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Structural changes in helium implanted $Zr_{0.8}Y_{0.2}O_{1.9}$ single crystals characterized by atomic force microscopy and EXAFS spectroscopy

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Abstract

The present work is devoted to investigate the local atomic environment (of Zr, Y and O) as well as surface modifications associated with excess helium in the cubic phase of (1 0 0)-oriented $Zr_{0.8}Y_{0.2}O_{1.9}$ single crystal substrates. Commercially available oxide crystals have been implanted at various fluences in the range 0.15–2.0 × 10^{16} He-atoms/cm^2 using a 2.74 MeV He^+ ion beam passing through a 8.0 μm Al foil. The microstructure and surface morphology of the irradiated surface are examined using atomic force microscopy (AFM). The local atomic environments of Zr, Y and O in the implanted layer are studied using synchrotron radiation and by extended X-ray absorption fine structure (EXAFS) measured at glancing angles to probe the implanted layer. From AFM studies it was observed that the surface roughness increases as fluence increases and above a critical fluence stage, small blister-like structures originating from helium bubbles are scattered on the irradiated surface. The radial distribution functions (RDFs), derived from EXAFS data at the Zr K-edge, have been found to evolve continuously as a function of ion fluence describing the atomic scale structural modifications in YSZ by helium implantation. From the pristine data, long range order (beyond the first- and second-shell) is apparent in the RDF spectrum. It shows several nearest neighbour peaks at about 2.1, 3.6, 4.3 and 5.4 Å. In the implanted specimens, all these peaks are greatly reduced in magnitude and their average positions are changed, typical of damaged material. A simple model taking into account only the existence of lattice vacancies has been used for the interpretation of measured EXAFS spectra.

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Keywords: Helium implantations; Stabilized zirconia; Point defects

1. Introduction

Understanding the effect of helium in stabilized cubic zirconia is crucial for the development of materials resistant to irradiation under fusion and fission conditions. Cubic zirconia is also a potential candidate as inert host matrix fuel (IMF) for transmutation of minor actinides in the management of high-level nuclear waste as well as specifically-devoted nuclear reactors. These applications are based on zirconia's inherent properties in a wide range such as low thermal conductivity and excellent chemical durability, high melting point and toughness, high solubility for actinides and exceptional stability under irradiation conditions. Therefore, the behaviour of helium in zirconia has been extensively studied, both theoretically and experimentally, since many years [1]. A variety of experimental techniques such as transmission electron microscopy (TEM), Rutherford backscattering spectrometry and channeling (RBS/C), positron annihilation spectroscopy, etc. has been

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used for understanding the defect structures and materials modifications in helium implanted zirconia. Cationic disorder and oxygen disorder are among the main factors which affect the transport properties of helium in the implanted layer. Some work has also concentrated on the aspects of helium retention and remission [2], helium thermal desorption [3], transport mechanism and related phenomena [4]. It is now established that the degree of radiation swelling and properties of IMF strongly depends on its microstructures and testing scenario [5]. Although the basic helium migration mechanisms are well known, however, due to the complexity of the problem there are still many unknowns regarding He migration in the presence of defects. Thus, an atomic scale description of the lattice disorder in zirconia, which is local in particular and element-specific providing definitive information on the near-neighbour atomic environment, is essential. In this work, we have studied local structural changes of the atomic distributions in helium implanted $Zr_{0.8}Y_{0.2}O_{1.9}$ single crystals using X-ray absorption fine structure (XAFS) spectroscopy technique, both extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). Other experimental techniques mentioned above already employed for the description of lattice disorder in zirconia are not sensitive to any small change in the local atomic distributions. To simulate defects at various levels the oxide crystals were implanted with helium ions at various fluences. Finally, the changes of surface morphology as well as defects at the irradiated surface have been examined using atomic force microscopy (AFM).

2. Experimental and XAFS data analysis

Details of the experimental arrangement for helium implantations are described in one of our recent publications [1] and only a short description is provided here. Commercially available single crystals of cubic zirconia stabilized with yttria [$Zr_{0.8}Y_{0.2}O_{1.9}$ (1 0 0), hereafter YSZ] have been used in the present study. The size of each crystal was $10 \times 10 \times 0.5\ mm^3$ and they were polished to optical finish by the manufacturer. In order to heal the intrinsic (native) point defects as well as near-surface defects induced during polishing, the as-received crystals were preannealed for 1.5 h at about 1250 °C in air and slowly cooled inside the furnace. Thereafter, separate substrates have been implanted at room temperature with a beam of 2.74 MeV He^+ ions passing through a 8.0 μm Al foil, covering a fluence range from 1.5×10^{15} to 2.0×10^{16} He-atoms/cm^2. The use of absorber foil provides a wide depth distribution of incorporated He due to large energy straggling of projectile ions in the Al foil. It also brings the implanted layer closer to the surface which was convenient for later analyses.

After the samples preparation the surface morphology of the as-implanted and annealed specimens was observed with a commercial AFM (Nanoscope III from Digital Instruments Ltd.) operated in the tapping mode. The images were treated with a second-order flattening routine and the root-mean-square (rms) values for the surface roughness were determined. Flattening and rms determination were carried out using the manufacturer's software. Unless otherwise stated, rms values were calculated based upon $5 \times 5\ \mu m^2$ scan images, taken at a resolution of 512×512 points.

In order to determine the local atomic configuration of constituent elements in irradiated YSZ, i.e. the nearest-neighbour atomic distance, the relative coordination number and similar information for some successive shells, we utilized the X-ray absorption spectroscopy (XAS) facility available at the Hamburg synchrotron radiation laboratory (HASYLAB at DESY, Hamburg), on the ROEMO-1 beam line under dedicated ring conditions (4.5 GeV, 140 mA). All measurements have been made in the reflection mode using grazing incidence geometry (of 3.0° providing an X-ray attenuation length ~1.2 μm at 18 keV) to enhance the contribution of the implanted layer. The incident X-ray intensities were measured by means of a gas-flow proportional counter. The specimens were held at room temperature and the fluorescence excitation spectra at the Zr K-edge were collected with an energy dispersive solid-state silicon detector. Data were also recorded from a pristine YSZ for use as structural comparators and reference spectrum. For calibrating the energy output of cooled Ge (1 1 1) double-crystal Bragg monochromator, the K-edge excitation energy of 17998 eV measured from a high purity zirconium metallic foil, was set equal to the maximum of the first derivative of the XANES data. The experimental station is currently equipped with a diffractometer which gives great freedom to the process of sample alignment, e.g. exposing the ion implanted area with X-ray beam, very precise control of the glancing angle of incidence, adjustment of the specimen height, etc. These were indeed very important in the present work for carrying out the measurements.

XAFS data processing and numerical analysis were performed using the computer program IFEFFIT [6]. Considering the measurements geometry, an appropriate correction has been applied to all the measured data for the self-absorption effect [7]. The first step in the data analysis was a background subtraction. We used a linear function in the pre-edge region and a spline fit above the absorption edge. The threshold position E_0 was determined from the maximum of the first derivative of an absorption curve. Thus, background removed EXAFS function $\chi(k)$ was extracted and normalized by the edge jump height. $\chi(k)$ was then multiplied by k^3 to emphasize the higher k region. Thereafter, k^3-weighted EXAFS was Fourier transformed (FT) into real space to obtain a radial distribution function (RDF) of the near-neighbours around the absorber atom. Transform termination effects were minimized by choosing an appropriate window range bounded by minima in $|\chi(k)|$ and using a Hanning window function that smoothed the ends of the region to zero. Phase shift corrected real distances were determined by the Fourier filtering technique for the spectra.