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Stoichiometry effect on the irradiation response in the microstructure of zirconium carbides

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ABSTRACT

Zone-refined ultra high pure ZrC with five C/Zr ratios ranging from 0.84 to 1.17 was irradiated using a 2 MeV proton beam at 1125 °C. The stoichiometry effect on the irradiation response of ZrC microstructure was examined using transmission electron microscopy following the irradiation. The irradiated microstructures generally feature a high density of perfect dislocation loops particularly at away from the graphite precipitates, and the C/Zr ratio shows a notable effect on the size and density of dislocation loops. The dislocation loops are identified as interstitial type perfect loops, and it was indirectly proved that the dislocation loop core likely consists of carbon atoms. Graphite precipitates that form with excess carbon in the super-stoichiometric ZrC are detrimental, and the dramatic increases in the size of and density of dislocation loops in the vicinity of graphite precipitates in ZrC phase were observed. Irradiation-induced faceted voids were only observed in $ZrC_{0.95}$, which is attributed to the pre-existing dislocation lines as biased sinks for vacancies.

1. Introduction

ZrC, with a cubic NaCl type crystal structure, has high melting point, exceptional hardness and good thermal and electrical conductivities. A comprehensive review on the properties of ZrC for nuclear fuel application was recently published by Katoh et al. [1]. ZrC has been considered for the deep burn TRISO (Tristructural-isotropic) fuel as an oxygen getter in the kernel, a coating layer for fission product retention, or a combination of these two functions as a direct coating on the fuel kernel. As a component of the TRISO fuel particle, ZrC is expected to experience high dose irradiation under the fuel operating temperature ranging from 850 to 1350 °C in a high temperature gas-cooled reactor (HTGR) [2]. Beside its potential nuclear fuel and nuclear propulsion applications, ZrC was also considered for many other industrial applications attributed to its high temperature stability and extreme hardness at room temperature.

Historically, the irradiation effects on ZrC were quite poorly understood and the majority of the available data were from the temperatures well below 850 °C [3–8]. Our previous work on commercial grade $ZrC_{1.01}$, proton irradiated at 800 °C, reveals that the irradiated microstructures are dominated with a high density of faulted dislocation loops, and slight changes in the lattice parameter, hardness and fracture toughness were also observed [4]. More recently, Snead et al. [9] studied zone-refined $ZrC_{0.93}$ irradiated with fast neutrons over a temperate range of 635–1480 °C. The microstructures were dominated with dislocation loops which gradually evolved from Frank loops to perfect loops as the irradiation temperature increased above 1280 °C.

It was widely reported that the properties of ZrC_x are often sensitive to the stoichiometry (C/Zr ratio) [10], and based on the Zr–C phase diagram (Fig. 1) [11], the carbon stoichiometry “x” ranges from slightly less than 0.6 to ~1.0. The high concentration of carbon vacancies or excessive graphite precipitates can significantly affect the various properties of ZrC_x, and the effect of C/Zr ratio on microstructures and properties was summarized by Katoh et al. [1]. The irradiation behavior is very likely affected by the C/Zr ratio. As a potential candidate coating layer for replacing the SiC coating of the Triso-coated fuel particle, the fabrication of ZrC coating has been investigated using chemical vapor deposition (CVD) methods by a number of groups [12–14], and it was revealed that the stoichiometry of the ZrC coating is very sensitive to the processing route and conditions and the ZrC deposited by CVD tends to have a hyper-stoichiometric C/Zr ratio. Therefore, it will be pertinent to systematically study the radiation response over a range of stoichiometry, and it is speculated that the radiation

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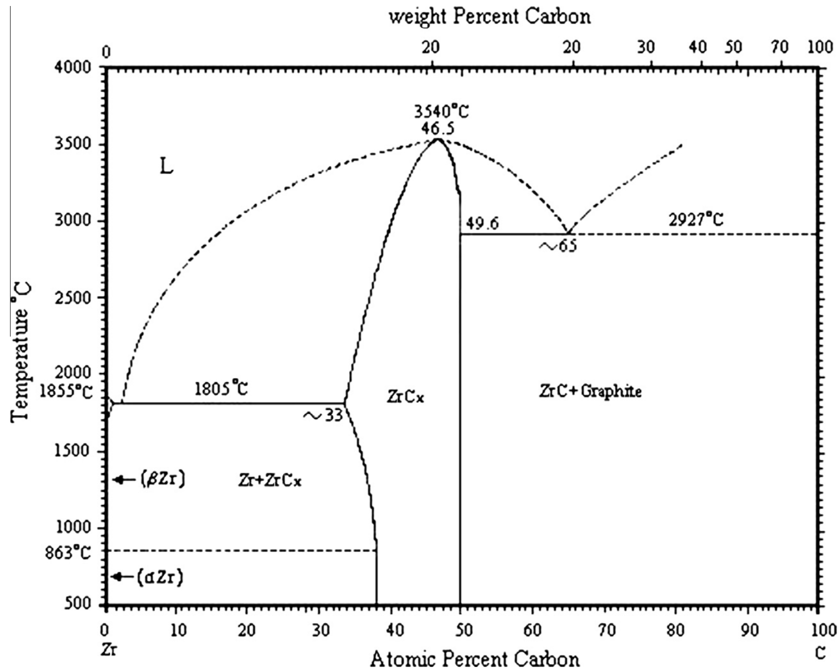

Fig. 1. Phase diagram of Zr–C system, modified from [11].

damage to sub-stoichiometric materials is relatively less than the nearly-stoichiometric or hyper-stoichiometric ones since the large number of carbon vacancies may provide a sink for irradiation produced defects in sub-stoichiometric ZrC.

This work investigated the effect of stoichiometry on the radiation response of high-purity ZrC irradiated at HTGR relevant temperature. The fundamental understanding on the radiation response over a range of stoichiometry will provide a baseline for a practical fabrication of ZrC-Triso (ZRISO) particle fuel from the aspect of radiation behavior.

Table 1
List of ZrC_x with five stoichiometries.

Sample	Target stoichiometry	Measured overall C/Zr	Measured C/Zr in matrix using WDS	Dimension
1	$ZrC_{0.8\pm0.05}$	0.84	0.81 ± 0.02	3 mm rod
2	$ZrC_{0.9\pm0.05}$	0.89	0.84 ± 0.03	
3	$ZrC_{1.0\pm0.05}$	0.95	0.92 ± 0.03	
4	$ZrC_{1.1\pm0.05}$	1.05	0.95 ± 0.01	
5	$ZrC_{1.2\pm0.05}$	1.17	0.98 ± 0.01	

2. Experiments

A series of high purity, zone-refined ZrC samples were provided by Oak Ridge National Laboratory (ORNL), and the materials were fabricated by Applied Physics Technologies, Inc. McMinnville, Oregon. These samples were prepared with five nominal C/Zr atomic ratios ranging from 0.8 to 1.2. As listed in Table 1, the overall bulk C/Zr ratios were determined by the vendor using mass-percent carbon analysis, and these ratio will be used to identify each material. The exact C/Zr ratio in the ZrC_x matrix was determined using a JEOL 733 Superprobe equipped with wavelength dispersive spectrometers (WDS). Consistently with the phase diagram, for the materials with a C/Zr ratio above one, the ZrC matrix is nearly stoichiometric with excessive carbon as graphite precipitates.

A set of 3 mm discs with a nominal 350 μm thickness were sliced from the ZrC rods and then mechanical polished down to a final finish of 50 nm using silica colloid for proton irradiation experiment. The proton irradiation was conducted using a Tandem accelerator the beam energy of 2 MeV. All the samples were irradiated in the same irradiation batch with two discs for each stoichiometry. The damage profile for the stoichiometric ZrC, calculated using TRIM2013 (Transport of Ions in Matter) [15] with the threshold displacement energies of 35 eV for zirconium and 25 eV for carbon, is shown in Fig. 2. Those threshold energies were used by Gosset [6] and they were based on the values observed in TaC. The K-P model was used the dpa (displacement per atom) calculation. The depth of the greatest interest is the shadowed region of 10–15 μm from the sample surface, and this region has a relatively constant radiation damage level. A fluence of 2.0×10^{19} protons/cm^2 was achieved, which corresponds to 2 dpa for the stoichiometric ZrC with a dose rate of approximately 1.8×10^{-5} dpa/s. Fig. 2 also shows the distribution of the measured irradiation temperature with a mean of 1125 °C. During the irradiation, the temperatures were monitored by two stage-embedded thermocouples, and the tips of thermocouple were spot-welded on the backsides of two Mo dummy discs that were irradiated together with the ZrC discs. The experimental temperature was achieved by heating the sample with a Pyrolytic Boron Nitride (PBN) heater and the proton beam, simultaneously.

After irradiation, a layer of 5 μm was removed for the irradiated surface, and then the samples were back thinned to about 15 μm using a wedge polisher. The TEM specimens were finally finished with ion milling at low angle to electron transparency. The cross-sectional TEM specimen was also prepared for the irradiated $ZrC_{0.89}$. Post-irradiation microstructural characterization was conducted using a Philips CM200 transmission electron microscope (TEM) and a Cs-corrected FEI Titan TEM for Z-contrast image at an atomic resolution. The characterizations were performed to reveal irradiation-induced defects including dislocation loops, voids, dislocation networks or new precipitate phases. For comparison, the unirradiated microstructures of ZrCs were also examined using TEM.