Electron irradiated ZrC layers in surrogate TRISO fuel particles

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1. Introduction

High temperature gas-cooled reactors (HTGRs) employ Tri-isotropic (TRISO) particle fuels, consisting of fuel kernels coated with buffer carbon, inner pyrolytic carbon, SiC, and outer pyrolytic carbon layers. Among the coatings, SiC layer is the most significant as it offers fission product retention and mechanical stability in irradiation environments. However, the SiC coating is prone to microstructural changes at temperatures around 1350 ℃ and may release fission products such as Pd and Ag. Consequently, post-irradiation experiments have revealed numerous failures in SiC coatings, decreasing the performance and safety of TRISO particle fuels during reactor operation. To overcome the limitations of SiC coatings, several solutions have been proposed.

One such solution is the replacement of SiC coatings with ZrC coatings, which offer superior properties such as high melting temperature, excellent thermal conductivity, low neutron absorption cross-section, and resistance to fission products. However, ZrC coatings are prone to changes in stoichiometry, and their microstructural and mechanical properties are susceptible to irradiation [1]. To address these limitations, the use of ZrC-SiC multi-layer coatings has been proposed, which has been used for the deep burn of specific isotopes in the core of TRISO particle fuels [2].

Despite numerous irradiation studies, very few experiments have utilized actual ZrC layers coated using Fluidized Bed Chemical Vapor Deposition (FBCVD) [3, 4], and none have utilized electrons for irradiating ZrC layers, which offer several advantages, including high-temperature irradiation and in-situ microstructure observation. This study aims to deposit ZrC and SiC coatings in surrogate TRISO particles using FBCVD and irradiate the ZrC layer using high-voltage electron microscopy to investigate the influence of irradiation on ZrC coating. Various material analyses, including in-situ microstructure investigation, defect observations, and selected area diffractions, will be carried out at irradiation temperatures of 15 ℃ and 700 ℃ and varying irradiation doses.

2. Experimental

The surrogate TRISO fuel particles including ZrC and SiC coatings were fabricated using FBCVD. Detailed preparation methods were reported elsewhere [5, 6] and are not provided in this study. For electron irradiation experiments utilizing HVEM (JEM ARM 1300S, JEOL Ltd.) with 1250 keV, thin-foil specimens were extracted at the interface between ZrC-SiC coating layers via the focused ion beam (FIB) method. The HVEM chamber was maintained at 2×10^{-6} Pa during irradiation and microstructure observations. The irradiation was carried out at 15 ℃ and 700 ℃ for varying durations ranging from 30 minutes to 3 hours, resulting in various damage doses. The electron irradiation damage was calculated using the following equation [7]:

$$D = J\alpha_d \quad (1)$$

Here, D represents the damage, J denotes the electron fluence, and α_d is the electron displacement cross-section. The estimated electron irradiation damages were found to be 0.4 dpa/h and 1.1 dpa/h at 15 ℃ and 700 ℃, respectively.

3. Results

The prepared surrogate TRISO particles with ZrC-SiC coatings are shown in Fig. 1. The ZrO_2 beads with a diameter of ~500 μm were coated with a ~100 μm thick porous buffer layer, a ~35 μm thick IPyC layer, and ZrC and SiC layers. The microstructures of both the ZrC and SiC coating layers appeared to be sound without any noticeable cracks, and their interfacial contact was excellent without any gaps or pores visible in the images.

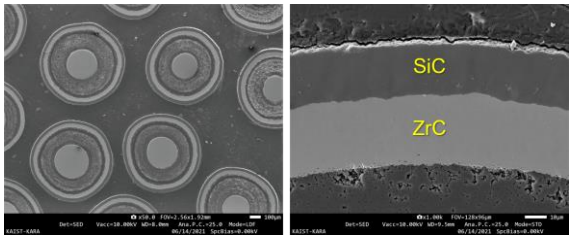

Fig. 1. SEM micrographs of as-coated ZrC and SiC layers in surrogate TRISO fuel particles.

Fig. 2 presents in-situ bright field transmission electron microscopy (BFTEM) images of ZrC layers irradiated with electrons at 15 ℃ between 0.4 and 1.2 dpa in three different magnifications. The irradiated specimens showed the production of numerous black-dot defects, and their densities increased with higher damage doses. It has been established in the literature

that the black dots observed in irradiated ZrC are typically defect clusters or dislocation loops [8]. Previous work by Gesset et al. [9] has suggested that the black dots observed in Au ion irradiated ZrC were small faulted interstitial loops based on the results of molecular dynamic simulations. Interestingly, the uniform distribution of black dots observed in the ZrC grain at 0.4 dpa became inhomogeneous in EIL-0.8 and EIL-1.2. The black-dot density near the grain boundary appeared to be higher than that in the center when exposed to higher damage doses. This phenomenon is known as a defect preferred zone, which extends to approximately 100 nm from the grain boundary and occurs because the grain boundary is a good sink for defect transport. The highest magnification images reveal the diffusion of defects and related material transport. The pore was filled by ZrC, while the ZrC region turned into a porous area with a higher irradiation damage. These observations suggest that defect diffusion and material transportation readily occur with electron irradiation and relatively low estimated damage dose.

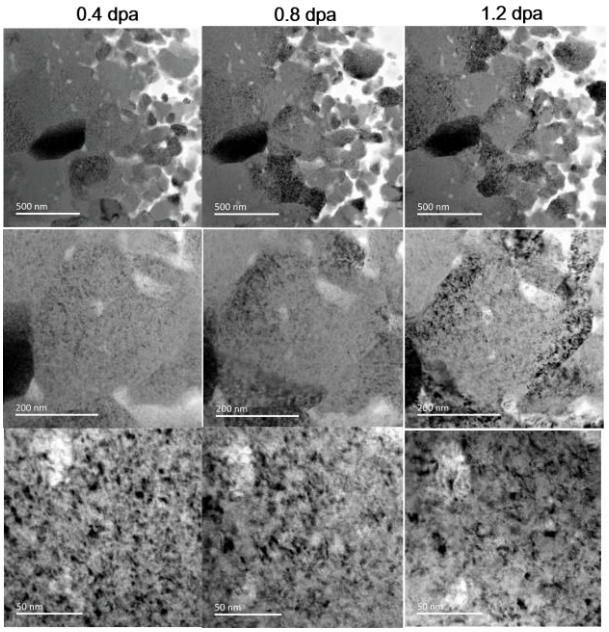

Fig. 2. In-situ BF-TEM profiles of ZrC electron irradiated up to 1.2 dpa at 15 ℃ in three different magnifications.

Fig. 3 shows BFTEM images of ZrC electron irradiated up to 3.3 dpa at 700 ℃ taken at two different magnifications. The formation of black dots with increasing damage dose is much more pronounced than that observed at 15 ℃ (see Fig. 2). The intense formation of black dots covered the grain boundary, obscuring the grains even after 1.1 dpa irradiation. The observed defect preferred zone near the grain boundary in the specimen irradiated at 15 ℃ was not observed at 700 ℃. Instead, the cluster of black dots is observed with increasing damage dose. The active defect transfer between neighboring grains is also revealed. Another interesting observation is the formation of nanocrystals in the original ZrC grain electron irradiated at 3.3 dpa. The fact that the recrystallization temperature of ZrC is between 1800 ℃ and 1900 ℃ implies that the irradiation temperature of 700 ℃ is not the main driving force for the emergence of the nanocrystals. Therefore, this phenomenon should be the result of irradiation-induced recrystallization. Before the formation of nanocrystals, the original ZrC grain was difficult to recognize, and the distinct grain boundary of non-irradiated ZrC became unclear with increasing dose to 3.3 dpa. This process could be amorphization, which commonly occurs before irradiation-induced recrystallization [10]. It is also known that irradiation-induced amorphization can occur in complex ceramics, except oxides. Although the irradiation-induced recrystallization of ZrC has not yet reported in the literatures, it is often observed in most commercial nuclear fuels including UO_2 [11].

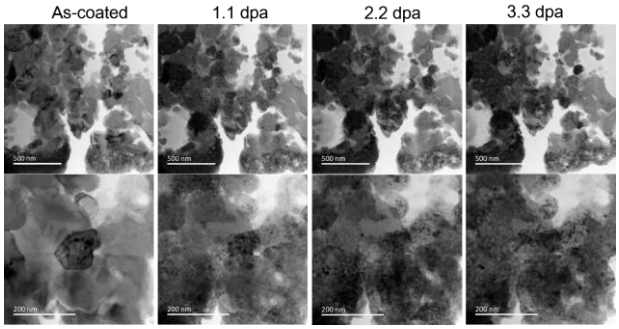

Fig. 3. In-situ BF-TEM profiles of ZrC in ZrC electron irradiated up to 3.3 dpa at 700 ℃ at two different magnifications.

4. Conclusions

The electron irradiation of ZrC at relatively low doses has resulted in substantial microstructural changes. Increasing irradiation dose has led to a greater formation of black dots, and active transfer of defects through grain boundaries has been observed. Notably, the irradiation-induced recrystallization of ZrC has been observed, characterized by a process involving the decomposition of original grains, amorphization, and the formation of nanostructures. This phenomenon has a significant impact on the swelling behavior of ZrC in reactor environments. Further research is required to evaluate the properties of ZrC in high-dose and high-temperature reactor core environments.

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