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Journal of the European Ceramic Society 25 (2005) 639–648

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Anisotropic X-ray diffraction peak broadening and twinning in diaspore-derived corundum

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Received 28 December 2003; accepted 6 March 2004

Abstract

Corundum produced by dehydration of diaspore at temperatures between 400 and 1000 °C was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The broadening of XRD peaks and the size of corundum twin domains are related to the dehydration temperature. At low dehydration temperatures (<450 °C) as well as at high temperatures (>700 °C) large twin domains are obtained which yield sharp XRD peaks for all reflections. Dehydration between 450 and 600 °C leads to twin domains smaller than 10 nm. In this temperature range, significant peak broadening is observed, however, only for reflections, which structure factors are dominated by the aluminum sublattice and which are not common to both twin variants of corundum. The experimental results show that XRD peak broadening is only caused by fine twinning. Porosity in corundum as a reason for XRD peak broadening is excluded: the lamellar pore system is well ordered in corundum produced at low temperatures, however narrow peaks are observed. The reasons for the development of twin domains with differing sizes at different dehydration temperatures are discussed in detail.

Keywords: Dehydration; Al_2O_3; Twinning; X-ray diffraction; Electron microscopy

1. Introduction

Aluminum oxides and hydroxides are widespread in nature and of utmost industrial importance. Bauxites, aluminum ores containing different hydroxides and oxyhydroxides, are most important resources for the aluminum production, while the oxides are important ceramic materials. As initial step of all production, the thermal conversion of hydroxides into water-free, highly-porous oxides is very critical.

One of the reactions involved in this process is the dehydration of diaspore, α-AlOOH, which is the most stable aluminum oxide hydroxide. Whereas all other hydroxides and oxide hydroxides of aluminum dehydrate to metastable transition aluminum oxides diaspore (D) directly transforms to corundum (C), α-Al_2O_3 upon dehydration:

$$2AlO(OH) \rightarrow Al_2O_3 + H_2O.$$

The first study of that reaction revealed that the transformation is topotactic with the lattice planes $(1\,0\,0)_D \parallel (00.1)_C$ and $(0\,1\,0)_D \parallel (11.0)_C$.[1] The hexagonal stacking of close-packed oxygen layers, ABABAB, is preserved during the reaction. Hence, the dehydration reaction requires only short range cationic rearrangement. From the reaction equation, however, it follows that a quarter of the oxygen atoms is removed during dehydration. This loss of oxygen atoms (and hydrogen) is accompanied by the formation of pores in the dehydration product.[2] In a more recent study, it has been shown that at low temperature (400 °C) dehydration of diaspore the pores are two-dimensionally aligned in lamellae parallel to the basal plane in the product, and the lamellae appear periodically at a distance of approximately 3.7 nm.[3] Dehydration at higher temperatures gradually degenerates the uniform pore structure. It has been shown that these pores act as diffusion paths for the water molecules to escape from the system during the reaction. Hence, the anisotropy of the dehydration of diaspore crystals can be understood considering the geometry of pores, cracks and cleavage planes.[3]

The subject of the present paper is the anisotropic peak broadening in powder X-ray diffraction (XRD) measurements of the dehydration product. This characteristic phenomenon has rarely been studied for diaspore-derived corundum,[2,4] where authors discussed XRD results without

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0955-2219/$ – see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2004.03.027

Table 1
Heat treatment (temperature and time) of powder samples and single crystal specimens

Dehydration temperature (°C)	Powder (for XRD)	Single crystals (for TEM)
400	–	28 days[a]
410	50 days	–
430	2 days	1 day[a]
445	30 h	–
460	20 h	
500	–	90 min[a]
525	1 h	–
550	–	30 min[a]
600	1 h	3 min[a]
650	1 h	–
700	1 h	1 h
800	1 h	1 h
1000	1 h	1 h

[a] Only partial transformation.

further TEM investigation. However, for the analogous dehydration reaction in the iron oxide system—goethite (α-FeOOH) to hematite (α-Fe_2O_3)—a number of investigations have been reported over the past decades. In both systems, the diffraction peaks of the types (01.2), (10.4), (11.6), (02.4), (01.8) and (21.4) are significantly broadened compared to the (11.0), (11.3) and (30.0) reflections. So far, the anisotropic broadening has been observed exclusively in low-temperature dehydration products, e.g. for goethite-derived hematite at temperatures lower than 600 °C. Regarding these previous studies, two different approaches have been made to explain that phenomenon: One refers to the crystal shape anisotropy due to the pore lamellae,[5–10] while the other ascribes the broadening to cationic disorder, caused by either very fine twinning[11–14] (domain sizes of about 5 nm) or residual hydroxyl groups.[15–17]

Up to now, for both of these interpretations series of papers have been published on the goethite/hematite system, however, no agreement has been achieved yet. In the present study, XRD peak broadening of diaspore-derived corundum as a function of dehydration temperature has been examined in direct correlation with high resolution and dark field TEM studies on twinning—an investigation which has not been performed so far. The results of the combined XRD and TEM study will be discussed with respect to the crystal structure and the microstructure of the dehydration product. In addition, high angle reflections in X-ray powder scans will be considered which provide further information and support for the interpretation given in the present paper. Finally, we shall be able to explain the anisotropic peak broadening with fairly simple arguments.

2. Experimental

All studies were performed on dehydration products of natural gem-quality diaspore from the Menderes region, Turkey. For the XRD measurements, parts of the crystal were crushed to a fine powder before heating. For the different reaction temperatures, the reaction time was chosen as listed in Table 1. The samples were directly placed into the hot tube furnace, and were quickly removed after the reaction time. This was done to avoid modification of the product by the heating or cooling procedure. In any of the thermal treatments listed in Table 1 complete conversion to corundum was achieved.

Natural diaspore powder consists of (0 1 0) plate-shaped crystals. To avoid falsification of intensity due to the (0 1 0) texture the X-ray diffraction intensities were acquired in Debye–Scherrer geometry. The data were collected on a STOE diffractometer, Stadi P (Cu Kα radiation), equipped with a position sensitive detector (PSD, 0.03° angular resolution). The XRD scans were evaluated using DIFFRAKT 97, which allows profile fitting with high accuracy for each of the reflections separately.

For TEM studies the diaspore crystals were cut into blocks with dimension of 6 mm × 1.8 mm × 0.3 mm, where cutting was performed along all principal planes of diaspore, respectively. The samples were annealed in air at temperatures ranging from 400 to 1000 °C for different times, which led to partial or total transformation to corundum (see Table 2). Again, the samples were directly placed into the hot tube furnace and were quickly removed and cooled down by dropping them on a cold metal plate. The oriented TEM specimens were prepared in cross-section using common procedures for TEM specimen preparation. The TEM studies were performed on electron microscopes type Philips CM30ST and type Philips CM300UT, both operated at 300 kV.

Table 2
Size and shape of twin domains as function of dehydration temperature

Dehydration temperature (°C)	Size of twin domains (along × normal to basal plane)	Shape	Twin boundary plane
400	1 μm × 200 nm	Elongation ‖ (0 0 0 1)	Favorably (0 0 0 1)
430	100 nm × 40 nm	Elongation ‖ (0 0 0 1), less pronounced	Still favorably (0 0 0 1)
500–600	10 nm × 10 nm	Random	Random
800	40 nm × 100 nm	Elongation ‖ ($\bar{1}$ 1 0 0)	Favorably ($\bar{1}$ 1 0 0)
1000	100 nm × 300 nm	Elongation ‖ ($\bar{1}$ 1 0 0), less pronounced	Favorably ($\bar{1}$ 1 0 0)