

Extreme deviations from stoichiometry in alumina nanopowders



Vladimir B. Vykhodets^{a,*}, Emily A.A. Jarvis^b, Tatiana E. Kurennykh^a, Igor V. Beketov^{c,d}, Sviatoslav I. Obukhov^a, Oleg M. Samatov^c, Anatoly I. Medvedev^{c,d}, Andrey E. Davletshin^a

^a Institute of Metal Physics, Russian Academy of Sciences, Ural Division, 620990 Yekaterinburg, Russia

^b Department of Chemistry and Biochemistry, Loyola Marymount University, Los Angeles, CA 90045, USA

^c Institute of Electrophysics, Russian Academy of Sciences, Ural Division, 620016 Yekaterinburg, Russia

^d Ural Federal University, 620000 Yekaterinburg, Russia

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ABSTRACT

Alumina's importance has motivated detailed exploration of α -Al₂O₃(0001). Under certain conditions, this surface undergoes a $(\sqrt{31} \times \sqrt{31})R9^\circ$ reconstruction resulting in a layer of aluminum, Al(111), over a stoichiometric substrate. γ -Al₂O₃ is less understood but dominates material applications. We show that γ -Al₂O₃ nanopowders present aluminum-enriched surfaces similar to those of the reconstructed α -Al₂O₃(0001). Employing nuclear reaction analysis supported by density functional calculations, we quantitatively identify the elemental composition of γ -Al₂O₃ and find a transition to pure aluminum termination.

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1. Introduction

The fundamental and practical importance of alumina has motivated numerous experimental and theoretical studies of the atomic structure of its surface, particularly for competing terminations of the basal growth plane for the high temperature crystalline phase, α -Al₂O₃(0001) [1–5]. The thermodynamically favored termination depends on temperature and ambient oxygen pressure and may be influenced by strain and dislocations [6,7]. When the α -Al₂O₃(0001) surface is depleted of oxygen content or aluminum is deposited, a $(\sqrt{31} \times \sqrt{31})R9^\circ$ reconstruction achieves a surface termination of a layer of aluminum metal, Al(111), over an apparently stoichiometric substrate [8–11]. α -Al₂O₃ has a well-defined hexagonal crystal structure, but the lower symmetry γ -Al₂O₃ is subject to ongoing debate even though the surface chemistry of this phase dominates alumina materials and nanopowder applications. It is generally considered a spinel structure [12] (such as Fd-3m) of alternating octahedrally and tetrahedrally coordinated cations in a regular oxygen lattice with cation vacancies introduced to achieve stoichiometry.

Studies exploring the surface structure and stoichiometry of aluminum oxide typically use electron-spectroscopy and microscopy-based methods. Employment of spectroscopy methods purports preparation of pure and homogeneous surfaces with the attested structure. Such conditions are difficult to provide even for single crystals; these

techniques are inapplicable for ascertaining surface stoichiometry in oxide nanopowders. This limitation is essential, since the main factor determining scientific and practical interest in the oxide nanopowders is just their high specific surface and associated surface chemistry. We have assumed that the average concentration of oxygen in a nanopowder of the Al₂O₃ oxide would differ from that for a massive sample if there were an oxygen deficit in the surface layer of the nanoparticle. To explore the detailed stoichiometry, we required the use of a method for direct elemental assignment, namely, nuclear reaction analysis (NRA).

2. Materials and methods

2.1. Alumina powder preparation and characterization

We produced alumina powders using laser evaporation of a ceramic target and subsequently measured the oxygen concentration in these powders via NRA. Finding the relative oxygen to aluminum content of the nanopowders is difficult due to the presence of adsorbed oxygen-containing molecules; therefore, the investigation was performed on powders with an oxygen subsystem enriched in ¹⁸O which has only 0.2% natural abundance. The initial alumina powder was annealed in flowing gaseous oxygen enriched in ¹⁸O to 80% and was fine-grained with a specific surface of 46 m²/g. These features are important for the realization of the oxygen isotope exchange because of very low diffusion coefficients *D* of oxygen in the aluminum oxide, i.e., $D \approx 10^{-28}$ m²/s at 1000 °C [13]. Under these conditions, an essential contribution to the enrichment of powders in isotope ¹⁸O was made by the oxygen isotope

* Corresponding author.

E-mail addresses: vykhod@imp.uran.ru (V.B. Vykhodets), emily.jarvis@lmu.edu (E.A.A. Jarvis).

exchange in the atomic-scale surface layer of the nanopowder particles. From the initial powder, tablets with a density 35–40% of the theoretical one were produced by pressing. The tablets were placed in an aluminum tube for annealing with an oxygen pressure of 1 atm at 1000 °C for 100 h.

The ^{18}O -enriched powder was ground in a mortar made of zirconium oxide. The micropowder was pressed in air at room temperature to produce a 60 mm diameter target. Laser evaporation of the target was performed in the mode of irradiation modulation with rectangular pulses of a microsecond duration with the use of a ytterbium fiber laser with a wavelength of irradiation of 1.07 μm and maximal intensity of 1 kW. To exclude the exchange of oxygen isotopes upon synthesis of the nanopowders, the laser evaporation was carried out in an inert atmosphere. The powders with the specific surface, S , lower than 200 m^2/g were synthesized in an argon atmosphere, while those with S higher than 200 m^2/g were synthesized under helium.

The X-ray diffraction (XRD) analysis of the nanopowders was performed using the DISCOVER D8 (Bruker) diffractometer operating at 40 kV and 40 mA with Cu-K α radiation ($\lambda = 0.1542$ nm) equipped with a graphite monochromator on a secondary beam and scintillation detector in Bragg–Brentano configuration. Bruker TOPAS-3 software with Rietveld full-profile refinement was employed for the quantitative analysis. The average size of coherent diffraction domains (nanoparticle size) was estimated by using the Scherrer approach.

2.2. Nuclear reaction analysis

The NRA study was carried out at a 2 MV Van de Graaff accelerator. To measure concentrations of isotopes ^{16}O and ^{18}O , the aluminum oxide particles were pressed into copper powder. Rutherford backscattering spectrometry in the zone of analysis verified that only oxygen and aluminum atoms were present and atoms constituting the copper substrate were absent. The thickness of the oxide layer on the copper surface did not exceed 10 μm . To measure the concentration of the isotope ^{16}O , we used the reaction $^{16}\text{O}(d,p_1)^{17}\text{O}^*$ at an energy of deuterons of 900 keV, and for the ^{18}O isotope, the reaction $^{18}\text{O}(p,\alpha)^{15}\text{N}$ at an energy of protons of 762 keV. According to the NRA data, the degree of enrichment of the oxygen subsystem of the target material in the isotope ^{18}O was $\alpha = 0.13$ (13%). The registration of products of nuclear reactions (protons and α -particles) was performed by means of silicon surface-barrier detector 10 mm in diameter with an angle of registration of 160°. The diameter of the incident beam of deuterons ranges from 0.5 to 1 mm. The number of particles in the incident beams (irradiation dose) was determined with the help of a secondary monitor, the statistic error of the measurements being about 0.5%.

2.3. Computational methods

To further investigate the features of an aluminum enriched surface, we performed density functional calculations on model $\gamma\text{-Al}_2\text{O}_3$ surfaces depleted of oxygen as in the well-studied $\alpha\text{-Al}_2\text{O}_3(0001)$ ($\sqrt{31} \times \sqrt{31}$)R9° reconstruction. Density functional calculations were performed on periodic surface cells derived from a $\gamma\text{-Al}_2\text{O}_3$ spinel unit cell without cation vacancies since our interest was in aluminum enriched surfaces and only near sub-surface layers are represented in periodic slab models. The cubic bulk unit cell had Fd-3m symmetry with 7.9910 Å lattice vectors. The periodic surface cells maintained >10 Å (six or more layers) of the regular oxygen lattice separating the equivalent aluminum enriched surfaces which were separated by 10 Å of vacuum normal to the surface. The Perdew–Burke–Ernzerhof non-local gradient-corrected exchange functional was used to calculation the exchange-correlation energy and potential [14]. All calculations employed Monkhorst–Pack grids resulting in a k-point mesh of 0.05 Å $^{-1}$ or finer spacing and a planewave basis cutoff of 340 eV for the valence electron density with ultrasoft pseudopotentials [15] used to describe ion–electron interactions as implemented in CASTEP [16].

The low index (111), (100), and (110) surfaces of $\gamma\text{-Al}_2\text{O}_3$ were studied with aluminum enrichment through oxygen loss of two oxygen monolayers nearest to the surface, analogous to that observed in the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface reconstruction. All calculations employed a convergence of 2.0×10^{-6} eV/atom for the SCF cycles and within the geometry optimization convergence criteria were set to 2.0×10^{-5} eV/atom energy change, 0.05 eV/Å maximum force, and 2.0×10^{-3} Å maximum displacement between cycles.

3. Results and discussion

XRD spectra of the nanopowders are shown in Fig. 1, and results using the BET method [17] for assigning specific surface and nanoparticle size as well as phase analysis from XRD are summarized in Table 1. The symmetry of $\gamma\text{-Al}_2\text{O}_3$ was treated as defect spinel with Fd-3mz space group. Detailed understanding of the $\delta\text{-Al}_2\text{O}_3$ crystal structure is not available, so we considered that structure to be tetragonal with P43212 space group. In Fig. 1, the principal peaks for phases are marked by symbols γ and δ , respectively. In some cases, XRD analysis failed to reliably determine the parameters of crystal lattices and the sizes of nanoparticles due to overlap of the peaks from the γ and δ phases. These cases are marked by dashes in Table 1. It was not possible to quantitatively determine the amorphous phase mass fraction in the

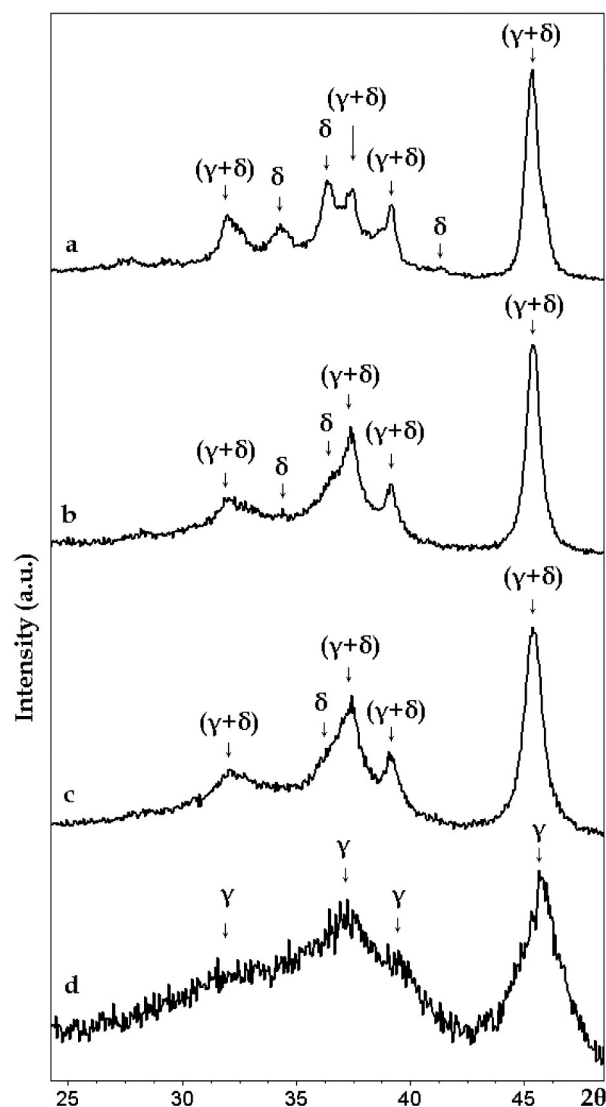


Fig. 1. XRD spectra for the nanopowders with a, b, c, and d depicting spectra for powders with the specific surface $S = 55, 82, 122,$ and 267 m^2/g , respectively.

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