



Early stage oxidation of ZrC under 10 MeV Au³⁺ ion-irradiation at 800 °C

Raul Florez^a, Miguel L. Crespillo^b, Xiaoqing He^{c,d}, Tommi A. White^{c,e}, Gregory Hilmas^f, William G. Fahrenholtz^f, Joseph Graham^{a,f,*}

^a Nuclear Engineering Program, Missouri University of Science and Technology, 65409, Rolla, MO, United States

^b Department of Material Science and Engineering, University of Tennessee, 37996, Knoxville, TN, United States

^c Electron Microscopy Core, University of Missouri, Columbia, MO 65211, United States

^d Department of Mechanical and Aerospace Engineering, University of Missouri, Columbia, MO 65211, United States

^e Department of Biochemistry, University of Missouri, Columbia, MO 65211, United States

^f Department of Materials Science and Engineering, Missouri University of Science and Technology, 65409, Rolla, MO, United States

ARTICLE INFO

Keywords:

ZrC
ZrO₂
Oxidation
Ion irradiation
Electron microscopy
GIXRD

ABSTRACT

The effects of irradiation on the morphology and microstructure of the oxide formed on the surface of ZrC_{0.99 ± 0.02} during irradiation with 10 MeV Au³⁺ ions at 800 °C were investigated. Nanosized oxide islands were observed on unirradiated and irradiated sample areas, indicating that the early stage oxidation of ZrC proceeded via nucleation and growth. Radiation shifted the particle size distribution (PSD) to smaller diameters, increased the circularity of the islands, and reduced the surface coverage of the specimen. Additionally, nanometric cavities were observed in oxide islands for doses above 2.5 dpa. The underlying mechanisms driving these changes were discussed.

1. Introduction

Zirconium carbide (ZrC_x) is an ultra-high-temperature ceramic (UTHC) material with outstanding mechanical strength, high thermal and electrical conductivity, and low neutron absorption cross section [1,2]. This unusual combination of properties makes ZrC_x an attractive material for a variety of applications, including nuclear reactors [2], aerospace and propulsion devices [3], high power density microelectronics [4], and solar power concentrators [5]. Particularly in the nuclear field, ZrC_x ceramics have gained significant interest as promising contenders for future advanced Generation-IV nuclear reactors and fusion systems. In these type of nuclear reactors ZrC_x could potentially be used as an inert fuel matrix [6], a plasma facing component (PFC) [7], an oxygen getter for microencapsulated fuels [8], an alternative cladding for advanced non-light water reactors [9], and a fission product barrier in Tri-structural Isotropic (TRISO) fuel particles [10]. As a potential in-core material for the next generation of nuclear systems, ZrC_x would be subject to extreme operation conditions combining high radiation fluxes, elevated temperatures, mechanical stresses, and aggressive chemical environments.

The primary coolant system considered for Gen-IV high-temperature and very-high-temperature gas-cooled reactors (HTGRs and VHTRs) is helium gas, which is known for its chemical inertness [11]. Although

the primary coolant system of HTRs and VHTRs is fitted with purification systems, impurities including H₂, CO, H₂O, CO₂, CH₄, O₂, and N₂ are inevitable in the coolant [12–14]. These impurities might arise from different sources including leaks into the cooling system, gas desorption from the nuclear fuel and other structural components, and nuclear fission reactions. Under prototypic operation conditions for gas-cooled reactor, the concentrations of impurities in the coolant system are in the part per million range [15]. Despite that, these impurities can induce corrosion reactions at high temperatures (> 500 °C), which can strongly affect the properties of the in-core reactor materials [16]. Previous studies have demonstrated that oxygen partial pressures (P_{O₂}) as low as 10^{−5} Pa can lead to the oxidation of ZrC_x ceramics at temperatures above 500 °C [17]. As a result, the oxidizing impurities in the helium coolant bear the risk of oxidation of the ZrC_x-based components during the operation of high temperature gas-cooled reactors. In-service oxidation of ZrC_x may induce significant changes in the thermophysical and mechanical properties of ZrC_x [2]. Furthermore, the oxidation of ZrC can enhance the release of gaseous fission products such as xenon (Xe) and helium (He) [18,19]. Since the properties of ZrC_x can be seriously compromised by in-service oxidation, it is important to elucidate the morphological and structural changes induced by oxidation of ZrC_x during operation of high temperature gas-cooled reactors.

Although the high temperature oxidation behavior of ZrC_x has been

* Corresponding author at: Nuclear Engineering Program, Missouri University of Science and Technology, 65409, Rolla, MO, United States.

E-mail address: grahamjose@mst.edu (J. Graham).

<https://doi.org/10.1016/j.corsci.2020.108609>

Received 15 September 2019; Received in revised form 13 February 2020; Accepted 16 March 2020

Available online 18 March 2020

0010-938X/ © 2020 Elsevier Ltd. All rights reserved.

extensively investigated during the last three decades [20–28], experimental data are lacking for the oxidation of ZrC_x under normal operating conditions of HTGRs and VHTRs. Until now, most of the published work has dealt with the oxidation of ZrC following a loss of coolant accident (LOCA) [23,24]. Moreover, these studies have focused only on the oxidation behavior of ZrC_x in the absence of radiation, which is critical to consider in a reactor environment. Unlike oxidation under LOCA scenarios, the in-service oxidation of ZrC_x occurs in oxygen-deficient atmospheres under radiation conditions. Radiation can significantly modify the oxidation behavior of ZrC_x by changing the properties of the ceramic matrix, the oxide formed on the surface, and the oxidizing environment [29,30]. Consequently, one can expect that the oxidation rate, surface composition, and oxide structures would be different from those observed during LOCA scenarios without radiation. To the best of our knowledge, no previous studies have investigated on the in-pile oxidation of ZrC. Thus, more research is needed to understand the effects of irradiation on the oxidation behavior of ZrC under the prototypical operation conditions of high temperature gas cooled reactors. This goal could be achieved by directly exposing ZrC to impure helium coolant and neutron irradiation in test nuclear reactors. However, such experiments are costly and time-consuming to perform due to construction, in-core insertion, handling, and post-irradiation examination (PIE) of neutron-irradiated materials.

Alternatively, heavy ion beam irradiations can serve as a good proxy to mimic the radiation damage processes and microstructural features observed in materials irradiated with fission neutrons [31,32]. Both heavy ions and fission neutrons have similar weighted primary recoil spectra $W_p(T)$ [33]; thus, similar damage regions are produced by the primary recoils of these particles. Previous studies have shown that comparable radiation-induced defects and dislocations microstructures are produced in neutron [34] and heavy ion-irradiated ZrC [35–37] over the temperature range relevant to HTGRs. Due to their high damage rates, heavy ions can produce the expected high damage levels anticipated for advanced nuclear reactors in much shorter times without inducing radioactivity, making it cost and time effective in comparison to neutron irradiations. Additionally, heavy ion irradiations allow the possibility to carefully and systematically control irradiation conditions (temperature, damage rate, damage level) over a wide range of doses in order to explore the effect of single irradiation parameters on a determined phenomenon. Single-effect ion irradiation studies can provide a more fundamental and scientific understanding of the physical mechanisms that control the degradation of nuclear materials during combined oxidation and irradiation.

The purpose of this paper was to investigate the microstructure of the oxides formed on the surface of ZrC_x during ion irradiation with Au^{3+} ions at 800 °C. The oxides were characterized for both the irradiated and unirradiated specimens to understand the effect of irradiation on the morphology and microstructure of the oxide scale. The results provide new insights into the early stage oxidation of ZrC_x under irradiation conditions that are relevant to its potential use in high temperature gas-cooled nuclear reactors.

2. Experimental procedure

2.1. Sample preparation

A pellet of ZrC was prepared by hot-pressing commercial ZrC powder (Alfa Aesar, Reactor Grade, USA). The as-received powder was hot pressed in a 25.4 mm cylindrical graphite die lined with BN-coated (SP-180 Cerac, Milwaukee, WI) graphite foil (2010-A; Mineral Seal Corp, Tucson, Arizona). Before hot pressing, the powder was loaded into the die and cold compacted in a uniaxial press at ~ 2 MPa. The powder was then heated under vacuum to 1600 °C with an average heating rate of 20 °C/min. At that time, the furnace was backfilled with helium and a uniaxial pressure of 32 MPa was applied to the powder compact. The furnace was then heated at 50 °C/min to 2200 °C. After

90 min, the furnace was cooled at ~ 50 °C/min. The load was removed when the die temperature dropped below 1600 °C.

Following densification, specimens for microscopy and ion irradiations were cut parallel to the hot pressing of the billet direction with a slow-speed diamond saw and then ground and polished to mirror-finish. The metallographic preparation was carried out by grinding the specimens with 100, 320, 600 and 1200 grit SiC pads with water as the lubricant. Felt pads and water-based diamond slurry suspensions were used for abrasive sizes from 3 μm to 0.25 μm . After polishing, the specimens were ultrasonically cleaned with ethanol for 15 min at room temperature.

2.2. Ion irradiations

A rectangular ZrC foil (13 $\times$ 8 mm) was irradiated in the Ion Beam Materials Laboratory (IBML UT-ORNL) at the University of Tennessee, Knoxville [38] with 10 MeV Au^{3+} ions at 800 °C using a 3.0 MV tandem accelerator. Five different regions of the ZrC foil (3 $\times$ 3 mm each) were irradiated to doses of 0.5, 2.5, 5, 10, and 15 dpa. The total sample area comprised the five non-overlapping irradiated regions and one unirradiated control spot. Adjustable beam slits were used to define the irradiation areas. The ion beam was defocused and rastered in the horizontal and vertical directions with the aim of producing a region that was homogeneously irradiated. The flux was set at $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ for all fluences. Low beam current densities in the range of 5 nA mm^{-2} were used to reduce any undesired effect and charge accumulation on the sample [39]. The vacuum chamber pressure was observed to be below $5 \times 10^{-8} \text{ torr}$ prior heating. Sample heating caused the pressure in the irradiation chamber to rise initially, but it decreased into the range of $3 - 5 \times 10^{-7} \text{ torr}$ during irradiation. The maximum outgassing of the specimen was observed around 170 °C with vacuum pressure levels of $7.8 \times 10^{-6} \text{ torr}$ (Fig. 1a). The Stopping and Range of Ions in Matter binary collision approximation (BCA) code 2013 version (SRIM-2013) [40] was used to estimate the displacement damage depth profile. Cascades were performed in full-cascade mode assuming a density of 6.447 g/cm^3 and threshold displacement energies of 37 eV for Zr and 16 eV for C [41]. To compare ion and neutron irradiation results, the use of the Full Cascade mode option in SRIM to compute radiation damage exposure in multi-elemental targets has been recommended within the nuclear community [42]. The predicted electronic (S_e) and nuclear (S_n) energy deposition, damage dose in displacements per atom

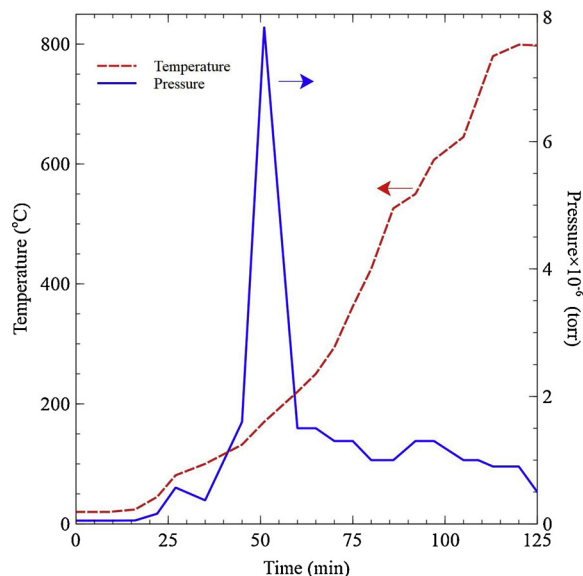


Fig. 1. Pressure and temperature evolution of the ion chamber before to the onset of ion irradiation.

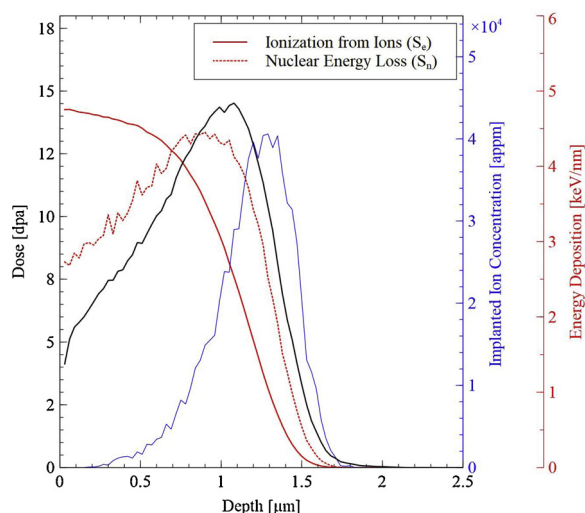


Fig. 2. Damage dose (dpa), energy deposition, and Au concentration as a function of depth for a fluence ion fluence of $1.8 \times 10^{15} \text{ cm}^{-2}$.

Table 1

Range, straggling, and electronic deposition for 10 MeV Au^{3+} ions for a fluence ion fluence of $1.8 \times 10^{15} \text{ cm}^{-2}$.

Ion Average Range	1.18 μm
Straggling	0.25 μm
Ion Lateral Range	0.16 μm
Straggling	0.20 μm
Ion Radial Range	0.26 μm
Straggling	0.13 μm
Surface	$S_e = 4.753 \text{ keV/nm}$ $S_n = 2.728 \text{ keV/nm}$
Peak Damage	$S_e = 2.529 \text{ keV/nm}$ $S_n = 4.126 \text{ keV/nm}$

(dpa), and the implanted Au ion profile are shown in Fig. 2 for a fluence of $1.8 \times 10^{15} \text{ cm}^{-2}$. The peak dose under 10 MeV Au irradiation was located around $1.1 \mu\text{m}$ nm below the surface. Table 1 summarizes the main results of the SRIM simulation.

The 10 MeV Au^{3+} ion irradiation was chosen for simulation of neutron damage that is expected to occur in the core of high temperature gas-cooled reactors. In this study, heavy ion irradiation was employed to emulate neutron damage due to the degree of similarity in the weighted average recoil spectra between heavy ions and fission neutrons [33]. Heavy ions create dense damage cascades that are comparable in density and morphology to those produced by fission neutron. Consequently, the defects and deformation microstructures produced by heavy ion irradiations are similar to those observed in neutron irradiated ZrC. The selection of the ion type and energy was performed according to the general guidelines to emulate neutron damage using charged particles suggested by Zinkle et al. [31]. Irradiations were performed with Au ions because of their relatively inert nature and large nuclear stopping cross section, which allows for a high damage rate per incident ion and minimal artifacts induced by the injected ions (Fig. 1b). It is worth noting that 10 MeV energy beam was chosen to obtain a damage profile to a depth of $1.1 \mu\text{m}$ (Fig. 1b). This length scale of the irradiation damage range provides a much larger intermediate-depth irradiated region to extract microstructural information without near-surface or implanted ion artifacts. The temperature and range of doses were selected with the goal of studying radiation damage mechanisms in regimes relevant to the conditions in Gen-IV high temperature gas cooled reactors and advanced fission and fusion reactor systems [43].

2.3. Material characterization

2.3.1. Density and chemical analysis

The bulk density of the hot-pressed billet was measured by the Archimedes' method using distilled water as the immersing medium, according to ASTM C73-88 [44]. The relative density was calculated by dividing the Archimedes' density by the estimated theoretical density of ZrC ($\rho = 6.71 \text{ g/cm}^3$). The chemical analysis for carbon, oxygen and nitrogen contents of the billet was conducted by direct combustion method using the infrared absorption detection technique. Carbon (CS600; Leco, St. Joseph, MI), oxygen and nitrogen (TC500; Leco, St. Joseph, MI) contents were measured by crushing dense specimens to ~ 200 mesh. Three measurements were conducted for each element to establish repeatability.

2.3.2. Grazing incidence X-Ray diffraction

Grazing incidence X-ray diffraction (GIXRD) measurements were performed to evaluate structural modifications in the near surface region following high temperature ion irradiations. GIXRD profiles were collected on a PANalytical X'Pert Pro Multipurpose Diffractometer (MPD) fitted with a Cu X-ray tube and a X'Celerator detector. The diffraction patterns were acquired in grazing incidence geometry over the 2θ range $25\text{--}90$ degrees with a step size of 0.03° and counting time of 0.5 s at each step. The analyzed 2θ range included six peaks of the typical rock salt structure of ZrC ($Fm\bar{3}m$) and the expected diffraction reflections for ZrO_2 polymorphs produced by the oxidation. X-ray tube operation conditions were 40 kV and 40 mA .

2.3.3. Electron microscopy

The surface morphology and composition were examined for both pristine and irradiated by focused ion beam (FIB)- scanning electron microscopy (FIB SEM, Scios™ DualBeam™, FEI, Hillsboro, Oregon) coupled with energy dispersive spectroscopy (EDS; Oxford Instrument Avignon UK). TEM specimens were also prepared using focused-ion-beam (FIB) lift out technique with a Scios™ DualBeam™ equipped with Ga focused ion beam. Before milling, a $2 \mu\text{m}$ thick Pt layer was deposited the top surface of the specimen to protect it from ion beam induced damage and unwanted surface milling during FIB preparation. Trenching was performed at an ion beam voltage of 30 kV with a beam current of a few nanoamps. After lift-out, thinning of the lamella was first conducted with a beam current of hundreds of picoamps at 30 kV at $\pm 5^\circ$ on both sides of the lamella using cleaning cross section mode until the lamella was $\sim 1 \mu\text{m}$ thick. Voltages and currents were gradually reduced, and the milling angles decreased as the lamella got thinner. To complete preparation, a gentle polishing with Ga^+ ions (5 keV and 48 pA) was used to remove damage caused by higher energy Ga bombardment. Microstructure characterization was performed using a 300 kV Technai F30 Supertwin transmission electron microscope (TEM). High resolution transmission electron microscopy (HRTEM) was used to reveal microstructural details of the oxide scale. Bright field (BF) imaging techniques were used to elucidate the radiation induced microstructural defects. Energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) were used for chemical composition studies.

2.3.4. Raman spectroscopy

Raman measurements were collected using a HORIBA Jobin Yvon LabRAM ARAMIS microRaman spectrometer (Horiba, Edison, NJ). The specimens were excited by a 632 nm He/Ne laser focused to a spot 500 nm in size on the sample using a $100\times$ microscope objective lens. Raman spectra were acquired in the backscattering geometry. The laser power was below 2 mW to prevent local heating of the sample.

3. Results

3.1. As-sintered sample

Gas fusion analyses indicated that as-sintered ZrC_x contained 11.62 wt% carbon, 0.144 wt% oxygen, and 0.0251 wt % nitrogen. Consequently, the carbon content of the fabricated billet corresponded to a carbon stoichiometry of $\text{ZrC}_{0.99}$. The uncertainty of the gas fusion analyses is estimated at ± 2 wt%, corresponding to an uncertainty in the stoichiometry of ZrC_x of about ± 0.02 . The bulk density of the as-sintered specimen measured by Archimedes' method was 6.447 g/cm³, corresponding to a relative density of approximately 97 %.

3.2. Annealed unirradiated sample

GIXRD patterns obtained at $\omega = 0.5^\circ$ for the control specimen before and after thermal annealing in the ion irradiation vacuum chamber are presented in Fig. 2a. After annealing, new peaks corresponding to ZrO_2 polymorphs were observed in the XRD pattern. This result clearly indicated that the near surface area of the specimen was oxidized after exposure to the residual vacuum ($< 10^{-7}$ torr) of the ion accelerator chamber at 800 °C. The assignment of type of ZrO_2 polymorph could not be done unambiguously due to the closeness of the XRD peak positions for monoclinic (m), tetragonal (t) and cubic (c) ZrO_2 in the evaluated 2θ range. The peak at $2\theta = 30^\circ$ is due to the presence of either t- or c- ZrO_2 polymorph(s) and/or oxygen-deficient m- ZrO_{2-x} . Fig. 2b shows GIXRD patterns, obtained at ω values of 0.5, 1, 1.5, 3 and 5° , from the unirradiated ZrC sample after annealing. It is noted that the intensity of the ZrO_2 peaks decreased as the incident angle ω increased, suggesting that the oxide phase was concentrated in the near surface region. Furthermore, the ZrC peaks shifted to higher angles when the X-ray incident angle decreased, indicating a contraction of the unit cell parameter of ZrC in the near surface area of the specimen. Such peak shifting could be attributed to the dissolution of adventitious oxygen into the ZrC lattice [45].

FESEM plain view micrographs of the annealed control specimen (Fig. 3a) showed that the surface was covered by discrete nanoprecipitates distributed homogeneously across the grains of the underlying ZrC . The nanoprecipitates ranged in sizes between 20 and 150 nm and seemed to grow preferentially within the grains. EDX elemental map-indicated that Zr, C and O were the major constituents on the surface area of the annealed control specimen (Fig. 3b). While the

concentration of zirconium and carbon was uniform across the analyzed area, the concentration of oxygen was lower at the grain boundaries. This suggests that the nanoprecipitates observed in the SEM images contain oxygen, which is consistent with the detection of zirconium oxide by GIXRD.

A Cross-sectional HRTEM image of the unirradiated specimen after annealing is shown in Fig. 4a. The surface of the ZrC specimen was covered by a nanocrystalline layer about ~ 4 nm thick. The chemical composition of the nanocrystalline layer was probed by EELS analysis. The STEM-high angle annular dark field (HAADF) image of the analyzed region (Fig. 4b) showed a dark layer (Point A) and a uniform gray layer (Point B). The EELS spectrum obtained at point A (Fig. 4c) confirmed that the amorphous layer was carbon rich, whereas point B (Fig. 4d) indicated that the nanocrystalline layer was most likely ZrO_2 . Underneath the nanocrystalline ZrO_2 layer (layer I), there was a layer of crystalline ZrC (layer II) that was oxygen rich compared to the bulk ZrC . The oxygen content decreased continuously from the top surface towards the unoxidized ZrC matrix, suggesting that the oxidation was promoted by the uptake of residual oxygen from the ion accelerator chamber during the annealing experiment. Fig. 5a shows a HRTEM image of an area of the annealed unirradiated sample where the continuity of the nanocrystalline oxide layer was interrupted by the formation of large nanosized islands. The chemical composition of the islands was consistent with ZrO_2 as confirmed by EELS analysis (Fig. 5d). A Fast Fourier Transform (FFT) pattern was acquired at the red squared region indicated in Fig. 5a. The obtained FFT pattern (Fig. 5b) can be well indexed along the $[-121]$ zone axis based on a tetragonal ZrO_2 structure (Inorganic Crystal Structure Database-66784). To confirm the validity of the indexing, a simulated electron diffraction pattern of the ZrO_2 tetragonal structure was obtained using the Crystallmaker™ software (Fig. 5c). Also, Fig. 5e shows that the precipitate was epitaxially grown on the ZrC surface with the epitaxial relationship being $(10\bar{1})_T // (002)_M$ and $[\bar{1}21]_T // [110]_M$.

3.3. Irradiated samples

3.3.1. ZrC matrix

The XRD patterns for the irradiated samples (Fig. S1) revealed the presence of defective but crystalline ZrC phase at all doses. The nature and evolution of the radiation-induced defects have been analyzed in detail in a sister paper [46]. At 800 °C, the irradiation response of ZrC is driven by in-cascade interstitial clustering. At low doses (0.5 dpa), the

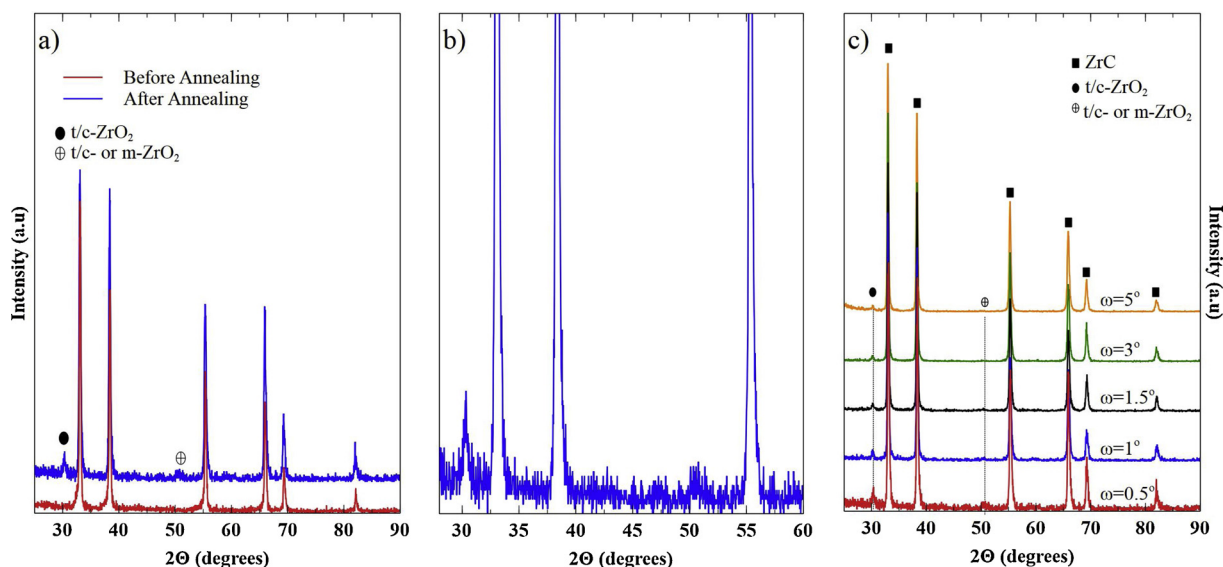


Fig. 3. (a) GIXRD patterns obtained from ZrC control sample before and after thermal annealing in the ion irradiation chamber at 800 °C, (b) (a) GIXRD obtained from ZrC control sample after thermal annealing collected at various x-ray incident angles.

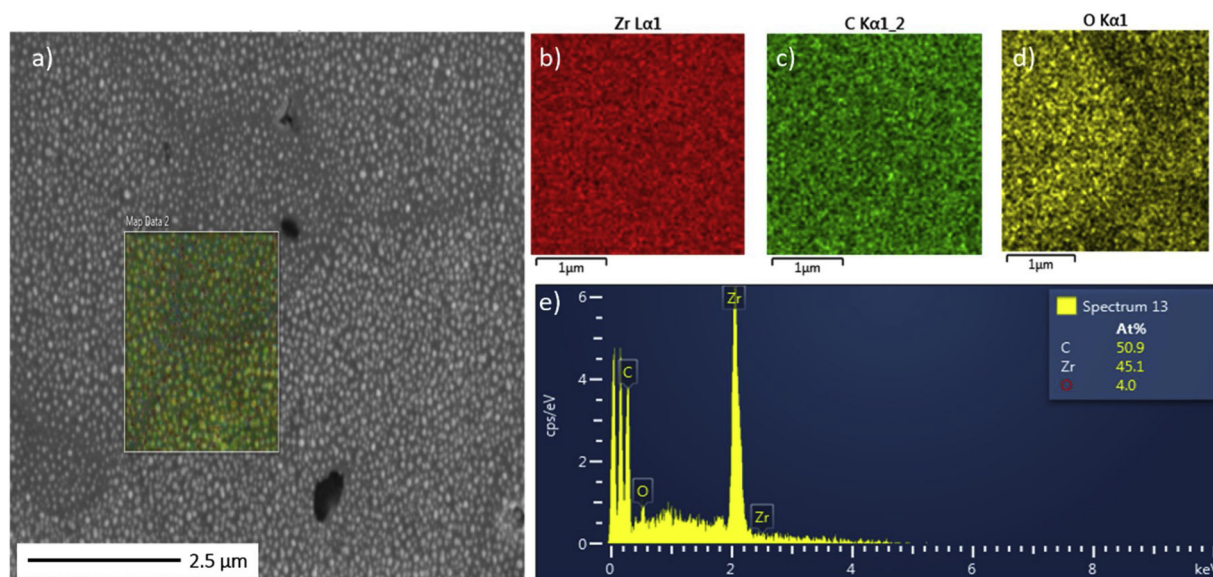


Fig. 4. (a) Secondary electron SEM image of the surface topography of the control sample showing presence of oxide nodules after thermal annealing in the irradiation chamber, (b) EDX compositional maps for C, Zr and O acquired in the box area in (a), (c) EDX spectra and standardless compositional quantification for the mapping area.

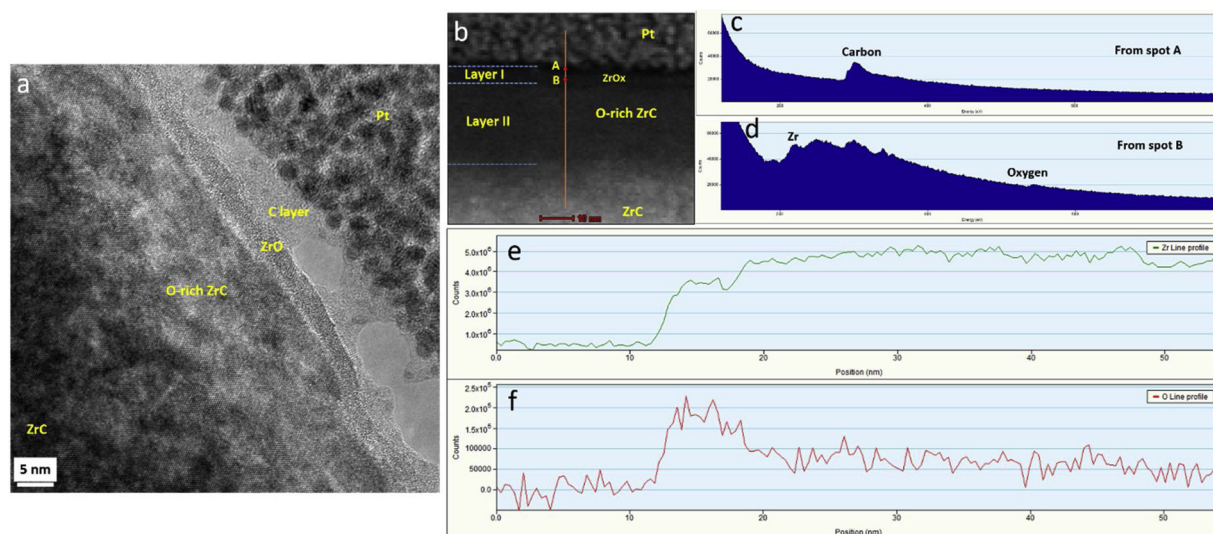


Fig. 5. (a) HRTEM image of the near surface area of the control specimen after annealing in the irradiation chamber (b) STEM-HAADF image with the EELS line profile. Two EELS spectrum are extracted from the spot A and spot B from the line profile, shown in the (c) and (d) respectively, confirming the amorphous C and nanocrystalline ZrOx layer in (a). Elemental line profile of Zr (e) and O (f).

microstructure contained primarily black-dot defects throughout the implanted layer. Upon increasing dose (> 5 dpa), entangled dislocation networks were observed in the specimens. Fig. 7a is a Bright Field Image of the specimen irradiated to 5 dpa showing the tangle dislocation network. A Centered dark field (DF) relrod TEM imaging of the same specimen was acquired by selecting the streak using a small objective aperture. The corresponding TEM images (Fig. 7b) of microstructure shows discontinuous bright lines on a relatively dark background. These lines correspond to faulted dislocation loops, which are the primary type of microstructural defects reported in neutron irradiated ZrC up to 1100 °C [34]. Fig. 7c shows a high resolution TEM image of the irradiated microstructure showing Frank loop defects.

Raman measurements were conducted to elucidate the evolution of point defects during ion irradiation of ZrC. The measurements were performed in transverse cross sections of FIB liftout to provide a more accurate comparison between the unirradiated and ion-implanted areas of the specimens. Fig. 8 shows the Raman spectra acquired at different

locations from the top surface of the 10 dpa FIB liftout. The spectra obtained at locations beyond the ion implantation range of the 10 MeV Au^{3+} ions ($> 1.5 \mu\text{m}$) showed four Raman bands in the 100–1000 cm^{-1} range, denoted by TA (204 cm^{-1}), LA (275 cm^{-1}), TO (515 cm^{-1}), and LO (600 cm^{-1}). These peaks were attributed to the acoustic and optical phonon lines of ZrC_{1-x} [47]. These phonon modes are forbidden in perfectly stoichiometric ZrC and only appear when carbon vacancies are present, confirming that the as-sintered ZrC specimen was substoichiometric. On the other hand, several changes were observed in the spectrum acquired at the ion irradiated area ($x = 0.65 \mu\text{m}$). Upon heavy-ion irradiation, the intensity of the ZrC defect-induced bands increased significantly, implying an increase in the number of carbon vacancies after irradiation. Additionally, new Raman bands were observed between 1000 and 1600 cm^{-1} . These new peaks were related to C–C bonds or disordered carbon, suggesting that carbon segregation occurred during ion irradiation. Therefore, the ion irradiation induced a local variation in stoichiometry of ZrC by increasing the number of

carbon vacancies and releasing carbon. Similar results were obtained by Pellegrino et al. [48].

3.3.2. Oxidation

Additionally, weak peaks were observed around $2\theta = 30^\circ$ in some of the irradiated specimens; although the intensity of this peak was too weak to be clearly deconvoluted from the background. The low intensity of the ZrO_2 peak in the irradiated samples could be because the volume fraction of ZrO_2 was too small to produce XRD peaks that were discernible from the background signal. The surfaces of irradiated samples were analyzed as discussed below to characterize changes that occur during irradiation.

Fig. 9 presents high resolution SEM micrographs of the surface of the control specimen and samples irradiated to 2.5, 10 and 15 dpa. Each image is shown together with the normalized particle size distributions of the ZrO_2 precipitates. From the SEM images, major changes are observed in the size, shape, and surface coverage of the oxide precipitates as the irradiation dose is increased. The relative change in the particle size with dose becomes apparent from the measured particle size distributions (PSD) shown in Fig. 9. For all specimens, the experimentally measured PSD is unimodal and can be well approximated using a log-normal distribution function ($r^2 > 98\%$). The mean and variance of fitting functions were calculated to give a more quantitative insight into the nanoisland size evolution under irradiation conditions. The results show that the PSD shifts progressively to smaller sizes and becomes narrower with increasing the irradiation dose. For the control sample (Fig. 6a), the PSD covers a broad range of diameter from 10 to 140 nm, while the peak of the distribution lies around of 55 nm. On the other hand, the peak region of the distribution decreases to around 39 nm and the upper bound of the distribution is found to be 60 nm as the irradiation dose increased to 15 dpa.

Radiation does not simply shift the PSD towards smaller sizes but also changes the shape and the surface coverage of the oxide nano-precipitates. Under irradiation conditions, the oxide precipitates assumed a more regular shape, with the formation of nearly circular nanoislands for the specimen irradiated to 15 dpa. To follow the shape change of the precipitates as the dose increases, circularity distributions of the oxide islands were calculated for each specimen (Fig. 10a). The

results indicate that the mean circularity value of the oxide nanoislands increases with increasing the irradiation dose. However, the average circularity does not increase because of a shift of the entire distribution, but rather to the increase of the main peak in the circularity distribution at expense of the tail at lower values. On the other hand, the areal density of oxide islands is also affected under irradiation conditions. Fig. 10b) shows the evolution of the surface coverage fraction with irradiation dose. It is found that the surface coverage of the oxide nodules steadily decreases with increased dose, going from around 34 % in the control specimen to $\sim 26\%$ in the specimen irradiated to 15 dpa. Thus, in light of the experimental results discussed above, it is clear that the observed morphological evolution of the oxide islands appears to be driven by radiation-induced processes.

High resolution TEM images of the oxide islands formed at different doses were taken from the $[110]$ zone axis of the ZrC matrix (Fig. 11) Morphological and interfacial changes were observed in the oxide nodules as the irradiation dose is increased. At low doses (0.5 dpa), the oxide particles showed a double cap morphology with approximately half of the oxide island semi-embedded into the ZrC matrix and the other half protruded above the surface. Further analysis of the interfacial area revealed no coherent relationship between the oxide nodule and the ZrC matrix. As dose increased, the oxide islands tended to become more faceted and the interfacial region became more diffuse (Fig. 11c–e). Interestingly, the phases of ZrO_2 tended to be monoclinic above 2.5 dpa after analyzing all the HRTEM images acquired, suggesting that irradiation affected the phase of the ZrO_2 that formed. Moiré fringes were observed at the oxide/matrix interface in some of the HRTEM images of irradiated samples. Faceted regions were also observed within the ZrO_2 islands irradiated above 2.5 dpa. Some of these regions had a characteristic octahedral shape with sizes ranging between 3 and 10 nm. Overfocus/underfocus TEM analysis was conducted on oxide nodules with faceted regions to elucidate the character of these microstructural features. Fig. 8 shows the Fresnel contrast change under different focusing conditions in an oxide nodule irradiated to 5 dpa. The faceted regions appeared as white features in under-focused conditions and black features in over-focused conditions. This contrast change is characteristic of cavities, suggesting that the faceted regions could be voids or bubbles that formed under irradiation

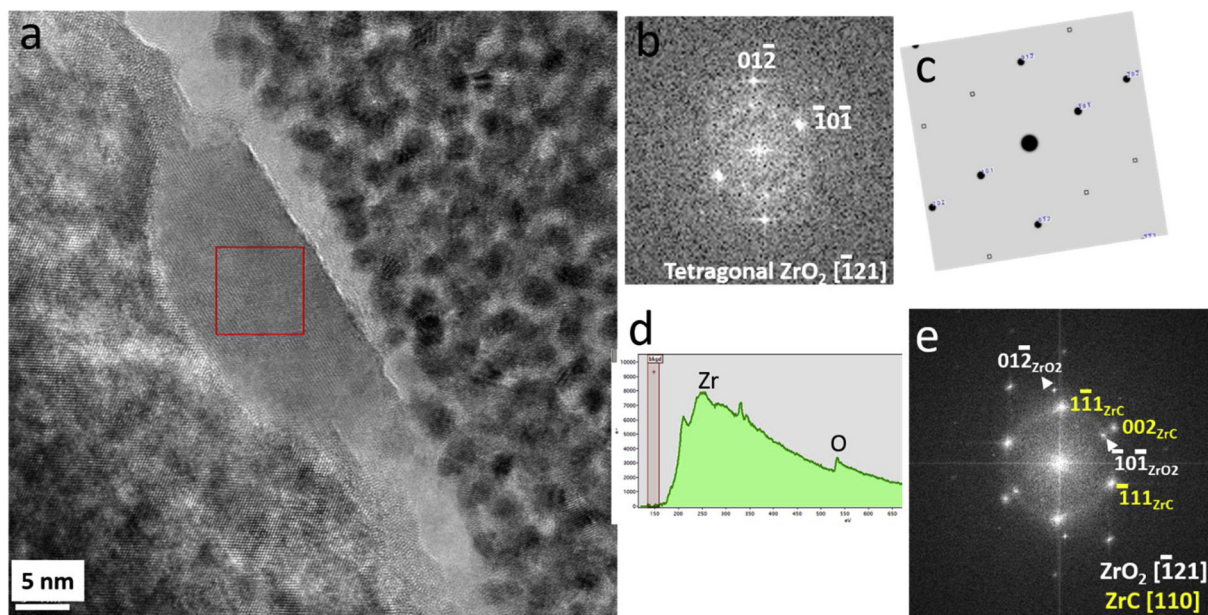


Fig. 6. (a) HRTEM image of a precipitate embedded in the ZrC matrix. (b) FFT pattern from the red squared region in a can be indexed to be tetragonal ZrO_2 along its $[121]$ zone axis. (c) The simulated electron diffraction pattern based on the tetragonal structure match well the experimental FFT. (d) EELS spectrum from the precipitate, confirming it is ZrO_2 . (e) FFT pattern from both ZrC and precipitate ZrO_2 showing the epitaxial relationship between them (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

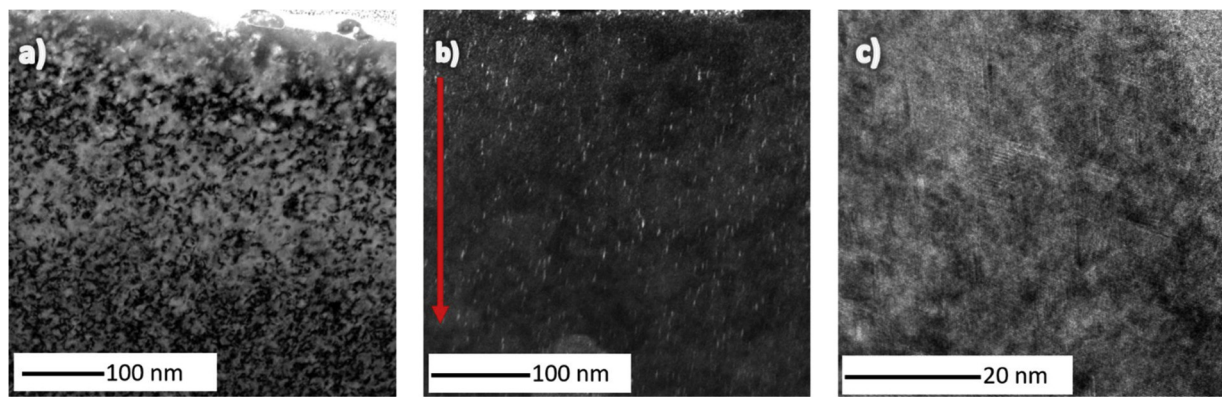


Fig. 7. (a) Bright Field Image of the specimen irradiated to 5 dpa showing the tangle dislocation network, (b) DF TEM relrod image of the sample irradiated at dpa with $g = 200$ near zone $[011]$, (c) High resolution TEM (HR-TEM) image of ZrC irradiated at 800°C to dpa. Arrows indicate the location of edge-on dislocation loops in the habit planes of $(-1,1,-1)$ and $(1,1,-1)$.

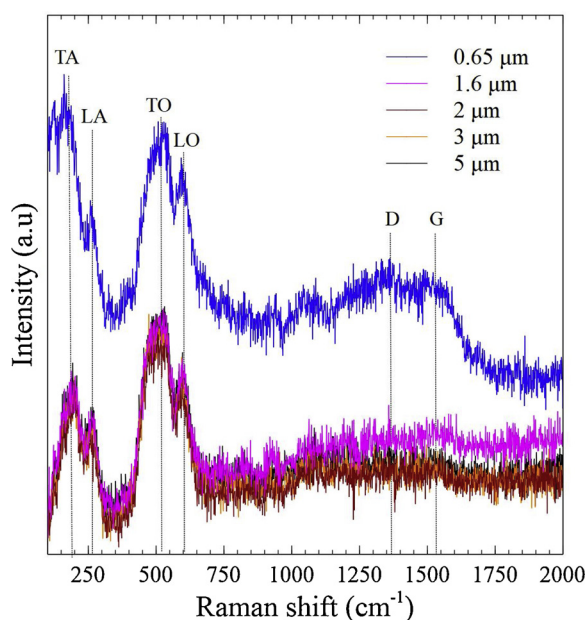


Fig. 8. A series of depth distribution of Raman spectra taken within the liftout region from the 5-dpa sample.

conditions [46].

4. Discussion

4.1. Early stage oxidation of ZrC

As shown in Fig. 1a, the gas pressure in the irradiation chamber increased substantially during heating of the target at temperatures between 150 – 170°C . This observation indicates that gases desorbed from the specimen during this stage of the heating processes. The chemical composition of the outgassing products could not be identified in this study because the ion accelerator chamber at the IBML is not fitted with a residual gas analyzer. However, the pressure increase was probably produced by the release of carbon impurities and/or water vapor previously trapped or adsorbed in the pellet during metallurgical preparation steps and handling of the sample. We speculate that these impurities could have played a role in the initial oxidation of ZrC. Similar outgassing processes could occur during the start-up and refueling stages of high temperature gas-cooled reactors [49]. Therefore, the experimental conditions inside the irradiation chamber observed in this experiment are akin to those expected in the nuclear reactor core.

The discrete oxide nanostructure observed on the surface of the unirradiated sample after annealing indicates that the oxidation process was on going. At the early stages, the oxidation of ZrC proceeds through nucleation and growth of oxide precipitates as depicted in Figs. 3 and 5. These results are similar to those obtained by Pipon et al. [18] after annealing $\text{ZrC}_{0.95}\text{O}_{0.05}$ at 1400°C in dynamic secondary vacuum (10^{-5} Pa) for 3 h. The early oxidation of other UTHCs and metals has also been found to proceed via nucleation and growth of oxide nanoislands under high temperature and vacuum conditions [50–52]. Alternatively, the formation of oxide islands can be due to dewetting of the thin oxide passivation layer formed at the early stages of the oxidation process. Due to excess surface free energy, thin oxide films are unstable and when they are heated, they will dewet to form islands [53]. Dewetting and nanopattern formation can be further induced by ion-irradiation [54]. Future *In-situ* oxidation experiments will be conducted in an environmental TEM to confirm the dewetting hypothesis at the early stages of ZrC_x oxidation.

The double-layer structure of the oxide scale observed in the unirradiated specimen after annealing (Fig. 4) is consistent with the morphological changes expected according to the oxidation mechanism proposed by Katoh [2]. In the present work, an oxygen gradient was detected by EELS analysis in the near surface area of the annealed specimen (Fig. 4b). The decrease in oxygen content with increasing distance from the surface suggests that oxygen dissolution occurred at the interface, forming an oxycarbide compound in the near surface area of the sample. Because of the sub-stoichiometric nature of the as-sintered billet used in this study it is conceivable that oxygen diffused towards carbon vacancies in ZrC_x (Eq. (1)):



Experimental work by Shimada and Ishil [20] showed that the ZrC_x containing dissolved oxygen becomes thermodynamically unstable after the oxygen concentration exceeds the solubility limit. As a result, the oxycarbide solution decomposes into a layer of amorphous zirconia and free carbon. Subsequently, ZrO_2 crystallites nucleate and growth from this amorphous layer and forms a continuous film at longer oxidation times. Similar results were obtained in this study for the oxidation of the unirradiated sample. Fig. 4a shows that an outer thin layer of nanocrystalline ZrO_2 (around 4 nm thickness) was formed on the top surface of the unirradiated sample after high vacuum thermal annealing.

Cross sectional TEM images of the oxide scale also revealed that the ZrO_2 crystallites were partially embedded into the underlying ZrC matrix rather than lying on the top surface (Fig. 5a). This embedding behavior has been previously observed in the early stage oxidation of other pure metals and alloys [55–57]. Embedding of the oxide embryos

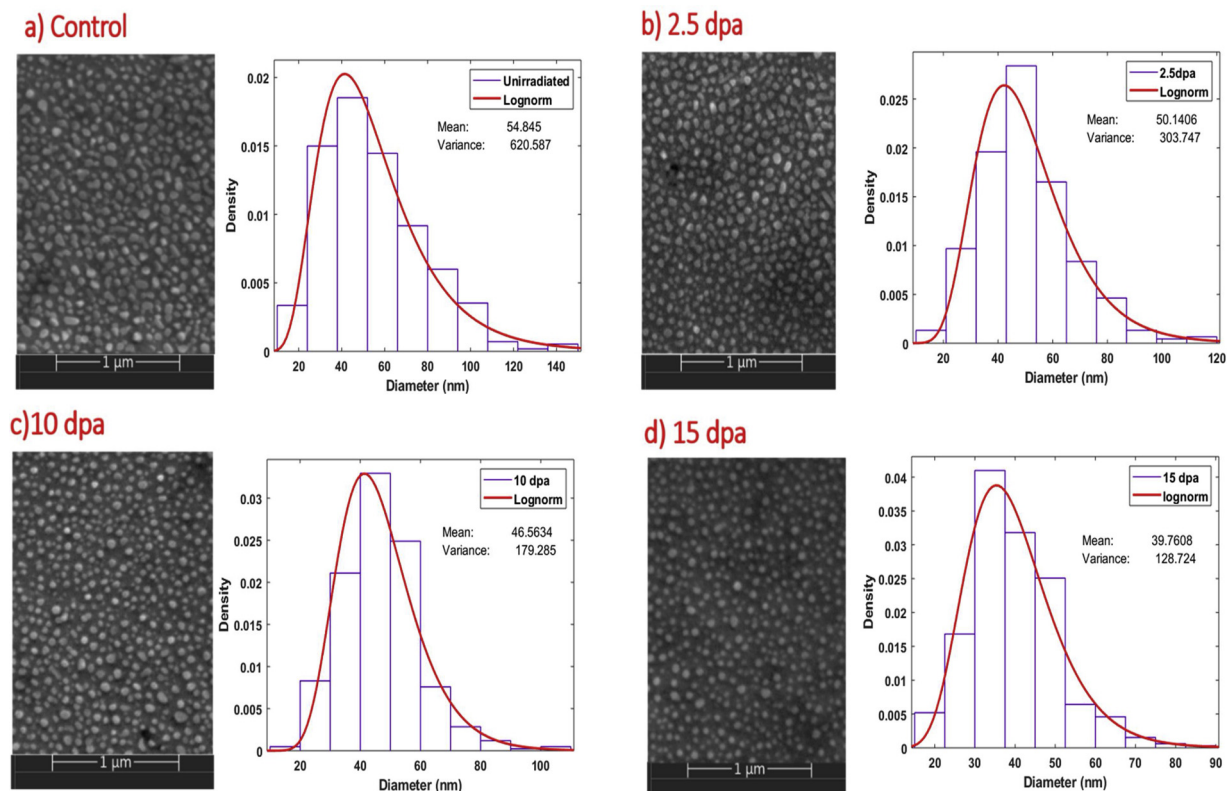


Fig. 9. Morphology of the nanostructured ZrO_2 nanoparticles obtained by SEM as a function of irradiation dose (a) Control samples, (b) 2.5 dpa, (c) 10 dpa, (d) 15 dpa. Statistical histograms of the oxide islands for each sample are reported below the SEM micrographs.

suggests that the oxide islands are formed by a 3D nucleation mechanism, which occurs when the surface mobility of oxygen is the dominant transport mechanism for the initial oxide formation [58]. Under such conditions, atomic oxygen diffuses over the surface and reacts with the underlying substrate atoms to form semi-buried oxide embryos. The formation of an internal oxide/substrate interface could also provide a fast pathway for oxygen diffusion into the matrix, which might contribute to further embedding of the oxide island during the growth stage.

The formation of sub-stoichiometric zirconia seems possible considering the low oxygen partial pressure and high temperature conditions used in this study. Ma et al. [59] have previously reported the formation of sub-oxides ZrO_{2-x} during the oxidation of Zr under high vacuum conditions ($\text{PO}_2 < 10^{-8}$ torr). Similarly, the occurrence of

oxygen deficient m- ZrO_2 has been observed at the interfacial region between the carbide and oxide during oxidation of ZrC_x [23]. On the other hand, the presence of t/c- ZrO_2 polymorph(s) cannot be dismissed either. Prior studies on ZrC oxidation have reported the formation of metastable t/c- ZrO_2 phases during the oxidation of ZrC [23,60]. The stabilization of t/c- ZrO_2 at temperatures below the conventional polymorphic stability range of these phases could be caused by several factors including crystallite size, strain, and structural defects.

4.2. Oxidation under irradiation conditions

For the irradiated samples, some of the large ZrO_2 nanoislands exhibits a series of structural defects (Fig. 6); however, they remained crystalline even after irradiation at the highest dose evaluated in this

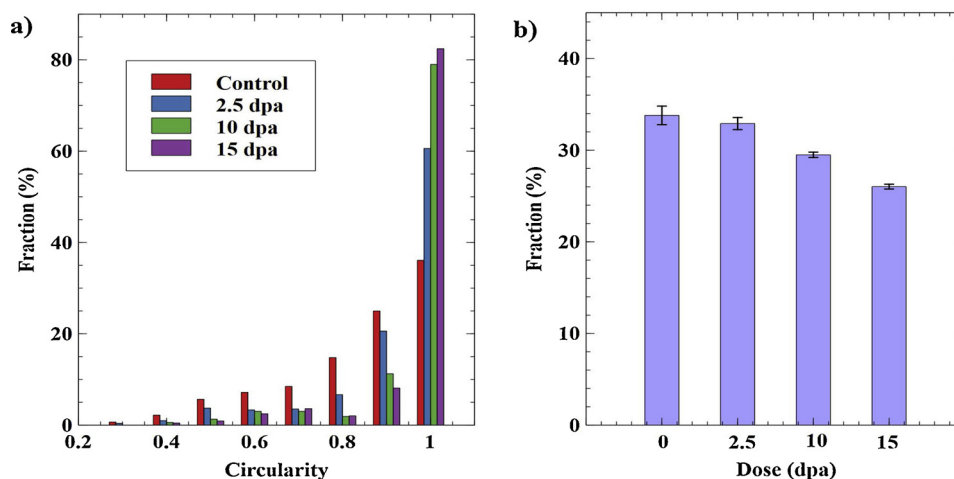


Fig. 10. Circularity distribution of oxide island as a function of the irradiation dose, (b) Coverage evolution of the oxide islands at different doses.

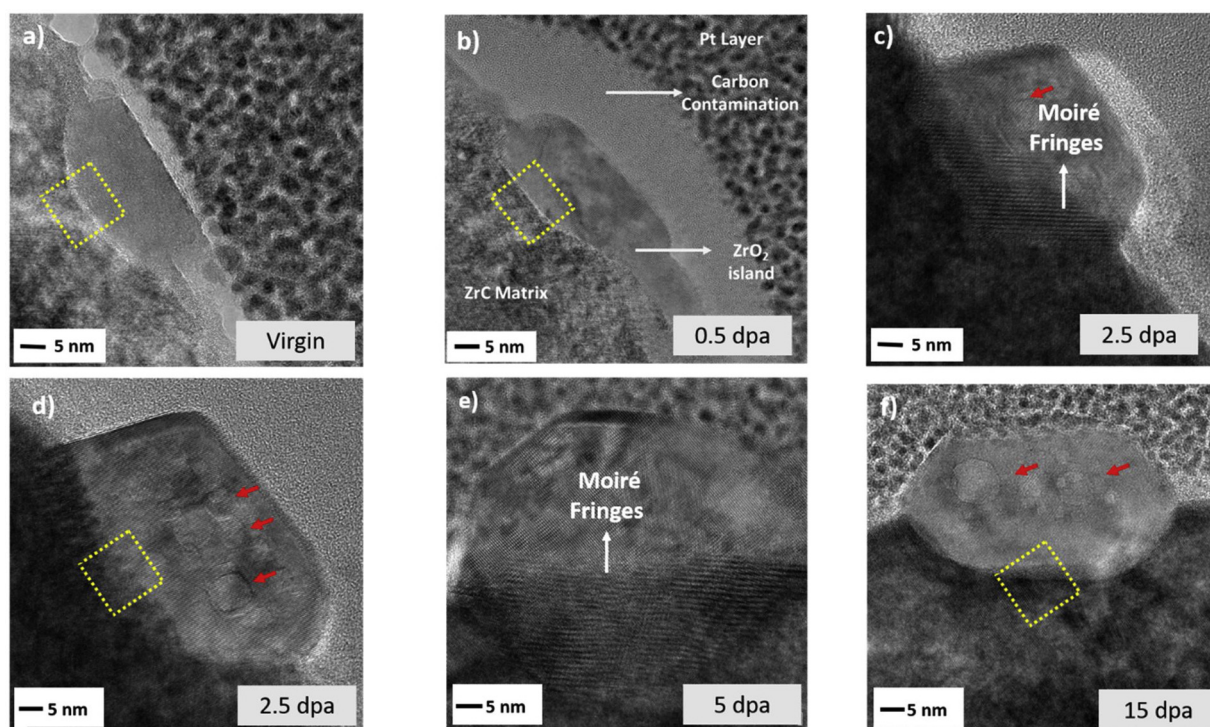


Fig. 11. HRTEM images of oxide island formed (a) control sample, and samples irradiated to (b) 0.5 dpa, (c) and (d) 2.5 dpa, (e) 5 dpa, and (f) 15 dpa.

work (15 dpa). This result agrees with previous experimental data [61,62] and first principle simulations [63,64], which indicate the high amorphization resistance for ZrO_2 polymorphs under irradiation conditions. The high radiation tolerance of ZrO_2 has been attributed to the large amount of native oxygen vacancies that enhances the dynamic recovery of the radiation induced defects [64].

Under irradiation conditions, the oxide islands are subject to several radiation-induced processes that determine their morphological and microstructural evolution (Fig. 9b). The protruded regions of the ZrO_2 nodules are sputtered by the incident ion beam. As shown in Fig. 6, the protruded regions of the nanoislands tended to become more faceted at higher doses. The reshaping of islands was more noticeable on the sides parallel to ion beam direction, suggesting that preferential ion sputtering occurred along this direction. Ballistic collisions with the Au^{3+} ions could also produce ion beam mixing at the ZrO_2/ZrC interface. As indicated by the yellow boxes in Fig. 6, irradiation tended to make the oxide/matrix interface more diffuse. Furthermore, Moiré fringes were observed in some of the irradiated precipitates. These observations were indicative that intermixing between the oxide particles and ZrC phases occurred during the ion irradiation of the specimens. Surface sputtering and ballistic mixing could enhance the dissolution of the oxide precipitates under radiation exposure. The atoms ejected out of the oxide particles might undergo three different processes: (i) dissolve into the ZrC matrix, (ii) diffuse back into the parent particle or being absorbed by other particles, and (iii) re-nucleate to form new particles with other solute atoms in the ZrC matrix. The last two process depend much on the diffusion of solute atoms, particularly oxygen atoms. Interestingly, no “halo” effect (i.e. formation of smaller oxide nanoparticles around the periphery the islands) was observed in the oxide/matrix interface for the irradiated samples. This suggests that the local composition of oxygen ejected from the islands does not exceed the solubility limit in the irradiated ZrC matrix. Thus, the nucleation and growth of smaller oxide cluster around the island is not possible. The absence of ‘haloing’ may be also related to other radiation-induced effects. Firstly, the supersaturation of defects created under irradiation conditions can increase the oxygen solubility in the matrix. Since the solubility increases during the irradiation, atoms ejected by ballistic

mixing may be in solution during irradiation. Secondly, the defect supersaturation can produce enhancement of diffusion processes. Radiation enhanced diffusion of sufficiently mobile species might occur either through vacancies or interstitials and can significantly alter the size and stoichiometry of the oxide islands. Previous experimental studies on sub-stoichiometric ZrC indicate that the presence of vacancies in the matrix can enhance the diffusion of oxygen towards the bulk [65]. It is conceivable that the diffusion of oxygen atoms in substoichiometric ZrC_x occur by an octahedral vacancy mechanism as observed experimentally in other group-IV carbides [66]. Additionally, other fast diffusion paths might be also operative under irradiation conditions, including dislocation loops and planar defects introduced in the irradiated microstructure as the dose increased.

As shown in Table 2, each of the irradiated areas in the ZrC foil endured different annealing times before and after ion irradiation. In general, longer pre-annealing time and lower doses lead to bigger oxide nodules on the surface of ZrC. It is noted that Increasing the post annealing time (i.e after ion irradiation) at higher doses does not produce coarsening of the oxide nanostructure. The region irradiated at the highest dose (15 dpa) was covered by small oxide precipitates. This behavior suggested that the nucleation and growth of the nanoislands is affected by the microstructure of the underlying ZrC substrate. At higher doses, more carbon vacancies and entangled dislocation networks are created in ZrC enhancing the dissolution of oxygen towards the bulk ceramic. Previously, we reported a coarsening of the

Table 2

Pre-annealing, irradiation and post-annealing times for each specimen.

Region	Dose (dpa)	Pre-annealing [min]	Irradiation [min]	Post-Annealing [min]
1	15	~140	30	~55
2	10	~170	20	~30
3	5	~180	10	~20
4	2.5	~190	5	~15
5	0.5	~195	1	~5
6	0	~196	0	0

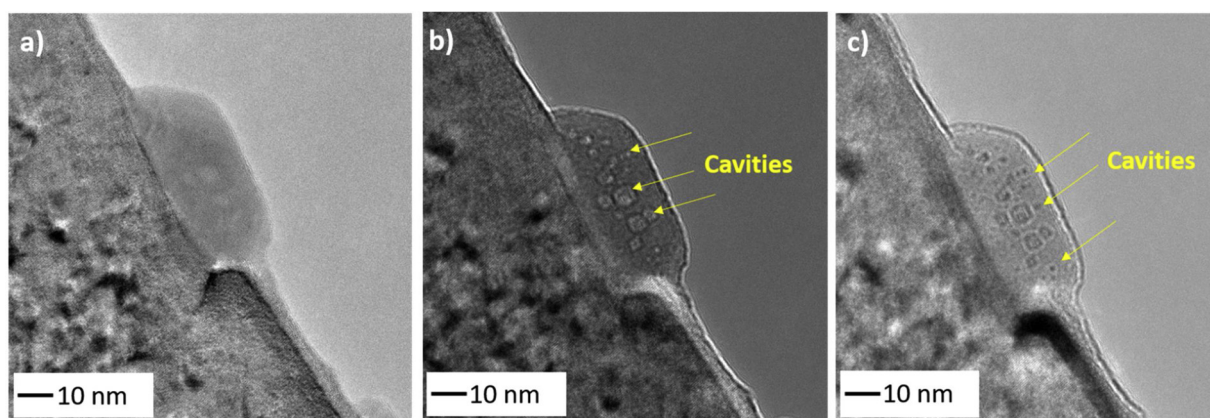


Fig. 12. Cavity morphology in the ZrO_2 island after irradiation to 5 dpa (a) in-focus, (b) underfocused, and (c) overfocused BF-TEM images showing changes in Fresnel contrast for the cavities.

microstructure in heavy ion irradiated ZrC at 800 °C driven by interstitial clustering [46]. At doses near 2.5 dpa, the dislocation loops began to coalesce forming entangled dislocation networks. This change in the dislocation structure could help to explain the oxide morphological evolution observed in Fig. 9. At doses below 2.5 dpa, the oxygen uptake is primarily driven by the formation of carbon vacancies, which were detected by Raman measurements. On the other hand, the formation of planar defects (i.e. cellular dislocation networks) at doses above 2.5 dpa could enhance the dissolution of oxygen towards the ZrC matrix as they act as fast pathways for oxygen diffusion. Thus, there is a threshold dose above which the planar defects formed and increased the diffusivity of oxygen towards the substrate.

Faceted pockets were also observed in the ZrO_2 islands for specimens irradiated at 2.5 dpa and above doses (Fig. 5d, f). These pockets were not observed in the oxide nodules for the control and 0.5 dpa-irradiated samples, indicating that radiation could have played a role on their formation. Furthermore, the pockets exhibited the characteristic Fresnel contrast of cavities in under-focus and over-focus BFTEM images (Fig. 12). This strongly suggested that pockets might be voids/bubbles that formed within ZrO_2 the islands under irradiation. Cavities were not expected from the published temperature/fluence damage mechanism maps for ZrO_2 . A possible mechanism for the formation and growth of cavities in the oxide nodules may be explained by oxygen diffusion and vacancy clustering processes. Due to small defect formation and migration barriers for oxygen compared to zirconium [67], the radiation response of ZrO_2 is mostly determined by the evolution of the surplus of oxygen point defects created during the irradiation. In the case of the oxide islands, the highly mobile oxygen atoms could migrate towards the free surface of the nodules and the ZrO_2/ZrC interface. The oxygen atoms that reach the free surface are no longer tightly bonded to the island and are lost; whereas those atoms that migrate towards the interface are dissolved into ZrC_x . Previous studies on ion irradiation of nanometric ZrO_2 indicate that a significant loss of oxygen occurs as the dose is increased [68]. Therefore, an accumulation of oxygen vacancy is expected in the ZrO_2 nodule upon irradiation. A supersaturation of vacancies may become the driving force for the nucleation and growth of cavities in ZrO_2 nodules at high doses. The process could be further assisted by the adsorption and absorption of inert gases present in the irradiation chamber, which may act to stabilize the void embryo and enhance their nucleation process. It can also be assumed that the voids are not pressurized because gas filled voids tend to have more spherical shapes rather than polyhedral ones.

5. Conclusion

This study investigated the morphology and microstructure of the oxidation scale formed on the surface of ZrC during irradiation with

Au^{3+} ions at 800 °C. GIXRD and electron microscopy (SEM/TEM) techniques were used to characterize the radiation response of the oxide at doses ranging from 0.5 to 15 dpa. Subsequent analysis was used to draw the following conclusions:

- The early stage oxidation of ZrC_x under prototypical operation conditions of high temperature gas cooled reactors proceeds via nucleation and growth of oxide islands rather than uniform oxide film growth. Cross-sectional TEM analysis suggested that the oxide nodules were formed by a 3D nucleation mechanism with embedding of the oxide embryos.
- Radiation affected the stability of the oxide islands at the early stages of ZrC oxidation. As dose increased, the PSD was shifted towards smaller diameters, the circularity of the islands was increased, and the surface coverage was reduced. The morphological and compositional analyses revealed that a combined effect of sputtering and ion-beam mixing results in the evolution of a nanoislands from extended to shrinking nanodots.
- The radiation response of the underlying ZrC matrix play a major role in the dissolution of oxygen towards the substrate. Radiation increased the amount of carbon vacancies in ZrC and led to the formation of entangled dislocation networks at higher doses. These radiation-induced defects can serve as fast pathways to diffusion of oxygen into the irradiated ZrC layer at high temperature. While carbon vacancies are the main oxygen diffusion route at low doses (< 2.5 dpa), entangled dislocation networks formed at doses above 2.5 dpa provide a new route for oxygen uptake.
- Ion irradiation introduced defects in the oxide nodules. Nucleation and growth of cavities was observed within the oxide nodules irradiated to 2.5 dpa and above. The driving mechanism for cavity formation could be associated with the loss of oxygen from the irradiated oxide nodules and the concomitant vacancy supersaturation.
- The oxide formed in ZrC has a high radiation-induced amorphization resistance. Although defects were observed in the oxide nodules, no amorphization of the ZrO_2 precipitates was observed under irradiation up to doses of 15 dpa. Some metastable phases of ZrO_2 were observed in the irradiated specimens.

CRediT authorship contribution statement

Raul Florez: Conceptualization, Methodology, Visualization, Writing - original draft. **Miguel L. Crespillo:** . **Xiaoqing He:** . **Tommi A. White:** . **Gregory Hilmas:** Supervision, Writing - review & editing. **William G. Fahrenholtz:** Supervision, Writing - review & editing. **Joseph Graham:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors of the paper of the manuscript “Early stage oxidation of ZrC under 10 MeV Au³⁺ ion-irradiation at 800 °C” have not conflict of interest to declare.

Acknowledgements

This research was supported by Nuclear Regulatory Commission Faculty Development Grant NRC-HQ-84-15-G-0044 and by the Ceramics program of the U.S. National Science Foundation as part of project DMR 1742086. The microscopy work was conducted at the Electron Microscopy Center EMC of the University of Missouri Columbia with partial funding through the EMC Excellence Microscopy Award. Material synthesis and X-ray diffraction measurements were performed using facilities of the Materials Research Center MRC located at the Missouri University of Science and Technology. Ion irradiations were performed at the Ion Beam Materials Laboratory located at the University of Tennessee, Knoxville.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.corsci.2020.108609>.

References

- [1] H.F. Jackson, W.E. Lee, Properties and characteristics of ZrC, in: R.J.M. Konings (Ed.), *Compr. Nucl. Mater.* Elsevier, Oxford, 2012, pp. 339–372.
- [2] Y. Katoh, G. Vasudevamurthy, T. Nozawa, L.L. Snead, Properties of zirconium carbide for nuclear fuel applications, *J. Nucl. Mater.* 441 (2013) 718–742.
- [3] X.T. Shen, L. Liu, W. Li, K.Z. Li, Ablation behaviour of C/C-ZrC composites in a solid rocket motor environment, *Ceram. Int.* 41 (2015) 11793–11803.
- [4] R. Ganter, R.J. Bakker, C. Gough, M. Paraliiev, M. Pedrozzi, F. Le Pimpec, L. Rivkin, A. Wrulich, Nanosecond field emitted and photo-field emitted current pulses from ZrC tips, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* 565 (2006) 423–429.
- [5] B. Pierrat, M. Balat-Pichelin, L. Silvestroni, D. Sciti, High temperature oxidation of ZrC-20%MoSi₂ in air for future solar receivers, *Sol. Energy Mater. Sol. Cells* 95 (2011) 2228–2237.
- [6] G. Vasudevamurthy, T.W. Knight, E. Roberts, T.M. Adams, Laboratory production of zirconium carbide compacts for use in inert matrix fuels, *J. Nucl. Mater.* 374 (2008) 241–247.
- [7] R. Liu, Z.M. Xie, J.F. Yang, T. Zhang, T. Hao, X.P. Wang, Q.F. Fang, C.S. Liu, Recent progress on the R&D of W-ZrC alloys for plasma facing components in fusion devices, *Nucl. Mater. Energy* 16 (2018) 191–206.
- [8] D. Wongsawaeng, Performance modeling of Deep Burn TRISO fuel using ZrC as a load-bearing layer and an oxygen getter, *J. Nucl. Mater.* 396 (2010) 149–158.
- [9] K.A. Terrani, Accident tolerant fuel cladding development: promise, status, and challenges, *J. Nucl. Mater.* 501 (2018) 13–30.
- [10] I.E. Porter, T.W. Knight, M.C. Dulude, E. Roberts, J. Hobbs, Design and fabrication of an advanced TRISO fuel with ZrC coating, *Nucl. Eng. Des.* 259 (2013) 180–186.
- [11] R. Wright, J. Wright, C. Cabot, Material performance in helium-cooled systems, in: R.J.M. Konings (Ed.), *Compr. Nucl. Mater.* Vol. 5 Elsevier, Oxford, 2012, pp. 251–277.
- [12] J. Berka, T. Hlinčík, I. Viden, T. Hudský, J. Vít, The design and utilization of a high temperature helium loop and other facilities for the study of advanced gas-cooled reactors in the Czech Republic, *J. Progress in Nucl. Energy* 85 (2015) 156–163.
- [13] N. Sakaba, T. Furusawa, T. Kawamoto, Y. Ishii, Y. Oota, Short design descriptions of other systems of the HTTR, *Nucl. Eng. Des.* 233 (2004) 147–154.
- [14] H. Chang, Z.X. Wu, H.J. Jia, Experimental study on cryogenic adsorption of methane by activated carbon for helium coolant purification of high-temperature gas-cooled reactor, *Ann. Nucl. Energy* 101 (2017) 367–374.
- [15] S. Hamamoto, Y. Shimazaki, T. Furusawa, T. Nemoto, H. Inoi, S. Takada, Investigation of chemical characteristics of primary helium gas coolant of HTTR (high temperature engineering test reactor), *Nucl. Eng. Des.* 271 (2014) 487–491.
- [16] V. Pauly, C. Tesch, J. Kern, M. Clark, D. Grierson, D. Singh, O. Ajayi, K. Sridharan, “High-temperature tribological behavior of structural materials after conditioning in impure-helium environments for high-temperature gas-cooled reactor applications, *J. Nucl. Mater.* 522 (2019) 311–323.
- [17] G. Gutierrez, N. Toulhoat, N. Moncoffre, Y. Pipon, A. Maître, M. Gendre, A. Perrat-Mabilon, Thermal behaviour of xenon in zirconium carbide at high temperature: role of residual zirconia and free carbon, *J. Nucl. Phys. Mater. Sci. Radiat. Appl.* 416 (2011) 94–98.
- [18] Y. Pipon, N. Toulhoat, N. Moncoffre, G. Gutierrez, A. Maître, M. Gendre, Influence of the Oxygen content on the thermal migration of Xenon in ZrC_xO_{1-x}, *J. Nucl. Mater.* 440 (2013) 546–552.
- [19] S. Agarwal, A. Bhattacharya, P. Trocellier, S.J. Zinkle, Helium induced micro-structure damage, nano-scale grain formation and helium retention behaviour of ZrC, *Acta Mater.* 163 (2019) 14–27.
- [20] S. Shimada, T. Ishii, Oxidation kinetics of zirconium carbide at relatively low temperatures, *J. Am. Ceram. Soc.* 73 (1990) 2804–2808.
- [21] S. Shimada, M. Yoshimatsu, M. Inagaki, S. Otani, Formation and characterization of carbon at the ZrC/ZrO₂ interface by oxidation of ZrC single crystals, *Carbon* 36 (1998) 1125–1131.
- [22] S. Shimada, Oxidation and mechanism of single crystal carbides with formation of carbon, *J. Ceram. Soc. Japan* 109 (2001) 33–42.
- [23] C. Gasparrini, R.J. Chater, D. Horlait, L. Van der Perre, W.E. Lee, Zirconium carbide oxidation: kinetics and oxygen diffusion through the intermediate layer, *J. Am. Ceram. Soc.* 101 (2018) 2638–2652.
- [24] C. Gasparrini, R. Podor, D. Horlait, R. Chater, W.E. Lee, Zirconium carbide oxidation: maltese cross formation and interface characterization, *Oxid. Met.* 88 (2017) 509–519.
- [25] G.A. Rama Rao, V. Venugopal, Kinetics and mechanism of the oxidation of ZrC, *J. Alloys. Compd.* 206 (1994) 237–242.
- [26] D. Gozzi, M. Montozzi, P.L. Cignini, Oxidation kinetics of refractory carbides at low oxygen partial pressures, *Solid State Ion.* 123 (1999) 11–18.
- [27] A. Bellucci, D. Gozzi, T. Kimura, T. Noda, S. Otani, Zirconia growth on zirconium carbide single crystals by oxidation, *Surf. Coatings Technol.* 197 (2005) 294–302.
- [28] B. Wei, D. Wang, Y. Wang, H. Zhang, S. Peng, C. Xu, G. Song, Yu Zhou, Corrosion kinetics and mechanisms of ZrC_{1-x} ceramics in high temperature water vapor, *RSC Adv.* 8 (2018) 18163–18174.
- [29] X. Iltis, F. Lefebvre, C. Lemaignan, Microstructural study of oxide layers formed on Zircaloy-4 in autoclave and in reactor Part i: impact of irradiation on the micro-structure of the zirconia layer, *J. Nucl. Mater.* 224 (1995) 109–120.
- [30] A. Garner, F. Baxter, P. Frankel, M. Topping, A. Harte, T. Slater, P. Tejland, J. Romero, E. Darby, A. Cole-Baker, M. Gass, M. Preuss, Investigating the effect of zirconium oxide microstructure on corrosion performance: a comparison between neutron, proton, and nonirradiated oxides, in: R.J. Comstock, A.T. Motta (Eds.), *Zirconium in the Nuclear Industry: 18th International Symposium, ASTM STP1597*, ASTM International, West Conshohocken, PA, 2018, pp. 491–523.
- [31] S.J. Zinkle, L.L. Snead, Opportunities and limitations for ion beams in radiation effects studies: bridging critical gaps between charged particle and neutron irradiations, *Scr. Mater.* 143 (2018) 154–160.
- [32] G.S. Was, Z. Jiao, E. Getto, K. Sun, A.M. Monterrosa, S.A. Maloy, O. Anderoglu, B.H. Sencer, M. Hackett, Emulation of reactor irradiation damage using ion beams, *Scr. Mater.* 88 (2014) 33–36.
- [33] G.S. Was, R.S. Averback, Radiation damage using ion beams, in: R.J.M. Konings (Ed.), *Compr. Nucl. Mater.* Elsevier, Oxford, 2012, pp. 195–221.
- [34] L.L. Snead, Y. Katoh, S. Kondo, Effects of fast neutron irradiation on zirconium carbide, *J. Nucl. Mater.* 399 (2010) 200–207.
- [35] C.J. Ulmer, A.T. Motta, M.A. Kirk, In situ ion irradiation of zirconium carbide, *J. Nucl. Phys. Mater. Sci. Radiat. Appl.* 466 (2015) 606–614.
- [36] D. Gosset, M. Dollé, D. Simeone, G. Baldinozzi, L. Thomé, Structural evolution of zirconium carbide under ion irradiation, *J. Nucl. Mater.* 373 (2008) 123–129.
- [37] D. Gosset, M. Dollé, D. Simeone, G. Baldinozzi, L. Thomé, Structural behaviour of nearly stoichiometric ZrC under ion irradiation, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 266 (2008) 2081–2805.
- [38] Y. Zhang, M.L. Crespillo, H. Xue, K. Jin, C.H. Chen, C.L. Fontana, J.T. Graham, W.J. Weber, New ion beam materials laboratory for materials modification and irradiation effects research, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 338 (2014) 19–30.
- [39] M.L. Crespillo, J.T. Graham, Y. Zhang, W.J. Weber, Temperature measurements during high flux ion beam irradiations, *Rev. Sci. Instrum.* 87 (2016) 024902.
- [40] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, SRIM - the stopping and range of ions in matter (2010), *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 268 (2010) 1818–1823.
- [41] M.J. Zheng, I. Szlufarska, D. Morgan, Ab initio prediction of threshold displacement energies in ZrC, *J. Nucl. Mater.* 471 (2016) 214–219.
- [42] W.J. Weber, Y. Zhang, Predicting damage production in monoatomic and multi-elemental targets using stopping and range of ions in matter code: challenges and recommendations, *Curr. Opin. Solid State Mater. Sci.* 23 (2019) 100757.
- [43] S.J. Zinkle, G.S. Was, Materials challenges in nuclear energy, *Acta Mater.* 61 (2013) 735–758.
- [44] ASTM, ASTM C373-14 Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products, *ASTM C373-88*, 1999.
- [45] F. Réjasse, O. Rapaud, G. Trolliard, O. Masson, A. Maître, Experimental investigation and thermodynamic evaluation of the C–O–Zr ternary system, *RSC Adv.* 100 (2016) 100122–100135.
- [46] R. Florez, M.L. Crespillo, X. He, T.A. White, G. Hilmas, W. Fahrenholtz, J. Graham, The irradiation response of ZrC ceramics under 10 MeV Au³⁺ ion irradiation at 800 °C, *J. Eur. Ceram. Soc.* (January) (2020).
- [47] H. Wipf, M.V. Klein, W.S. Williams, Vacancy-induced and two-phonon raman scattering in ZrC_x, NbC_x, HfC_x, and TaC_x, *Phys. Status Solidi* 108 (1981) 489–500.
- [48] S. Pellegrino, P. Trocellier, L. Thomé, S. Miro, J.M. Costantini, E. Jouanny, Raman investigation of ion irradiated TiC and ZrC, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* (2019).
- [49] H.L. Brey, H.G. Olson, The Fort St. Vrain high temperature gas-cooled reactor. II. Helium circulators, *Nucl. Eng. Des.* 53 (1979) 125–131.
- [50] R. Bès, S. Gavarrini, N. Millard-Pinard, S. Cardinal, A. Perrat-Mabilon, C. Peaucelle, T. Douillard, Influence of crystallographic orientation on the early stages of oxidation of polycrystalline titanium nitride, *J. Nucl. Mater.* 427 (2012) 415–417.

- [51] S. Gavarini, R. Bes, N. Millard-Pinard, S. Cardinal, C. Peaucelle, A. Perrat-Mabilon, V. Garnier, C. Gaillard, A comparative study of TiN and TiC: oxidation resistance and retention of xenon at high temperature and under degraded vacuum, *J. Appl. Phys.* 109 (2011) 014906.
- [52] J. Baillet, S. Gavarini, N. Millard-Pinard, V. Garnier, C. Peaucelle, X. Jaurand, S. Cardinal, A. Duranti, C. Bernard, R. Rapegno, L. Dernoncourt, T. De Echave, Influence of grain size and microstructure on oxidation rate and mechanism in sintered titanium carbide under high temperature and low oxygen partial pressure, *J. Eur. Ceram. Soc.* 36 (2016) 3099–3111.
- [53] R.V. Zucker, G.H. Kim, W. Craig Carter, C.V. Thompson, A model for solid-state dewetting of a fully-faceted thin film, *C. R. Phys.* 14 (2013) 564–577.
- [54] R. Lo Savio, L. Repetto, P. Guida, E. Angeli, G. Firpo, A. Volpe, V. Lerardi, U. Valbusa, Control of the micrometric scale morphology of silicon nanowires through ion irradiation-induced metal dewetting, *Solid State Commun.* 240 (2016) 41–45.
- [55] L. Luo, Y. Kang, J.C. Yang, G. Zhou, Nucleation and growth of oxide islands during the initial-stage oxidation of (100)Cu-Pt alloys, *J. Appl. Phys.* 117 (2015) 065305.
- [56] G. Zhou, J.C. Yang, Formation of quasi-one-dimensional Cu₂O structures by in situ oxidation of Cu(100), *Phys. Rev. Lett.* 89 (2002) 106101.
- [57] G. Zhou, J.C. Yang, Initial oxidation kinetics of Cu(100), (110), and (111) thin films investigated by in situ ultra-high-vacuum transmission electron microscopy, *J. Mater. Res.* 20 (2005) 1684–1694.
- [58] G. Zhou, Nucleation thermodynamics of oxide during metal oxidation, *Appl. Phys. Lett.* 94 (2009) 201905.
- [59] W. Ma, F.W. Herbert, S.D. Senanayake, B. Yildiz, Non-equilibrium oxidation states of zirconium during early stages of metal oxidation, *Appl. Phys. Lett.* 106 (2005) 101603.
- [60] S. Shimada, A thermoanalytical study on the oxidation of ZrC and HfC powders with formation of carbon, *Solid State Ion.* 149 (2002) 319–326.
- [61] J.M. Costantini, F. Beuneu, W.J. Weber, Radiation damage in cubic-stabilized zirconia, *J. Nucl. Mater.* 440 (2013) 508–514.
- [62] K.E. Sickafus, H.J. Matzke, Th. Hartmann, K. Yasuda, J.A. Valdez, P. Chodak III, R.A. Verrall, Radiation damage effects in zirconia, *J. Nucl. Mater.* 274 (1999) 66–77.
- [63] D.S. Aidhy, Y. Zhang, W.J. Weber, Radiation damage in cubic ZrO₂ and yttria-stabilized zirconia from molecular dynamics simulations, *Scr. Mater.* 98 (2015) 16–19.
- [64] E. Zarkadoulas, R. Devanathan, W.J. Weber, M.A. Seaton, I.T. Todorov, K. Nordlund, M.T. Dove, K. Trachenko, High-energy radiation damage in zirconia: modeling results, *J. Appl. Phys.* 115 (2014) 083507.
- [65] W. Hu, J. Xiang, S. Liu, Y. Zhang, C. Chen, P. Wang, H. Wang, B. Xu, J. He, D. Yu, Y. Tian, Z. Liu, Low-temperature diffusion of oxygen through ordered carbon vacancies in Zr₂C_x: the formation of ordered Zr₂C_xO_y, *Inorg. Chem.* 51 (2012) 5164–5172.
- [66] M. Schuhmacher, P. Eveno, Oxygen diffusion in titanium carbide, *Solid State Ion.* 12 (1984) 263–270.
- [67] U. Brossmann, R. Wüschum, U. Södervall, H.E. Schaefer, Oxygen diffusion in ultrafine grained monoclinic ZrO₂, *J. Appl. Phys.* 85 (1999) 7646.
- [68] P.D. Edmondson, Y. Zhang, F. Namavar, C.M. Wang, Z. Zhu, W.J. Weber, Defect- and strain-enhanced cavity formation and Au precipitation at nano-crystalline ZrO₂/SiO₂/Si interfaces, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 269 (2011) 126–132.