Available online at www.sciencedirect.com

ScienceDirect

Nuclear Instruments and Methods in Physics Research B 266 (2008) 2877–2881

NIM B Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Electron energy-dependent formation of dislocation loops in CeO_2

K. Yasunaga [a,*], K. Yasuda [a], S. Matsumura [a], T. Sonoda [b]

[a] Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka 819-0395, Japan

[b] Nuclear Technology Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), Komae, Tokyo 201-8511, Japan

Available online 31 March 2008

Abstract

High-voltage transmission electron microscopy (HVTEM) was used to examine the formation of dislocation loops as a function of incident electron energy to reveal the formation of defects and kinetics in CeO_2. In the case of electron irradiation methods with an energy range from 200 to 1250 keV, interstitial-type non-stoichiometric dislocation loops of the 1/9<1 1 1>{1 1 1} type were formed by the aggregation of oxygen ions. In contrast, interstitial-type perfect dislocation loops of the 1/2<1 1 0>{1 1 0} type were formed with electron irradiations with an energy range from 1500 to 3000 keV. The formation of perfect dislocation loops induced by incident electrons above 1500 keV indicated the displacement of both constituent ions with elastic collisions of electrons. Based on the findings of the formation and growth behavior of each interstitial-type dislocation loop caused by different displacement conditions, we estimated the threshold displacement energies of the sublattices and the migration energy of Ce vacancy in CeO_2.

PACS: 61.72.Cc; 61.72.Ff; 61.72.Lk; 61.72.Nn; 61.80.Fe; 61.82.Ms; 68.37.Lp

Keywords: High-voltage electron microscopy (HVEM); Fluorite structure; Cerium dioxide (CeO_2); Point defects; Dislocation loops; Migration energy

1. Introduction

Metallic oxides with a cubic fluorite structure including ceria (CeO_2) and yttria-stabilized cubic zirconia (YSZ) are ion conduction ceramics due to their high mobility of oxygen vacancies. Recent studies on the behavior of oxygen vacancies in CeO_2 have been conducted for the possible application to fuel-cell electrodes at lower operation temperatures than that for YSZ [1]. However, up until now, only limited information has been available for the Ce ion and its point defects in CeO_2. We investigated the radiation response induced by energetic particles in CeO_2 as simulation material of UO_2. Therefore, it is necessary to understand the fundamental properties of point defects not only of oxygen ions but also cerium ions and to confirm the similarities in the formation of secondary defects.

Fluorite-type oxides are polyatomic systems with significantly different properties for cations and anions. There is a big difference in mass between the cation and anion sublattices in CeO_2; therefore, the displacement conditions for the cations and anions would vary depending on the incident electron energy. In fact, in a more recent article, we showed the formation of non-stoichiometric dislocation loops in CeO_2 under electron irradiation conditions below 1000 keV [2]. The dislocation loops can be referred to as oxygen platelets formed after the selective displacements of the oxygen sublattice.

Due to the large difference in mass between the Ce and O ions, the structures of the defect clusters formed under electron irradiation are expected to depend on the incident electron energy. Therefore, it is expected to be able to extract the threshold displacement energy of each sublattice and the migration energy of each point defect, independently, in CeO_2. The present study aimed to clarify the structures of the dislocation loops in CeO_2 under the condition whether the displacement of Ce ions occurs. The nucleation and growth processes of the dislocation loops in CeO_2 were systematically investigated as a function of incident electron energy by high voltage electron microscopy.

* Corresponding author. Tel./fax: +81 92 802 3488.
E-mail address: yasunaga@nucl.kyushu-u.ac.jp (K. Yasunaga).

0168-583X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2008.03.204

2. Experimental

CeO_2 pellets were prepared by compacting CeO_2 powders (99.99% purity, Rare Metallic Corporation) by uniaxial pressing using a pressure of 50 MPa and subsequent hydrostatic pressing in water (150 MPa) for densification. Polycrystalline CeO_2 specimens with grain size of about 5 μm in diameter were obtained by sintering the pellets at 1673 K for 12 h. These pellets were covered by CeO_2 powders to avoid direct contact between the pellets and an alumina melting pot during sintering.

Disk specimens of 3 mm in diameter and 100 μm in thickness were prepared by mechanical polishing, followed by mechanical dimpling and Ar-ion thinning processes to prepare wedge-shaped thin foil specimens suitable for transmission electron microscopy. The thin foil specimens were subjected to *in situ* observations under electron irradiation. Three kinds of electron microscopes, i.e. a conventional TEM (JEM-2000EX, JEOL Ltd.) and a high voltage electron microscope (JEM-1000, JEOL Ltd.) at the HVEM laboratory of Kyushu University; and an ultra-high voltage electron microscope (H-3000, Hitachi Ltd.) at the UHVEM center of Osaka University, were used to cover a wide range of electron energy from 200 to 3000 keV. The irradiation temperatures ranged from 300 to 1073 K and the electron beam flux (ϕ) was 1×10^{23} and 3×10^{23} e^-/m^2 s.

3. Results and discussion

3.1. Non-stoichiometric dislocation loops in CeO_2 below 1250 keV of electron irradiation

Fig. 1 shows the bright-field images of the dislocation loops in CeO_2 formed with 200–1250 keV electrons to an identical fluence of 3×10^{26} e^-/m^2 at 296 K. In these bright-field images, the dislocation loops show black elliptical strain contrast. Larger dislocation loops with lower density were seen noticeably with 200 and 500 keV electron irradiations, accompanied with strong strain contrast which indicated the existence of large strain fields in the lattice. Although the size and density of these dislocation loops depend on the incident electron energy, they have the same nature. Image contrast and trace analyses revealed that the nature of the dislocation loops involved faulted-interstitial loops lying on the {1 1 1} planes with the Burgers vector parallel to the <1 1 1> directions and normal to the habit plane [2].

High-resolution transmission electron microscopy (HRTEM) imaging of a dislocation loop lying between the arrowheads on the (1 1 1) plane, as shown in Fig. 2(a), also confirmed the stacking fault. Since an additional

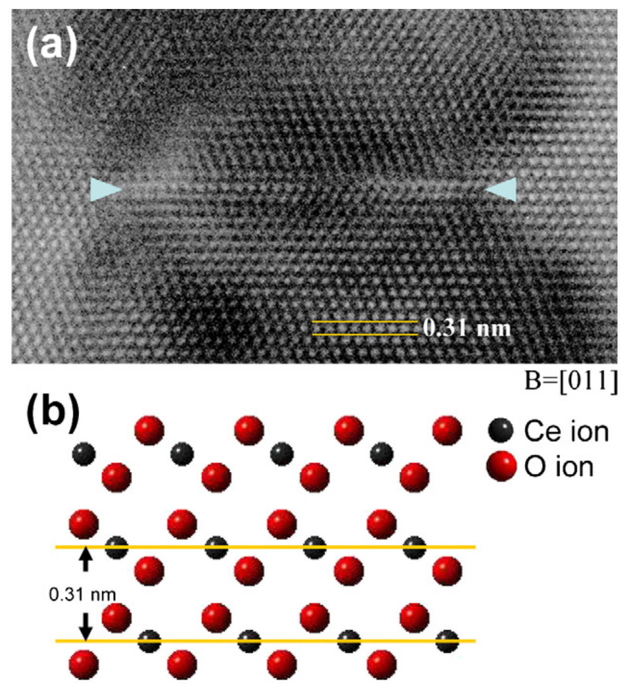

Fig. 2. HRTEM image of a dislocation loop on (1 1 1) in CeO_2, showing the stacking fault (a) and the stacking sequence on (1 1 1) of the fluorite structure (b). This micrograph is taken along the [011] direction with an acceleration voltage of 400 kV.

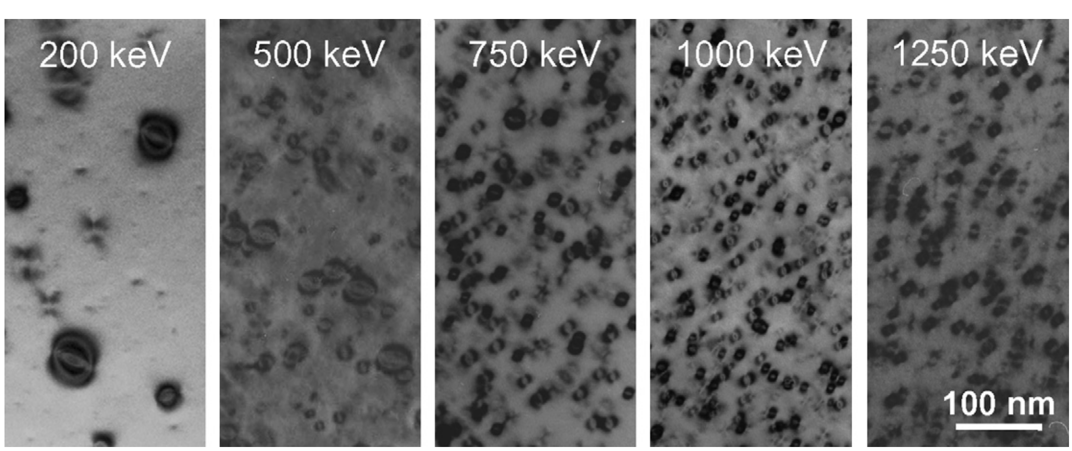

Fig. 1. Bright-field images of interstitial-type non-stoichiometric dislocation loops formed with 200–1250 keV electrons to a fluence of about 3×10^{26} e^-/m^2 at 296 K in CeO_2. These micrographs are taken along the [0 1 1] direction with $g = 11\bar{1}$.