Using BSE analysis, the graphitic matrix can be distinguished from other locations that are likely pores, but may also contain another carbonaceous phases. Utilizing MATLAB image segmentation and analysis software, a BSE image was converted to a binary image and analyzed to determine the relative amount of the image comprised of each phase [4]. Figure 3 is an BSE image of the same material shown in Figures 1 and 2. Figure 4 is an image of the same BSE data with the graphitic phases and zirconia “masked”, or selected, prior to conversion to a binary image. Figure 5 is the binary image resulting from removal of the masked phases (now shown as white space).

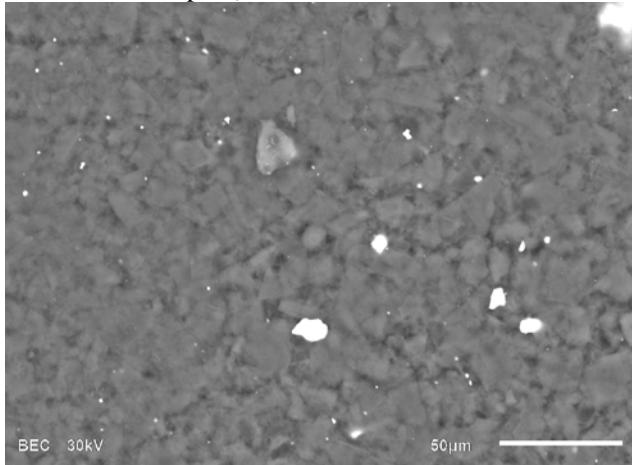


Fig. 3. BSE SEM image of a TREAT LEU conversion compact (500x Magnification).

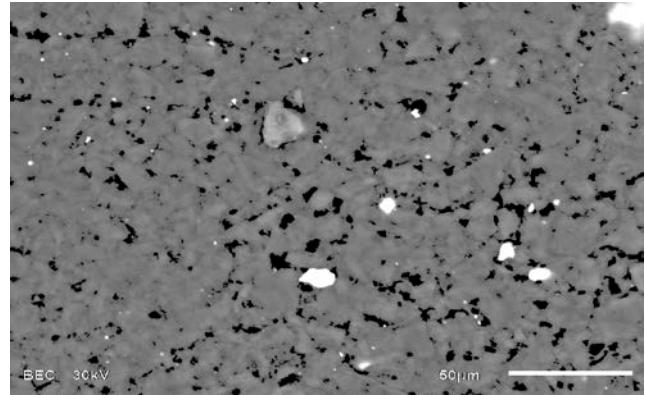


Fig. 4. BSE SEM image (500x magnification) of a TREAT LEU conversion compact with zirconia and graphitic phase “masked” based on contrast. Non-graphitic phases are shown as black.

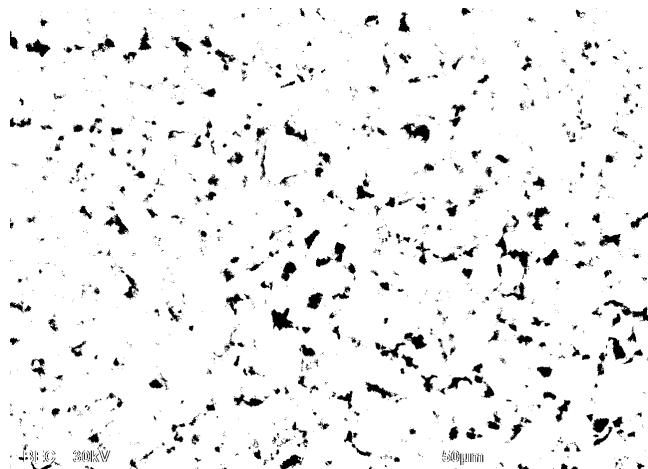


Fig. 5. BSE SEM image (500x magnification) of a TREAT LEU conversion compact after conversion to a binary – black and white – image by removal of the masked phases. The white portions of the image represent zirconia and graphitic phases. Non-graphitic phase are shown as black.

The amount of zirconia and graphitic phases can be estimated by determining the relative areas of the image occupied by each phase. The area occupied by zirconia and graphite was calculated to be approximately 94.3%. The area of zirconia alone was also determined (images not shown) to be approximately 1.43%. Subtracting the area of zirconia from the combined area yields an approximate graphitic phase percentage of 92.8%.

X-ray Diffraction (XRD)

XRD was used primarily as a quantification tool. Various quantitative and semi-quantitative methods exist for interpreting XRD spectra for graphite composites, such as spectra peak ratios, interlayer distance ratios, and full spectra Fourier transform degree of graphitization analysis [2].

A 0.5 mm x 8 mm section of one compact was analyzed using XRD. The XRD testing was conducted at the Molecular Analysis Facility (MAF) at the University of Washington. A Bruker D8 Discover with GADDS 2-D XRD System Diffractometer was used for this analysis. The Bruker D8 features a Cu (with a wavelength of 1.54056 nm) anode X-ray source.

The interlayer distance (d_{002}) was determined to be 3.360 angstroms (or 0.3360 nm), based on the 002 plane reflection identified at 26.504 degrees 2θ . Graphite content can be determined by comparing the d-spacing of fully graphitized material with that of carbonaceous sample according to

$$\% \text{ graphite} = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \times 100 \quad (1)$$

where 0.3354 nm represents a fully graphitized material and 0.3440 represents a non-graphitized material. Using the d-spacing value for the fuel matrix in this expression yields a graphite percentage of 93.02%.

Raman Spectroscopy

Similarly to XRD, Raman spectroscopy was used for carbon phase quantification. Using quantitative and semi-quantitative methods similar to those used for XRD, such as peak ratios or full spectra regression analysis, Raman can be used to determine graphite content. In various industries, Raman analysis is used to perform highly accurate quantifications using reference standards to which newly produced samples are compared [5].

Raman spectroscopy was performed on the matrix material at MAF, using a Renishaw InVia Raman Microscope with a 514 nm⁻¹ beam, and a 60 sec integration time on four areas. Typical graphite characteristic spectra peaks were identified at about 1580 cm⁻¹ for the G band and 1350 cm⁻¹ for the D band. Additionally, a relatively large 2D band at about 2700 cm⁻¹ was identified. Figure 6 is a plot of the four Raman spectra.

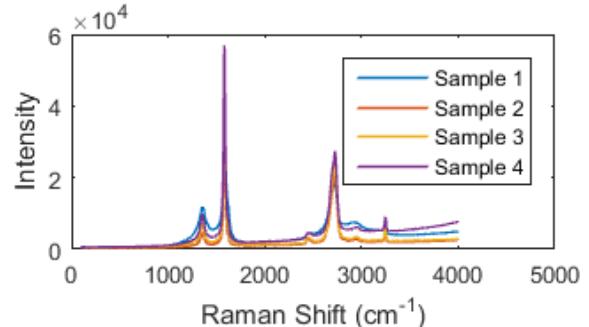


Fig. 6. Raman spectra using a 514 nm laser and a 60 second integration time at four locations on a TREAT LEU conversion compact sample.

A semi-quantitative calculation often used when characterizing graphite is the I_D/I_G ratio, which has been shown to be inversely proportional to the in-plane crystallite size. For perspective, the I_D/I_G ratios have been calculated by Magampa et al. [6] for synthetic graphite, 0.12, natural graphite, 0.18, and carbonized novolac phenolic resin, 0.9.

TABLE 1. Raman Spectra Peak Intensity Ratios (I_D/I_G) Ratio Calculation for TREAT Compact Samples

	I_D	I_G	I_D/I_G ratio
Sample 1	11,785.70	47,459.20	0.31
Sample 2	4,561.64	41,644.00	0.11
Sample 3	7,066.18	49,125.40	0.14
Sample 4	9,555.37	56,942.00	0.17
Average	8,242.22	48,792.65	0.17

If one assumes the synthetic graphite used by Magampa et al. was pure (i.e. 100%) multi-crystalline graphite, the carbonized resin is non-graphitic (e.g. 0% graphite), and an approximately linear relationship, the relative graphite content of the TREAT compact analyzed by ISU can be estimated.

$$(1\% \text{ of the Magampa matrix}) = \frac{|0.9 - 0.12|}{100} = 0.0078, \quad (2)$$

$$\text{therefore, graphite (\%)} = \frac{(0.17 - 0.12)}{0.0078} = 93.6\%$$

Obviously, any non-linearity or other major deviations from the restrictive assumptions would alter or null the calculated graphite percentage from the I_D/I_G ratio; however, this exercise does give a rough idea of the amount of graphite in the compact samples.

RESULTS

Although no one type of analysis has provided a complete determination of the quantities and identities of all carbon phases present in the fuel matrix, additional information has been gathered and is being used to refine future analysis methods. From the three types of quantification performed, results have been within 1% (92.8%, 93.02% and 93.6% for BSE image analysis, XRD and Raman spectroscopy, respectively). More work remains to identify any trace crystalline carbonaceous phases that may be present, quantify any traces that are identified, and develop and use further complementary bulk phase quantification techniques.

Future Work

There are plans for the performance of optical microscopy with polarized light and transmission electron microscopy, the latter having greater promise for seeing non-graphitic minor phase crystallites that may form within the amorphous carbon. Also planned is electron backscatter diffraction (EBSD) to distinguish between graphitic and non-graphitic phases in the matrix.

Traditional XRD has been used for analysis as already reported; however, this technique is not amenable to small quantities of various low Z phases in a sea of a dominant phase. Graphite is the major phase, but the remaining carbonaceous material represents a small quantity of possibly multiple phases. However, it has been very challenging to characterize the non-graphitic carbonaceous materials using regular tools, including XRD, due to the short-range structure compared with graphite. Hence, we propose to use high-energy synchrotron XRD techniques to identify and quantify these phases. The high energy XRD, i.e. short wavelength, enables the full coverage of reflections from multi-phases with high detection sensitivity. Furthermore, the high angular resolution of high energy XRD resolves the overlapping peaks from multiple phases. The high energy XRD has been employed successfully to provide detailed local structure for graphite like materials (grain size < 6 Å).

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