Using a Spherical Crystallite Model With Vacancies to Relate Local Atomic Structure to Irradiation Defects in ZrC and ZrN

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Abstract

Zirconium carbide and zirconium nitride are candidate materials for new fuel applications due to several favorable physicochemical properties. ZrC and ZrN have been irradiated at the Advanced Test Reactor National Scientific User Facility with neutrons at 800 C to a dose of 1 dpa. Structural examinations have been made of the ZrC samples using high resolution transmission electron microscopy, and the findings compared with a previous study of ZrC irradiated with protons at 800 C. The use of X-ray absorption fine structure spectroscopy (XAFS) to characterize the radiation damage is also explored including a model based on spherical crystallites that can be used to relate EXAFS measurements to microscopy observations. A loss of coordination at more distant coordination shells was observed for both ZrC and ZrN, and a model using small spherical crystallites suggested this technique can be used to study dislocation densities in future studies of irradiated materials.

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1. Introduction

Zirconium carbide was one of six ceramics that met melting temperature, neutronic, and irradiation performance requirements for composite fuels in gas-cooled fast reactors (GFR) [1]. Those properties and the ability to retain fission products also make ZrC a possible replacement for SiC in tri-isotropic (TRISO)-coated fuel particles in high temperature applications [2, 3]. ZrN has been proposed as a suitable material for fast neutron systems from the beginning of the development of nuclear fuel options [4]. Its high thermal conductivity, high melting point, and low neutron capture cross section make it an attractive choice for fast reactors and accelerator-driven transmutation systems [5].

The design for the Very High Temperature Reactor (VHTR) fuel for example must be able to withstand accident temperatures of 1600 °C, fast neutron fluences of about 6×10^{25} n/m², and have good performance up to a burnup of 20% fissions per initial metal atom [6]. ZrC has a melting point of 3540 °C, and its eutectic melting point with carbon of 2850 °C should ensure temperature compatibility with new reactor applications [7]. Stoichiometric ZrN has a melting point of 2952 °C, while the non-stoichiometric phase has a reduced melting point down to 2952 °C [8]. ZrN also has favorable chemical behavior with steel cladding, sodium, and nitric acid make it a candidate for homogeneous diluents for PuN and PuO₂ fuel [9].

The response of ZrC and ZrN to irradiation has been studied, but often using Au or Kr ions, or protons [10]. Neutrons have been used, but often irradiation takes place within a few hundred degrees of room temperature, far away from pebble bed or helium gas cooled design requirements [10]. In this work we study high temperature, 800 °C, neutron irradiated ZrC and ZrN using electron microscopy and Extended X-ray Absorption Fine Structure (EXAFS) techniques. Using both a traditional EXAFS analysis as well as technique for determining the size of undamaged regions, we aim to demonstrate EXAFS can be used as a complementary technique to TEM which has been widely used for studying irradiated microstructures.

2. Methods

Commercial grade ZrC rods (CERCOM Inc.) 3 mm wide, with a stoichiometric ratio of C/Zr of 1.01, were fashioned into TEM sample disks by slicing with a low speed diamond saw, followed by wet grinding to 250 μm , and polishing with 1 μm diamond paste [11]. TEM examination showed no bubbles or voids, up to the image resolution of 1 nm, and SEM images revealed a surface with low porosity with no visible inclusion phases, and an average grain size of about 24 μm [11]. ZrN TEM sample disks were similarly prepared [12] using commercial grade ZrN rods (CERCOM Inc.) The ZrN was sub-stoichiometric, with ratio of N/Zr of 0.80, and also contained small amounts of carbon and oxygen impurities [12].

ZrC and ZrN TEM discs (3 mm wide, 0.25-0.3 mm thick) were subsequently neutron irradiated at the Advanced Test Reactor National Scientific User Facility (ATR-NSUF). The samples were held at 800 °C as they were irradiated up to a dose of 1 displacement per atom (dpa). Temperature was controlled during irradiation by adjusting coolant gas flow in the envelope around the sample capsule. Based on the position of the samples in the reactor, the fast neutron flux (energy greater than 1 MeV) was $1 \times 10^{14} \text{ n cm}^{-2} \text{ s}^{-1}$ [13]. Dose to the samples, located in GFR-F1 capsule, was calculated by ATR-NSUF staff taking into account reactor configuration, power output, and operating history as described elsewhere [14, 15].

The EXAFS measurements were conducted at the Materials Research Collaborative Access Team (MRCAT) beamline at the Advanced Photon Source. EXAFS measurements at the MRCAT undulator beamline have been described in detail elsewhere [16, 17]. An undulator produced polychromatic X-rays and wavelength was selected using a Si(111) double crystal monochromator. Higher harmonics were removed with the use of a Pt coated harmonic rejection mirror [18, 19]. The energy was calibrated to the Zr K-edge (17998 eV) of a Zr foil (The EXAFS Company) run in transmission geometry with incident and transmitted X-ray flux monitored by ionization chambers (Boyd Technologies).

The ZrC and ZrN samples were measured in fluorescence geometry using a Lytle detector (The EXAFS Company). The I_0 ion chamber used a gas mix of 85% N_2 : 15% Ar, the I_t and fluorescence ion chamber used 100% Ar as the fill gasses.

High Resolution TEM imaging was performed on the very same samples brought to the beamline using a Phillips CM200 TEM, and the rel-rod dark field images were taken using a JEOL 200CX TEM. TEM discs were mechanically dimpled to 10 μm at the center and 100 μm at the edge with sufficient mechanical integrity. The dimpling was performed using a Fischione dimpling grinder (model 200). The thickness of the discs was frequently monitored using an optical profilometer (Zygo NewView 7000) particularly after each step of changing to finer diamond grits. The perforation of TEM discs was completed by ion milling (Fischione 1010 ion mill), and the TEM specimens were finally cleaned using a 3 kV ion beam at an angle of 9° to eliminate an ion damage during previous high energy ion milling.

3. Results and Discussion

Figure 1(a) shows a high resolution TEM image of the irradiated microstructure of ZrC, and the revealed streaks correspond to individual dislocation loops. The dislocation loops lie on the on habit plane of $\{111\}$ and display an angle of 70° between the dislocation loops lying on habit planes of $(-1, 1, -1)$ and $(1, 1, -1)$, respectively, in the beam direction of $[011]$. A previous study was performed on the same material irradiated using a 2.6 MeV proton beam at $800^\circ C$ [11]. The Z contrast spherical aberration corrected STEM image of proton irradiated ZrC further confirms that those loops are interstitial type dislocation loops[20]. This indicates that the dislocation loops might be surrounded by C vacancies that have a much lower mobility as compared with C interstitials, however, there is no direct experimental evidence to confirm this yet. The rel-rods image and rel-rods streaks in the diffraction pattern of Fig. 1(b) further show that the dislocation loops contain stacking faults.

Figure 1: (a) High resolution TEM (HR-TEM) image of ZrC, neutron irradiated at 800 °C to 1dpa. Arrows indicate the location of edge-on dislocation loops in the habit planes of $(-1, 1, -1)$ and $(1, 1, -1)$. (b) Rel-rods dark field image of faulted dislocation loops in irradiated ZrC.

The distance between dislocation loops is the distance between cores of two dislocation loops, calculated by considering each dislocation loop to be isolated in a cubic box. The average distance between dislocation loops is 13 nm. The number density of the dislocation loops for ZrC is $4.26 \times 10^{23} \text{ m}^{-3}$ and the average loop size (accounting for projection effects) is $6.5 \pm 0.2 \text{ nm}$. These numbers are close to, but slightly higher than those found for the ZrC proton irradiated to 1.5 dpa, $3.37 \times 10^{23} \text{ m}^{-3}$ and $5.8 \pm 0.578 \text{ nm}$, respectively [11]. The size of the undefected regions, taken as approximately equal to the average distance between loops minus the average dislocation diameter, is estimated as $6.5 \pm 0.2 \text{ nm}$.

High magnification TEM results were also obtained for ZrN, Figure 2, however, no rel-rod image could be obtained, which may have been due to interference from Moiré fringes. The number density of the dislocation loops is $5.2 \times 10^{22} \text{ m}^{-3}$, and the average loop size (accounting for projection effects) is $7.1 \pm 0.6 \text{ nm}$. These numbers are much higher than for ZrN, proton irradiated to 0.75 dpa at 800 °C, $1.12 \times 10^{16} \text{ m}^{-3}$ and 2.35 nm, respectively [12]. The size

between undefected regions is estimated to be 19.9 ± 0.6 nm for ZrN, suggesting under these irradiation conditions ZrN is less prone to accumulation of dislocation loops than ZrC. The TEM observations for both samples were conducted at room temperature, the number of dislocations was observed to be constant even after a prolonged TEM session, suggesting escaping dislocations was not an issue.

The EXAFS data was analyzed according to the standard EXAFS analysis procedures [21, 18], data reduction including alignment, summation, calibration, and error correction was done with Athena [22]. Spectral fitting to determine structural parameters was performed using Artemis [22] with theoretical EXAFS paths created with FEFF6 [23, 24, 25, 26]. Error bars for each fitting parameter were determined by inversion of the covariance matrix [27].

The collected spectra suffered from self-absorption effects, altering the apparent amplitudes of the various scattering paths. Corrections were applied to the unirradiated samples using the method of Booth and Bridges [28] bringing their coordination numbers to the values expected from undamaged bulk samples. The same correction was then applied to the data from the irradiated samples, the resulting k^2 weighted EXAFS of the ZrC and ZrN samples in momentum space (k-space) and real-space (r-space) are shown in Fig. 3 and Fig. 4, respectively.

The FEFF model for the ZrC structure is based on the NaCl type, space group number 225 with lattice parameter $a = 4.6828$ Å [29]. Fitting of the EXAFS equation [18, 19],

$$\chi(k) = \sum_i \frac{N_i S_0^2 F_i(k)}{k R_i^2} \sin(2k R_i + \phi_i(k)) e^{(-2\sigma_i^2 k^2)} e^{\frac{-2R_i}{\lambda(k)}}, \quad (1)$$

to the measured $\chi(k)$ involved performing a non-linear least-squares fit summing over each scattering path used, i , in order to find the best values for the amplitude of each path, N_i , scattering half-path length, R_i , energy shift, ΔE_0 , and mean squared displacement, σ_i^2 , also known as the EXAFS Debye-Waller factor. The values for the effective scattering amplitude, $F_i(k)$, effective scattering phase shift, $\phi_i(k)$, and mean free path, $\lambda(k)$, were taken from the FEFF

Figure 2: High magnification TEM image of ZrN, neutron irradiated at 800 °C to 1dpa: high density of dislocation loops are identified.

Figure 3: Zr K-edge X-ray absorption fine structure data for the 0 and 1 dpa ZrC samples, shown as the magnitude of the Fourier-transformed k^2 weighted data (inset), highlighting the loss of coordination with irradiation.

Figure 4: Zr K-edge X-ray absorption fine structure data for the 0 and 1 dpa ZrN samples, shown as the magnitude of the Fourier-transformed k^2 weighted data (inset), highlighting the loss of coordination with irradiation.

Table 1: Fitting results for the simultaneous fit of the 0 and 1 dpa ZrC data. A single value of E_0 was used for all paths, the best fit was -1.12 ± 0.62 eV. Uncertainties determined by inversion of the covariance matrix.

Path ^a	$R_{\text{PerfectCrystal}}(\text{\AA})$	$R_{\text{Measured}}(\text{\AA})$	$\sigma^2(\text{\AA}^2)$	N, 0 dpa	N, 1 dpa	% Amplitude Difference
$\text{Zr}_0 \rightarrow \text{C}_1 \rightarrow \text{Zr}_0$	2.34	2.32 ± 0.02	0.008 ± 0.002	7.7 ± 2.6	6.6 ± 1.7	-14%
$\text{Zr}_0 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_0$	3.31	3.32 ± 0.02	0.004 ± 0.001	12.9 ± 3.5	9.3 ± 0.5	-28%
$\text{Zr}_0 \rightarrow \text{C}_1 \rightarrow \text{Zr}_2 \rightarrow \text{Zr}_0$	4.68	4.69 ± 0.02	0.005 ± 0.001	12.0 ± 2.0	7.8 ± 1.2	-35%
$\text{Zr}_0 \rightarrow \text{Zr}_3 \rightarrow \text{Zr}_0$	5.74	5.75 ± 0.02	0.003 ± 0.001	13.0 ± 3.5	6.0 ± 1.7	-53%
$\text{Zr}_0 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_4 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_0$	6.62	6.60 ± 0.02	0.005 ± 0.001	6.6 ± 1.8	2.8 ± 0.8	-57%

^a The subscript represents n^{th} coordination shell of a particular type of atom, 0 indicating the core scattering atom.

calculations.

Initially, both the ZrC 0 dpa and 1 dpa data sets were modeled individually and only minor changes in path length and Debye-Waller factors between data sets were observed. Most of the changes were due to reduction in scattering path amplitude with increasing distance. However, the amplitudes and Debye-Waller factors are highly correlated, having correlation between 85% and 95% for all paths in both data sets. Although the fits were satisfactory, this resulted in some of the amplitude changes as a result of radiation damage being accounted for in the minimization by changes in disorder. However, TEM images of the irradiated sample provided visual evidence that with the exception of dislocation loops the overall crystal structure remained largely intact after irradiation. This is expected based on both simulations of neutron irradiated ZrC and TEM images from proton irradiated ZrC [11], as well as TEM images from fast neutron irradiated ZrC [10]. With that in mind the data were fit again simultaneously, sharing all parameters except for path amplitudes. The energy shifts and changes in scattering path length were also correlated between 40% and 85%, but the differences between the independent fits was minimal and the results were consistent with the simultaneous fit. All other correlations were below 40%, and no fitting restraints were applied to the models. The fitting results are summarized in table 1 and the data along with the total fit and fitting paths for the 1 dpa ZrC sample are shown in Fig. 5 as an example.

The ZrN structure used to create the FEFF model was also based on the structure in Wyckoff [29], but with the lattice parameter, $a = 4.5835 \text{ \AA}$ taken

Figure 5: The magnitude of the Fourier-transformed k^2 weighted data and the fit for the 1 dpa ZrC sample are shown along with the fitting paths used in the model (reflected about the x -axis for clarity).

Table 2: Fitting results for the simultaneous fit of the 0 and 1 dpa ZrN data. A single value of E_0 was used for all paths, the best fit was 2.9 ± 0.9 eV, the Einstein temperature was 331 ± 50 K. Uncertainties determined by inversion of the covariance matrix.

Path ^a	$R_{\text{PerfectCrystal}}(\text{\AA})$	$R_{\text{Measured}}(\text{\AA})$	$\sigma^2(\text{\AA}^2)$	N, 0 dpa	N, 1 dpa	% Amplitude Difference
$\text{Zr}_0 \rightarrow \text{N}_1 \rightarrow \text{Zr}_0$	2.92	2.91 ± 0.03	0.012 ± 0.01	8.4 ± 4.7	5.3 ± 3.1	-36%
$\text{Zr}_0 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_0$	3.24	3.24 ± 0.005	0.003 ± 0.002	11.6 ± 1.1	10.2 ± 0.8	-12%
$\text{Zr}_0 \rightarrow \text{N}_2 \rightarrow \text{Zr}_0 \rightarrow \text{Zr}_0$	3.97	4.00 ± 0.2	0.012 ± 0.01	6.1 ± 3.0	8.6 ± 1.2	41%
$\text{Zr}_0 \rightarrow \text{Zr}_2 \rightarrow \text{Zr}_0$	4.59	4.67 ± 0.01	0.003 ± 0.005	9.3 ± 4.0	7.9 ± 2.7	-15%
$\text{Zr}_0 \rightarrow \text{Zr}_3 \rightarrow \text{Zr}_0$	5.62	5.62 ± 0.01	0.003 ± 0.005	12.8 ± 3.0	10.5 ± 1.2	-18%
$\text{Zr}_0 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_0$	6.48	6.46 ± 0.02	0.005 ± 0.01	6.7 ± 1.8	7.3 ± 1.2	9%
$\text{Zr}_0 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_4 \rightarrow \text{Zr}_1 \rightarrow \text{Zr}_0$	6.48	6.46 ± 0.02	0.006 ± 0.005	6.7 ± 1.8	2.8 ± 1.2	-58%

^a The subscript represents n^{th} coordination shell of a particular type of atom, 0 indicating the core scattering atom.

from Yang et al.[12]. Using the same technique as the ZrC fitting, the ZrN 0 dpa and 1 dpa data sets were fit simultaneously, with all parameters shared except for path amplitudes. The fit was satisfactory except for features around 2 Å (uncorrected) corresponding to the location of the first nitrogen shell, and around 3.8 Å (uncorrected) which did not correspond to any expected multiple scattering peaks. These structures, possibly arising from the impurity phases were responsible for most of the statistical misfit. The shape of the first nitrogen scattering peak, and the low scattering contribution of the second nitrogen and outer zirconium double scattering peak made the fitting parameters difficult to determine for those paths if they were unconstrained. An Einstein model [27] applied to the Debye-Waller factors of all the paths was chosen in order to constrain the unruly fitting parameters without setting them to ad hoc values and instead tie them to some quantity that was still optimized in the fitting procedure. Removing those paths would have removed the difficulty, but the improvement in the fit was determined to be statistically significant [30]. The fitting results are summarized in table 2, and the data along with the total fit and fitting paths for the 1 dpa ZrN sample are shown in Fig. 6.

The decrease in coordination number evident in the EXAFS analysis is not coming from amorphization of the sample, but rather from the change in local environment that the scattering atom sees as a result of being surrounded by dislocation loops. By analogy if we consider a spherical nanoparticle the atoms near the center will have a coordination environment much like the bulk mate-

Figure 6: The magnitude of the Fourier-transformed k^2 weighted data and the fit for the 1 dpa ZrN sample are shown along with the fitting paths used in the model (reflected about the x -axis for clarity).

rial, but those closer to the surface will suffer from a loss of neighbors. EXAFS however will sample all the atoms, and the effect only becomes noticeable as the particle size shrinks to the point where a significant fraction of the atoms are surface-like.

For example, using the distance to the first near neighbor in ZrC, 2.34 Å, for the diameter of the surface shell around a 5 nm particle, we find that about 13% of the atoms are on the surface, and so there should be a corresponding drop in first near neighbor amplitude. However, the EXAFS signal is sensitive to more than just the nearest neighbors, and so those atoms close to but not on the surface will show evidence of missing neighbors in extended coordination shells. The fraction of volume in the same 5 nm particle experiencing a termination effect at 5 Å for example jumps to about 27%.

Several models have been utilized to determine the average coordination numbers of nanoparticles in specific configurations, but often they utilize only the first near neighbor, and in any case they rely on knowing the particular morphology of the particle in question [31, 32, 33, 34]. In order to estimate the mean size of the undefected regions of the sample we employ a more widely applicable approach, at the expense of some precision based upon the technique used by Borowski et. al [35, 36] and Calvin et. al. [37, 34]. If we consider a spherical crystallite of radius R , the reduction in average coordination, compared to the bulk material, at a given distance r is given by [34, 38]:

$$N_{\text{nano}} = \left[1 - \frac{3}{4} \left(\frac{r}{R} \right) + \frac{1}{16} \left(\frac{r}{R} \right)^3 \right] N_{\text{bulk}}, \quad (2)$$

where N_{bulk} is the coordination number present in the bulk (undamaged) compound, and N_{nano} is the lowered coordination number due to size effects.

To investigate the applicability of the model, spherical clusters of ZrC were created using the programs *debyer* [39, 40, 41] and *gosam* [42]. Radial distribution functions (RDFs) [43] were calculated for each of the clusters. The RDF, calculated [43] by a summation

$$R(r) = \sum_{\nu} \sum_{\mu} \frac{b_{\nu} b_{\mu}}{\langle b \rangle^2} \delta(r - r_{\nu\mu}), \quad (3)$$

over atomic positions ν , and μ , and where b is a scattering factor and $r_{\nu\mu}$ is the magnitude of the separation of the atoms [43]. The RDFs for clusters of radius 5 Å, 10 Å, 15 Å, 25 Å, 50 Å, 100 Å, and 200 Å, were fit to the bulk coordination values using equation 2. The results indicate the excellent ability of the spherical model to fit the crystallite size. The largest misfit was for the 5 Å particle, 7.6%, which dropped to 1.2% or less for all the larger sizes.

It is also possible that point defects may alter the particle size as fit by the model. To study this possibility, spherical models of ZrC were again created using debyer [39, 40, 41] and gosam [42], but with vacancies created at random positions with fixed percentages of 0%, 1%, 2%, 5%, 10%, 15%, 20%, and 25%. The vacancies were randomly generated multiple times to gain a representative distribution. As the percentage of vacancies increases, the spherical model produces erroneously smaller fits, 13.26 ± 0.96 Å for a 25 Å radius particle with 25% random vacancies. By altering equation 2 to account for a fraction of atoms removed as vacancies,

$$N_{\text{nano}} = \left[1 - \frac{3}{4} \left(\frac{r}{R} \right) + \frac{1}{16} \left(\frac{r}{R} \right)^3 \right] (N_{\text{bulk}}(1 - v)), \quad (4)$$

where the new term multiplied by N_{bulk} accounts for the fraction of vacancies, v , in the crystal, it once more becomes possible to successfully model the computer generated clusters, as seen in Fig. 7.

The best fit values of cluster radii and vacancy populations were determined by fitting the self-absorption corrected Fourier transform from the irradiated sample to that of the unirradiated sample, using the vacancy corrected spherical model at each distance r . The diameter of the undefected regions of ZrC was found to be 1.8 ± 0.08 nm at the 95% confidence interval, as shown in Fig. 8. The vacancy percentage was equal to zero within the error bars. This is smaller than the undefected region size obtained via TEM, 6.5 ± 0.2 nm. The simplicity of the model, requiring only a single variable be fit, is also a potential limitation. The model will suffer inaccuracies if serious departures from spherical regions occur, additionally, if there is a broad distribution of crystallite sizes the result will be biased toward smaller sizes [34]. The ZrN fit with zero vacancies as

Figure 7: The radial distribution function calculated for a 25 Å radius spherical particle with 25% randomly placed vacancies, fit with the spherical and vacancy corrected spherical models (top), and the residual differences between the fits and the RDFs (bottom).

well, although to reign in the error bars required restricting the fitting range when using the vacancy corrected fit due to interference from the first carbon scattering peak. The diameter of the undefected region of ZrN was found to be 4.0 ± 0.4 nm at the 95% confidence interval, as shown in Fig. 9. This is also smaller than the TEM determination of 19.9 ± 0.6 nm.

We note that both EXAFS and TEM measurements show larger undefected region sizes in ZrN, with EXAFS predictions systematically 3.5 to 5 times smaller. It is well known that EXAFS measurements typically estimate a greater fraction of damaged material compared to TEM and X-ray diffraction (XRD) measurements[44, 45]. In the case of discrete particles, this type of EXAFS size estimate has been known to estimate particle sizes almost an order of magnitude smaller than XRD[37], and several times smaller than TEM[44]. Extra disorder caused by relaxation effects at the boundaries, coupled with the inability of TEM to capture the smallest sized defects in a material, are thought to be responsible for the disparity between the TEM measurements and our EXAFS results[44, 45].

This data suggests that the presence of dislocation loops, primary along the $\{111\}$ family of planes, might, through overlapping displacement fields introduce enough disorder to effectively isolate small regions from each other at least with respect to EXAFS measurements. Defects, even point defects, in a radiation damaged material displace neighboring atoms resulting in a complicated and extensive displacement field. These distortions some of which are below the capability of TEM to resolve, are partly responsible for the loss of amplitude seen in EXAFS spectra. We note the fact that the Zr data from these samples can be fit with such a simple model is not necessarily due to simplicity of the model, for it is not universally applicable to all cases of radiation damage. For example, in neutron irradiated mod.9Cr1Mo steel the damage around Mo was confined to the nearest neighbors[46], and equation 2 would not have been able to fit that data. Even with cause for skepticism about the absolute accuracy of the size determinations made, this technique should still produce a reliable relative metric for comparisons between different materials, as we have done

here, or as a way of tracking the evolution of a structure as a function of dose.

Equation 4 assumes a random distribution of vacancies in the particle, however, vacancies in the material can potentially form clusters, as seen in other materials with high enough doses [47] or in simulations [48] of ZrC, but not seen in TEM with proton irradiated ZrC [11] or in the present study at these low doses. However, since the limit of detection with our TEM study is approximately 1 nm, further simulations were carried out to determine the effects of small vacancy clusters on the spherical particle model. The program DISCUS [49] was used to generate spherical particles and randomly place vacancy clusters throughout, the RDFs were determined using debyer [39, 40, 41], and fit using Larch [50] with scripts similar to those used in the single point vacancy tests to compile the results.

Spherical particles with a 50 Å radius were created, and vacancy clusters were generated with five radii from 2.34 Å to 5.24 Å corresponding to the removal of the first through fifth near-neighbors. Fitting the particles with the model from equation 2 produces results with small error bars, less than 5% for all the variations tested, and best fit radii which underestimate the particle size. For example, with a vacancy fraction of only 0.8%, and a cluster size of 2.34 Å the particle radius fit to 46.7 ± 0.2 Å, and with a vacancy fraction of 7%, a cluster size of 5.24 Å the particle radius fit to 33.9 ± 0.3 Å. However, when vacancy clusters are present in large enough amounts, the model will fit with slightly higher values for coordination number for the first several shells, suggesting that if the EXAFS data represent a true measure of the coordination and if the fit is systematically high, that a high density of vacancy clusters could be present.

When fitting the particles with equation 4 the model would underestimate the fraction of vacancies present in the particle, an effect which worsened as the size and number of the vacancy clusters increased. At high vacancy fractions large error bars indicated a problem applying that model to this system, however, at low enough vacancy fractions clusters of vacancies could be reasonably fit, although with an underestimated cluster size. For example, with

7% vacancies caused by 5.24 Å radius clusters the 50 Å radius particle fit to 37.8 ± 0.7 Å. When the vacancy fraction increased to 30%, the particle radius fit to 21.7 ± 1.4 Å, an uncertainty of about 6%. Smaller vacancy clusters produced similar errors in fits, although at lower vacancy fractions. The smallest clusters, 2.34 Å had a similar error, 46.3 ± 2.3 Å, or about 5% with a vacancy fraction of only 8%.

Since the fits in figures 8 and 9 do not show a systematic overestimation of amplitude, and do not indicate a high concentration of vacancies, the results from the simulation suggest there is not a large concentration of vacancies or vacancy clusters below the TEM limit of detection. Keilholtz et al. [51] studied fast neutron irradiated ZrC at 130–355 °C[10], below the annealing temperature, and found a volume increase (up to 3%) primarily due to agglomerates of point defects or formation of gas bubbles, along with severe fracturing. Up to 1% volume increase was attributed to lattice expansion[51]. Further high temperature studies showed a reduction of volume expansion and elimination of sample fracture[10]. Our results are consistent with increased defect mobility at higher temperatures, leading to a reduced agglomeration of point defects. Gaining a better understanding of the effects a single defect in the structure has on the EXAFS of all the neighboring atoms may provide a way for this simple quantification to better describe the radiation damage in materials.

4. Conclusions

To summarize, we have demonstrated the use of EXAFS to model the size of defected regions in neutron irradiated ZrC and ZrN. ZrN was more radiation tolerant than ZrC under these irradiation conditions. The changes in local atomic structure were related to, and consistent with, microscopy observations. This technique should be applicable to studying further changes with irradiation dose, and having another technique available should prove useful as dealing with higher levels of radioactivity from activated samples makes post-irradiation examination more difficult. Additionally, these results may be useful for bench-

Figure 8: Fitting results of the unirradiated ZrC sample to the 1 dpa sample, using the vacancy corrected spherical crystallite model.

Figure 9: Fitting results of the unirradiated ZrN sample to the 1 dpa sample, using the spherical crystallite model.

marking molecular dynamics and kinetic Monte Carlo studies of radiation damage by providing a point of comparison for RDFs generated by simulations. Further applications of this technique on other materials are ongoing.

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Graphical Abstract