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Structure of ion tracks in ceria irradiated with high energy xenon ions

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ABSTRACT

Structure and accumulation behavior of ion tracks in CeO_2 irradiated with 200 MeV Xe ions were examined by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) to obtain fundamental knowledge on the microstructure evolution induced by fission fragments in nuclear fuels and transmutation targets, which is of importance for the development of advanced fuel/target materials at high burn-up conditions. Bright-field (BF) TEM images of ion tracks from an inclined direction showed Fresnel contrast along penetrating path of incident ions. The signal intensity of high-angle annular dark-field (HAADF) STEM images was decreased at the core damage region of ion tracks along the path of ions, revealing the reduction of atomic density inside the ion track. Preferential formation of smaller and larger ion tracks was observed at a high ion fluence of 1×10^{14} cm^{-2} compared to a low ion fluence of 1×10^{11} cm^{-2}. Results were discussed due to the coalescences and incomplete recovery of the core damage regions during the overlap of high density electronic excitation damage, which is induced during the repetition of the formation and recovery of ion tracks within an influence region.

1. Introduction

Oxide ceramics with a fluorite-type structure, such as uranium dioxide, fully stabilized cubic zirconia and cerium dioxide are known as radiation tolerant materials (Sickafus et al., 1999a), and those oxides have been incorporated as nuclear fuels in light water reactors and have potential applications as nuclear waste (Sickafus et al., 1999b), inert matrix forms (Yamashita et al., 1999; Pouchon et al., 2003; Degueldre and Yamashita, 2003; Degueldre, 2007), and a transmutation target (Delage et al., 2011). Among the radiation sources under those environments of fuels and target materials, radiation damage induced by fission fragments (FFs) that have typical kinetic energies in the range of 70–100 MeV, is one of the crucial issues: the electronic energy loss of FFs reaches around 20 keV nm^{-1}, which induces high density electronic excitation along the penetrating path of FFs to results in the formation of cylindrical or tubular defect of ion tracks, in which amorphous region or voids surrounded by a defective region is formed (Toulemonde et al., 2006).

Previous investigations of ion tracks by transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques in fluorite-type oxides such as UO_2 (Wiss et al., 1997; Sonoda et al., 2010; Ishikawa et al., 2013), Y_2O_3-ZrO_2 (Sickafus et al., 1998; Moll et al., 2009), ThO_2 (Tracy et al., 2014) and CeO_2 (Sonoda et al., 2006; Yasuda et al., 2013) have shown that the structure around individual ion tracks is not amorphous and retains the fluorite structure. Bright-field (BF) TEM observations have shown that ion tracks exhibit Fresnel contrast. Scanning transmission electron microscopy (STEM) observations with high-angle annular dark-field (HAADF) and annular bright-field (ABF) techniques revealed the retained fluorite structure of the ion tracks in CeO_2 from an end-on direction (Takaki et al., 2014). Analysis on STEM signal intensity showed the reduction of the signal intensity at the core damage region of the ion track, which was discussed to be attributed to the decrease in the atomic density at the core damage region of the ion track (Takaki et al., 2014).

It is also important to note that prolong irradiation under high fluence conditions has induced high density of dislocations and formed sub-micron size fine-grain structure (Garrido et al., 2009; Yasuda et al., 2013). Significant overlap of radiation damage with high density electronic excitation will be induced in nuclear fuels and target materials under the environment of nuclear reactors: the interval of the spike of FFs was estimated to be 100 s with an

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assumption of the ion track size of 20 nm in diameter (Kinoshita, 2006), corresponding to the damage overlaps in the order of 10^5 times during one year exposure. The development of fine-grain structure with a size of 100 nm or less with high density dislocations has been discussed to be a cause of *rim structure* formation (Kinoshita et al., 2009; Sonoda et al., 2010), which has been found in UO_2 nuclear fuels at high burn-up conditions (Une et al., 1992; Cunningham et al., 1992; Matzke and Spino, 1997). Therefore, detail knowledge on the structure and size of ion tracks in fluorite-type oxides is essential to understand the microstructure evolution and to assess the stability of fuel/target materials at the high burn-up radiation environments.

This paper deals with the structure of ion tracks in CeO_2, which has received attention as a surrogate material for UO_2 because of its identical crystal structure and similar thermal and physical properties (Sonoda et al., 2006; Yasunaga et al., 2006; Ishikawa et al., 2008; Guglielmetti et al., 2008; Kinoshita et al., 2009; Ye et al., 2011), irradiated with 200 MeV Xe ions. Results on TEM and STEM observations and analysis including atomic resolution observations of ion tracks are reported to further discuss the atomic structure and accumulation behavior of ion tracks in CeO_2.

2. Experimental

CeO_2 powders of 99.99% purity (Rare Metal Corp.) were compacted into pellets by uniaxial pressing, followed by hydrostatic pressing in water with a pressure of 150 MPa. These pellets were sintered at 1873 K for 12 h in air to obtain sintered compacts with 98.5% of the theoretical density. The size of grains was evaluated to be around 5 μm. Disk specimens with 3 mm in diameter and 150 μm in thickness were prepared by mechanical polishing, and were irradiated with 200 MeV Xe^{14+} ions at an ambient temperature to ion fluences of 3×10^{11}, 3×10^{12}, and 1×10^{14} cm^{-2} in a Tandem accelerator at Japan Atomic Energy Agency-Tokai. The irradiated specimens were mechanically dimpled at the centered part from the opposite side of the ion-irradiated surface, followed by the conventional Ar ion-thinning to prepare thin-foil specimens for plan-view observations around the irradiated surface region. The thin-foil specimens were finally polished with 0.5 keV Ar ions to minimize the Ar-ion damage. Also, the irradiated surface region was slightly polished with 0.5 keV Ar ions to remove the contaminated surface layer. The electronic (S_e) and nuclear (S_n) stopping power of 200 MeV Xe ions was calculated by the SRIM (Stopping and Range of Ions in Matter) code (Ziegler et al., 1985) to be 27 keV nm^{-1} and 0.1 keV nm^{-1}, respectively, at the irradiated surface region. The value of electronic energy loss of 200 MeV Xe ions at the surface region is rather high compared to the one induced by FFs in nuclear fuel/target materials (around 20 keV nm^{-1}). A higher electronic stopping power is used in the present study to investigate the structure of ion tracks under a condition well exceed the threshold value of ion track formation (15 keV nm^{-1}). It is also noted that most of incident ions penetrate the surface region (less than around 200 nm in thickness), at which TEM and STEM observations were performed in the present study. Microstructure observations were performed with BF imaging using a conventional TEM (JEM-2100HC, JEOL Ltd.) operated at 200 kV. The electron beam flux during microstructure observations is reduced to be around 1×10^{18} cm^{-2} s^{-1}, and the adjustment of diffraction condition and beam alignments were performed at a neighbor region to avoid electron beam damage. The morphology and density of ion tracks were confirmed not to be changed during taking micrographs at the observation condition, although a high intensity focused electron beam irradiation higher than 10^{19} cm^{-2} s^{-1} for a prolong time induce dislocation loops consist of oxygen ions (Takaki et al., 2013). Atomic resolution observations were also performed by STEM *Z*-contrast imaging using a TEM equipped with a spherical aberration corrector (JEM-ARM200F, JEOL Ltd.). Two kinds of STEM techniques, HAADF- and ABF-STEM imagings, were utilized for the atomic resolution observations: HAADF-STEM is advantageous for atomic scale imaging of heavy elements (Lee et al., 2011), or Ce-cation in the present study, as its signal intensity is proportional to the square of the atomic number (Z^2) (Pennycook and Jesson, 1991), and ABF-STEM is beneficial to detect light (O-anion) and heavy (Ce-cation) elements at the same time (Hojo et al., 2010; Ishikawa et al., 2011), owing to the rather weak dependence of the signal intensity on $Z^{0.3}$ (Findlay et al., 2010). The diffraction angles of electron beam to the inner and outer edge of the annular detector were 90 mrad and 170 mrad, respectively, for HAADF image and 11 mrad and 22 mrad, respectively, for ABF image. Microstructure observations for STEM Z-contrast were performed with a condenser aperture of 30 μm in size and a spot size of 8, which corresponds to the beam intensity of 26 pA. Adjustments for the diffraction and beam conditions were also performed at a neighbor region and the illumination of electron beam on the interested region was limited for the taking microstructure. It has been shown from the previous study that a high intensity focused electron beam induces the reduction in CeO_2 [Garvie and Buseck, 1999]. Microstructure of ion tracks and EELS (Electron Energy Loss Spectroscopy) spectrum were confirmed not be changed significantly during the observation conditions used in the present study.

3. Results and discussion

It is shown in previous TEM observations in fluorite-type oxides, such as UO_2 (Sonoda et al., 2010; Ishikawa et al., 2013), stabilized cubic zirconia (Moll et al., 2009), and CeO_2 (Sonoda et al., 2006; Yasuda et al., 2013) that ion tracks exhibit Fresnel contrast at defocused kinematical diffraction conditions in BF TEM images. TEM and X-ray diffraction analysis have revealed that the fluorite structure is retained (Sickafus et al., 1999a; Moll et al., 2009; Sonoda et al., 2006; Ishikawa et al., 2013), and the origin of Fresnel contrast of ion tracks was discussed in terms of the reduction of atomic density at the core damage region of ion tracks (Yasuda et al., 2013). Fig. 1 shows BF TEM images of an identical region in CeO_2 at the surface region from an inclined direction, irradiated with 200 MeV Xe ions to an ion fluence of 3×10^{11} cm^{-2}. The micrographs were taken with over- or under-focus kinematical diffraction conditions with defocus values of $\Delta f = \pm 0.5$ μm, where Δf is defined as the defocus value from the just focus condition. In Fig. 1, black or white rod-like contrasts are observed along the trajectory of incident ions with 2–3 nm in width for (a) over- and (b) under-focus conditions, respectively. Such reverse of contrast with focus conditions reveals that ion tracks appear as Fresnel contrast along the trajectory of ions, which indicates that the atomic density is decreased along the trajectory of ions at the core damage region of ion tracks. It is worth noting that Fresnel contrast appears as strings of dot-contrasts or with modulating the intensity of contrasts along the penetrating paths. Further, a part of ion tracks in Fig. 1(a) and (b) appears as bar contrasts with shorter lengths than others, although the value of electronic energy loss (27 keV nm^{-1}) well exceeds the threshold value of electronic energy loss for the track formation (15–16 keV nm^{-1}) (Sonoda et al., 2008). It has been shown in an amorphisable insulator of $Y_3Fe_5O_{12}$ (Houpert et al., 1989; Toulemonde et al., 2006) that the morphology of amorphous track region changes from individual spherical shape, discontinuous elongated bar, and continuous and homogeneous cylindrical shape with increasing electronic energy loss. The result shown in Fig. 1, therefore, suggests that the electronic energy loss to form continuous ion track in CeO_2 appeared as Fresnel contrast with BF