



Atomic structure and composition of the yttria-stabilized zirconia (111) surface

Vedran Vonk^{a,b,c,*}, Navid Khorshidi^b, Andreas Stierle^{c,d,b}, Helmut Dosch^{c,b}

^a Radboud University Nijmegen, Institute for Molecules and Materials, NL-6525AJ Nijmegen, The Netherlands

^b Max Planck Institute for Intelligent Systems (former Max Planck Institute for Metals Research), D-70569 Stuttgart, Germany

^c Deutsches Elektronen-Synchrotron (DESY), D-22607 Hamburg, Germany

^d Fachbereich Physik, Universität Hamburg, D-20355 Hamburg, Germany

ARTICLE INFO

Article history:

Received 23 January 2013

Accepted 21 February 2013

Available online 27 February 2013

Keywords:

Oxide surfaces

Surface structure

Solid-oxide fuel cell

SOFC

Cubic YSZ

Yttria stabilized zirconia

ABSTRACT

Anomalous and nonanomalous surface X-ray diffraction is used to investigate the atomic structure and composition of the yttria-stabilized zirconia (YSZ)(111) surface. By simulation it is shown that the method is sensitive to Y surface segregation, but that the data must contain high enough Fourier components in order to distinguish between different models describing Y/Zr disorder. Data were collected at room temperature after two different annealing procedures. First by applying oxidative conditions at 10^{-5} mbar O_2 and 700 K to the as-received samples, where we find that about 30% of the surface is covered by oxide islands, which are depleted in Y as compared with the bulk. After annealing in ultrahigh vacuum at 1270 K the island morphology of the surface remains unchanged but the islands and the first near surface layer get significantly enriched in Y. Furthermore, the observation of Zr and oxygen vacancies implies the formation of a porous surface region. Our findings have important implications for the use of YSZ as solid oxide fuel cell electrode material where yttrium atoms and zirconium vacancies can act as reactive centers, as well as for the use of YSZ as substrate material for thin film and nanoparticle growth where defects control the nucleation process.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Atomic structure, composition and characteristic defects of yttria-stabilized zirconia (YSZ) surfaces are key to a basic understanding of this application relevant material. YSZ is for example frequently used in solid oxide fuel cells (SOFCs), which are regarded as a very promising technology to generate in a clean way electricity by direct conversion from chemical energy [1]. In such SOFCs, YSZ acts as solid electrolyte for oxygen ions and the surface and its interface with the electrode material play a central role in the relevant reactions: it is involved in the adsorption and oxidation of hydrocarbons, the formation of H_2O and the oxidation of carbon monoxide at the anode as well as the dissociation and incorporation of oxygen at the cathode surface [1,2]. Hence, knowledge of the atomic structure and composition of YSZ surfaces and in particular characteristic defects is indispensable for a basic understanding of solid oxide fuel cell performance. Furthermore, details of the YSZ(111) atomic surface structure are crucial for an atomistic description of thin film and nanoparticle growth, for which YSZ is frequently used as substrate material [3].

The mostly used composition of YSZ contains 9.5 mol% yttria, which stabilizes the cubic phase of zirconia (C-YSZ) [4]. Density functional theory (DFT) calculations on low index C-YSZ surfaces predict that the non-polar, oxygen terminated (111) surface is the most

stable one [5]. Despite its technological importance, experimental investigations of the C-YSZ(111) surface are scarce. Only recently it was observed by scanning tunneling microscopy (STM) at elevated temperatures that this surface exhibits a high number of defects [6], which are known to be important for surface reactions. Furthermore, at typical operation temperatures above 1000 K, a variation of the Y to Zr ratio is reported to change the performance of fuel cell devices considerably [7]. Contradictory results on Y and Zr surface segregation are reported, making a reconsideration of related chemical potentials necessary [6,8–10].

Here we present a combined anomalous and nonanomalous surface X-ray diffraction (SXRD) study to resolve the atomic structure and composition of the (111) surface of a 9.5 mol% yttria doped ZrO_2 single crystal. Anomalous SXRD allows an X-ray scattering contrast variation between Zr and Y, which is essential for an element specific study of surface segregation [25]. To elucidate the role of the chemical environment on the surface structure and composition we employed two different sample treatments which are close to the conditions at the fuel cell cathode and the anode, respectively: A) heating the as-received sample at 700 K for 120 min at an oxygen pressure of 10^{-5} mbar (more oxidative), B) heating the sample to 1270 K for 145 min under ultra-high vacuum (UHV) conditions (more reductive). After these treatments the samples were quenched down to room temperature and it is to be expected that already segregated species remain in the near surface region.

Accompanying the data analysis we present surface structure factor calculations based on a statistical fluorite model for the YSZ

* Corresponding author at: Deutsches Elektronen-Synchrotron (DESY), D-22607 Hamburg, Germany. Tel.: +49 4089986012.

E-mail address: vedran.vonk@desy.de (V. Vonk).

bulk structure and the so-called Zr-shift model which is a more elaborate description based on the occupation of high symmetry sites by Y atoms and specific displacements of the surrounding Zr and O atoms. Although the final fits do not make use of the Zr-shift model, it is included here to show the sensitivity of the used technique and as a basis for future work.

2. Experimental details

Commercially available, wet-chemically polished YSZ single crystals with a miscut $<0.1^\circ$ were used. The experiments were carried out in a portable UHV chamber equipped with gas inlet and an electron bombardment sample heating. Prior to the synchrotron experiments, the preparation conditions for a chemically clean surface were established in a laboratory UHV system. Auger electron spectroscopy after treatment A showed that the sample surface was contamination free.

SXRD experiments were performed measuring crystal truncation rods (CTR) [11] at room temperature under UHV conditions at the Swiss Light Source (SLS) [12] and at the Ångström-Quelle Karlsruhe (ANKA) [13]. At the SLS, both anomalous and nonanomalous data were recorded. Anomalous SXRD was performed on the same sample at the Y (17.038 keV) and Zr K-edges (17.998 keV). Nonanomalous data were collected at a photon energy of 16 keV (SLS) and at 10 keV on a second sample at ANKA. For both experiments the incident angle was fixed near the critical angle for total external reflection to improve the signal to noise ratio. From the obtained SXRD data it can be concluded that the sample preparation is very reproducible.

Data integration and merging of symmetry equivalents were performed using standard procedures [14,15]. Table 2 gives a summary of the data collection and subsequent merging results. Structure refinement was carried out using the ANA-ROD package [14] including the option to fit anomalous CTR data [16]. All the data measured at different X-ray energies are used at once to refine one structural model. In this way the composition of Y and Zr atoms can be refined to much higher accuracy.

The hexagonal surface unit cell has axes \vec{a}_s , \vec{b}_s and \vec{c}_s , with $a_s = b_s = \frac{\sqrt{2}}{2}a_0$, $c_s = \sqrt{3}a_0$, whereby a_0 is the parameter of the primitive cubic unit cell. The experiment gives the following surface cell parameters: $a_s = b_s = 3.638 \text{ \AA}$, $c_s = 8.912 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ from which we obtain that for our sample $a_0 = 5.145(6) \text{ \AA}$. By making use of an empirical linear relationship between cell parameters and yttria doping level $a_0[\text{\AA}] = 5.1063 + 0.200x$ [17], we find $x = 0.19$, with the composition $(1-x)\text{ZrO}_2 \cdot x\text{YO}_{1.5}$ ($= \text{Y}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$). This is in good agreement with the supplier's specifications (Crystec) $\text{Y}_{0.174}\text{Zr}_{0.826}\text{O}_{1.913}$.

3. Bulk structure of YSZ and its (111) face

The idealized structure of cubic yttria-stabilized zirconia is of CaF_2 type, with space group $\text{Fm}\bar{3}\text{m}$, see Fig. 1 (a). Here, the Y and Zr atoms randomly occupy fcc (4a) sites, while the oxygens reside at interstitial (8c) $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ -type positions [26]. However, many neutron and X-ray diffraction studies conclude to distortions from the ideal positions (see e.g. [18] and references therein). Although a controversial topic for some time, consensus has been found with a description of the structure where the anions displace along the $\langle 100 \rangle$ and the cations along $\langle 111 \rangle$ and cubic symmetry-related directions [19,20]. An

Table 1
Anomalous dispersion corrections used in the structure factor calculations [21].

Energy (keV)	f'_Y	f''_Y	f'_{Zr}	f''_{Zr}
10.0000	0.00	0.00	0.00	0.00
16.0000	-2.00	0.50	-1.50	0.60
17.0384	-5.85	1.02	-2.44	0.57
17.8876	-2.01	3.38	-5.79	1.05

Table 2

Data reduction and refinement results. The agreement of merging symmetry equivalent data points is given by $R_{\text{merge}} = \frac{\sum_i \sum_{\text{hkl}} |F_i(\text{hkl}) - F_i(\text{hkl})|}{\sum_i \sum_{\text{hkl}} F_i(\text{hkl})}$. At the bottom are listed the residuals for the best fits. These are defined as $\chi^2 = \frac{1}{N-p} \sum_i \frac{(|F_i^{\text{obs}}| - |F_i^{\text{calc}}|)^2}{\sigma_i^2}$ and $R = \frac{1}{N} \sum_i \frac{|F_i^{\text{obs}}| - |F_i^{\text{calc}}|}{|F_i^{\text{obs}}|}$.

Energy (keV)	Treatment 1				Treatment 2	
	Sample 1		Sample 2		Sample 2	
	N	R_{merge}	N	R_{merge}	N	R_{merge}
10.0000	373	0.14				
16.0000					239	0.053
17.0384			431	0.096	370	0.082
17.8876			371	0.154	423	0.119
χ^2	0.86		1.03		1.40	
R	0.14		0.12		0.09	

elaborate combined anomalous X-ray diffraction and extended X-ray absorption fine structure (EXAFS) study showed that the average distortions could be refined, thereby revealing that the Y and Zr atoms reside in fact not at the same crystallographic positions [20]. The Zr atoms are displaced by 0.19 Å from the ideal fcc positions in the $\langle 111 \rangle$ and seven other symmetry-related directions, hence the name Zr-shift model. Since the formal valences of Y^{3+} and Zr^{4+} are different, it seems reasonable to assume that the local chemical environment around these ions is different, i.e. the coordination of Y is close to 6, while for Zr it is close to 7. As a result, part of the oxygens also displaces, however in the $\langle 100 \rangle$ and symmetry related directions. Fig. 1 (b) shows the Zr-shift structural model as the average over many different atom configurations, i.e. not every site displayed in Fig. 1 (b) is fully occupied by one atom. Within the Zr-shift model, all the atoms reside at positions compatible with $\text{Fm}\bar{3}\text{m}$ symmetry, with Y at the origin (4a) and Zr displaced to (32f) positions. Part of the oxygens is displaced from (8c) to (48g) positions. Such a description of the YSZ structure is in line with other studies, which showed that there is an accumulation of defects, giving rise to pronounced diffuse scattering [19] consistent with the displacements of cations and anions as described by the Zr-shift model.

Transformation between the cubic and the (111)-oriented surface unit cell (see Fig. 2) used for our SXRD measurements is carried out as presented in Appendix A.

4. Results

4.1. Anomalous dispersion and simulations

In this section the scattering along CTRs of the YSZ(111) surface is discussed for both the fluorite as well as the Zr-shift models. In order to distinguish between the scattering contributions of Y and Zr, it is needed to exploit the anomalous diffraction effect due to element specific X-ray-induced electronic transitions. Whereas the atomic scattering factors of Y ($Z = 39$) and Zr ($Z = 40$) far away from resonances (f_0) are almost identical, the X-ray absorption behavior is different. The scattering of a particular element near its absorption edge alters for which the following corrections are made to the atomic scattering factor f :

$$f(\mathbf{Q}, E) = f_0(\mathbf{Q}) + f'(E) + if''(E) \quad (1)$$

whereby \mathbf{Q} is the momentum transfer ($|\mathbf{Q}| = 4\pi n \sin(\theta)/\lambda$, with θ half the scattering angle and λ the wavelength), E the X-ray energy, f_0 the atomic scattering factor far away of resonances, f' the dispersion correction and f'' the absorption correction. Values of f' and f'' used in the present study are taken from the NIST database [21] and listed in Table 1.

By making use of the corrected atomic scattering factors (Eq. (1)) it is straightforward to compute CTRs [16]. Fig. 3 shows simulated

Download English Version:

<https://daneshyari.com/en/article/5422516>

Download Persian Version:

<https://daneshyari.com/article/5422516>

[Daneshyari.com](https://daneshyari.com)