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X-Ray Diffraction Line Profile Analysis of the Microstructure of Micro- and Nanosized Alumina Particles

E. Yu. Tarasova[a, *], **S. I. Kuznetsov**[a], **A. S. Panin**[a], **and S. A. Nefedov**[b]
[a] *Lebedev Physical Institute, Samara Branch, Russian Academy of Sciences, Samara, 443011 Russia*
[b] *Korolev Samara National Research University, Samara, 443086 Russia*
**e-mail: kat@fian.smr.ru*

Abstract—X-ray diffraction line profile analysis is adapted to investigate the microstructure of alumina. The structure of electrocorundum and corundum powders produced from pseudoboehmite with submicronic and nanometer-sized particles is analyzed. The lognormal size distribution parameters and their dependence on the conditions of corundum synthesis are determined. The structure of dislocations in corundum with different synthesis prehistories is analyzed, and structural features of the studied material are revealed.

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INTRODUCTION

Transmission electron microscopy (TEM) is the most informative way of studying microstructure defects. With corundum ceramics, this complicated technique allows us to characterize individual grains or small numbers of them.

X-ray diffraction analysis is an alternative to TEM. However, the standard analyses of the half-width or integral width of the diffraction lines provide too little information on a structure.

X-ray diffraction analysis (XRD) can be used [1–4] to determine the type of a defect and its concentration in corundum powders, along with the type of diffraction line distortion caused by defects. However, the authors of [1–4] only considered basal slip planes, and XRD based on variations in diffraction line half-width allow us to determine only the probability of a defect.

The last 20 to 30 years have seen the active development of line profile analysis, which is most often used for metals or nanoparticles. The formulas for analyzing the type of a defect and its concentration in metals can be applied to simple densely packed lattices only. With nanoparticles, particles of several or 10–20 nm are commonly studied, and their form and size distribution are analyzed without considering defect structure.

The aim of this work was to adapt diffraction line profile analysis to the microstructure of corundum, and to analyze the structure of corundum powder with defects and relatively large grains (50–100 nm). Such analysis is dictated by the need to study a less symmetrical system than metals and alloys, without a predominant source of broadening determining the line profile.

CALCULATION PROCEDURE

Our diffraction line profiles were studied by analyzing their Fourier transforms and the contributions from individual distortions to the general profile. A diffraction line profile is a convolution of profiles determined by all sources of its broadening. A Fourier transform (its real part) changes the integral convolution of functions into the product of their Fourier transforms:

$$A(L) = A^{\mathrm{Inst}}(L)A^{\mathrm{Size}}(L)A^{\mathrm{Disl}}(L), \tag{1}$$

where $A^{\mathrm{Inst}}(L)$ is a Fourier transform of the instrumental distortion profile, $A^{\mathrm{Size}}(L)$ is a Fourier transform based on the smallness of coherent scattering regions (CSRs) and their size distribution, and $A^{\mathrm{Disl}}(L)$ is a Fourier transform based on the defects of a crystalline lattice.

Fourier transforms are commonly used for both identifying instrumental distortions and separating dimensional and dislocation contributions to distortions. However, this approach is not entirely correct, since the real part of a Fourier transform yields a symmetric function, while instrumental distortions are always asymmetric. For relatively large grains (50–100 nm), the systematic error caused by ignoring asymmetry can total tens of percent of the calculated CSR size [5]. We therefore used Richardson–Lucy iteration to separate instrumental and intrinsic broadening [6, 7]. This method does not impose any restrictions on the types of developable and instrumental functions. According to [8], it also provides the best physical profile reconstruction, compared to all other iterative methods. After deconvolution, the profiles of the analyzed lines are symmetrical or nearly so; the use of Fourier analysis thus does not result in notable systematic errors.

Our Fourier transforms were modeled on the basis of a priori assumptions about particle structure. According to microscopy data, corundum particles are equiaxial and have a rounded shape. Our initial calculations were therefore performed by assuming CSRs are spherical and have a lognormal size distribution:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma}\frac{1}{x}\exp\left\{-\frac{(\ln(x/m))^2}{2\sigma^2}\right\}, \tag{2}$$

where σ is dispersion and m is the median distribution subject to determination. The Fourier transform of the broadening caused by a system of spherical crystallites with a lognormal distribution has the form

$$\begin{aligned} A^{\text{Size}}(L) = {} & \frac{m^3\exp\left(\frac{9}{4}\left(\sqrt{2}\sigma\right)^2\right)}{3}\operatorname{erfc}\left[\frac{\ln\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \frac{3}{2}\sqrt{2}\sigma\right] \\ & - \frac{m^2\exp\left(\sqrt{2}\sigma\right)^2}{2}|L|\operatorname{erfc}\left[\frac{\ln\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma} - \sqrt{2}\sigma\right] + \frac{|L|^3}{6}\operatorname{erfc}\left[\frac{\ln\left(\frac{|L|}{m}\right)}{\sqrt{2}\sigma}\right]. \end{aligned} \tag{3}$$

The value at the maximum when $L = 0$ is

$$A^{\text{Size}}(0) = \frac{2m^3\exp\left[\frac{9}{4}\left(\sqrt{2}\sigma\right)^2\right]}{3}. \tag{4}$$

Normalized profile $\frac{A^{\text{Size}}(L)}{A^{\text{Size}}(0)}$ is used in the calculation procedure. For such distribution, an average size of CSR is determined as

$$D_{\text{vol}} = \frac{3m\exp\left[\frac{7}{4}\left(\sqrt{2}\sigma\right)^2\right]}{4}. \tag{5}$$

The function for the Fourier coefficients of broadening due to lattice deformations caused by dislocations has the form

$$A^{\text{Disl}}(L) = \exp\left(-2\pi^2 d_{hkl}^{*\,2} L^2 \left\langle\varepsilon_L^2\right\rangle\right), \tag{6}$$

where d^*_{hkl} is the interplane distance in the reciprocal lattice, and $\left\langle\varepsilon_L^2\right\rangle$ represents mean-square strain, which is generally defined as

$$\left\langle\varepsilon_L^2\right\rangle = \left(\frac{b}{2\pi}\right)^2 \pi\rho C_{hkl} f\left(\frac{L}{R_{\text{e}}^*}\right), \tag{7}$$

where b is the Burgers vector modulus, ρ is the density of dislocations, C_{hkl} is the dislocation contrast factor, f is a function describing the distribution and interaction of dislocations, and R_{e}^* is a characteristic parameter (the outer cut-off radius).

To describe the structure of dislocations, we used the Wilkens model of a limited random distribution of dislocations that does not depend on hkl and slip systems [9]:

$$\begin{aligned} f(\eta) = {} & -\ln\eta + \left(\frac{7}{4} - \ln 2\right) + \frac{512}{90\pi}\frac{1}{\eta} + \frac{2}{\pi}\left(1 - \frac{1}{4\eta^2}\right)\int_0^{\eta}\frac{\arcsin V}{V}dV \\ & - \frac{1}{\pi}\left(\frac{796}{180}\frac{1}{\eta} + \frac{41}{90}\eta + \frac{2}{90}\eta^3\right)\sqrt{1-\eta^2} - \frac{1}{\pi}\left(\frac{11}{12}\frac{1}{\eta^2} + \frac{7}{2} + \frac{1}{3}\eta^2\right)\arcsin\eta + \frac{1}{6}\eta^2 \\ & \text{when } \eta \le 1, \end{aligned} \tag{8}$$

$$f(\eta) = \frac{512}{90\pi}\frac{1}{\eta} - \left(\frac{11}{24} + \frac{1}{4}\ln 2\eta\right)\frac{1}{\eta^2} \quad \text{for } \eta \ge 1, \tag{9}$$

where

$$f\left(\frac{L}{R_{\text{e}}^*}\right) = f(\eta), \quad \eta = \frac{1}{2}\exp\left(-\frac{1}{4}\frac{L}{R_{\text{e}}^*}\right).$$

Strictly speaking, formulas (8) and (9) were obtained only for screw dislocations, but Wilkens noted their suitability for other types of dislocations, along with other distributions of dislocations that differ slightly from the limited random varieties.

If a crystal is characterized by several types of dislocations and different slip systems, the resulting broadening for a given hkl is a convolution of all active slip systems, and the Fourier transform of the convolution has the form

$$\begin{gathered} A^{\mathrm{Disl}}(L) = \prod_{j=1}^{N} A_j(L) \\ = \exp\left[-\frac{\pi}{2} d_{hkl}^{*2} L^2 \frac{1}{N} \sum_{j=1}^{N} b_j^2 \rho_j C_{hkl}^{j} f(\eta_j)\right]. \end{gathered} \tag{10}$$

Analysis should yield dislocation densities ρ_j and the corresponding parameters of $R_{\mathrm{e},j}$. To simplify the calculation procedure in the first approximation, we assumed all values of $R_{\mathrm{e},j}$ were equal. According to [10], this was an entirely correct assumption and should not have introduced any appreciable errors into our calculations.

The density of dislocations was calculated by determining dislocation contrast factors that depended on hkl and the slip systems, and described the anisotropy of diffraction line broadening.

The general approach to determining the dislocation contrast for a crystal with arbitrary syngony and any type of dislocation was described in [11]. The dislocation contrast factor is the product of two tensors referred to as the geometric G_{ijmn} and elastic E_{ijmn} components:

$$C_{hkl} = \sum_{i,m}^{3} \sum_{j,n}^{2} G_{ijmn} E_{ijmn}. \tag{11}$$

Tensor G_{ijmn} is formed by multiplying directional cosines $\tau_i = \left(\frac{\mathbf{d}^*}{d^*}\right) \cdot \mathbf{e}_i$ of the angles between the diffraction vector and the axes of orthonormal coordinate system S associated with a dislocation:

$$G_{ijmn} = \tau_i \tau_j \tau_m \tau_n, \ (i,m) = 1,2,3, \ (j,n) = 1,2. \tag{12}$$

In the coordinate system $S = (\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$, vector $\mathbf{e}_3$ is directed along the line of a dislocation, $\mathbf{e}_2$ is perpendicular to the dislocation slip plane, and $\mathbf{e}_1 = \mathbf{e}_2 \times \mathbf{e}_3$. To calculate the geometric component of dislocation contrast G_{ijmn}, we must set reflecting plane indexes (hkl); slip system $\langle UVW \rangle \{HKL\}$ (the Burgers vector and slip plane); parameter ϕ, which depends on the type of dislocation; and tensors G_m, M, and $R(\phi, \mathbf{e}_2)$, which carry data on the crystal metrics and the rules of coordinate system transformation. All of the formulas needed to calculate G_{ijmn} were given in [11], while the rules for transforming a crystal's coordinate system were presented in [12].

The tensor of elastic components of dislocation contrast factor E_{ijmn} is generally defined in terms of the integral:

$$E_{ijmn} = \frac{1}{\pi} \int_0^{2\pi} \beta_{ij}(\varphi) \beta_{mn}(\varphi)\, d\varphi, \tag{13}$$

where the values of β_{ij} are proportional to partial derivatives $\partial u_i / \partial x_j$ of the field of dislocation motion, while φ is the polar angle. E_{ijmn} is calculated by estimating field u of the deformation of an isolated dislocation in an anisotropic elastic medium. According to [11], the field of crystal lattice deformation can be described via the Stroh formalism applied to problems of anisotropic elasticity.

Determining the fields of deformation in an anisotropic elastic medium using the Stroh tensor formalism is reduced to constructing intermediate tensors **Q**, **R**, and **T** composed of the crystal's elastic tensor components $\mathbf{C} = \{c_{ij}\}$, transformed into coordinate system S associated with the dislocation slip line [12]:

$$\begin{gathered} \mathbf{Q} = \begin{bmatrix} c_{11} & c_{16} & c_{15} \\ c_{16} & c_{66} & c_{56} \\ c_{15} & c_{56} & c_{55} \end{bmatrix}, \ \mathbf{R} = \begin{bmatrix} c_{16} & c_{12} & c_{14} \\ c_{66} & c_{26} & c_{46} \\ c_{56} & c_{25} & c_{45} \end{bmatrix}, \\ \mathbf{T} = \begin{bmatrix} c_{66} & c_{26} & c_{46} \\ c_{26} & c_{22} & c_{24} \\ c_{46} & c_{24} & c_{44} \end{bmatrix}. \end{gathered} \tag{14}$$

The Stroh formalism yields several matrix equations for determining the necessary intermediate values of p_α and vectors $\mathbf{A}_\alpha$, $\mathbf{L}_\alpha$ that make it relatively simple to determine fields u of deformation and their derivatives β_{ij} in anisotropic elastic media with low symmetry. However, applying it to a hexagonal lattice poses some mathematical challenges related to the degeneration of **Q**, **R**, and **T** matrixes, since many components of the elastic tensor are equal to zero, due to the high degree of symmetry. Even then, a solution is possible, but it must be calculated analytically, which is very laborious. We propose determining the values of p_α, $\mathbf{A}_\alpha$, and $\mathbf{L}_\alpha$ as eigen values and the eigen vectors of generalized elastic vector **N** [13]:

$$\mathbf{N} \begin{bmatrix} \mathbf{A}_\alpha \\ \mathbf{L}_\alpha \end{bmatrix} = p_\alpha \begin{bmatrix} \mathbf{A}_\alpha \\ \mathbf{L}_\alpha \end{bmatrix}, \tag{15}$$

where

$$\begin{gathered} \mathbf{N} = \begin{bmatrix} \mathbf{N}_1 & \mathbf{N}_2 \\ \mathbf{N}_3 & \mathbf{N}_1^{\mathrm{T}} \end{bmatrix}, \ \mathbf{N}_1 = -\mathbf{T}^{-1}\mathbf{R}^{\mathrm{T}}, \\ \mathbf{N}_2 = \mathbf{T}^{-1}, \ \mathbf{N}_3 = \mathbf{R}\mathbf{T}^{-1}\mathbf{R}^{\mathrm{T}} - \mathbf{Q}. \end{gathered} \tag{16}$$

Expression (15) defines a system of six equations that can be solved only numerically, but the Stroh formalism can in this case also be applied to lattices with high degrees of symmetry. After calculating eigen values p_α and eigen vectors $\mathbf{A}_\alpha$, $\mathbf{L}_\alpha$, the values of β_{ij} used to calculate the elastic component of dislocation contrast must be calculated as

$$\beta_{mn}(\varphi) = \mathrm{Im}\left[\sum_{\alpha=1}^{3} \frac{A_{m\alpha} D_\alpha p_\alpha^{(n-1)}}{\cos\varphi + p_\alpha \sin\varphi}\right], \tag{17}$$

where $(n-1)$ is an involution and $b = |\mathrm{b}|$ is the Burgers vector modulus, while intermediate values D_α are determined as

$$D_\alpha = -\frac{(\mathbf{L}_\alpha \cdot \mathbf{b})}{b(\mathbf{A}_\alpha \cdot \mathbf{L}_\alpha)}. \tag{18}$$

With a polycrystalline material having randomly oriented grains, the dislocation contrast factor must be averaged over N crystallographically equivalent slip systems for each j-th dislocation system:

$$\bar{C}^{\,j}_{hkl} = \frac{1}{N}\sum_{i}^{N} C^{\,i}_{hkl}, \tag{19}$$

where $\bar{C}^{\,j}_{hkl}$ is the average dislocation contrast for a j-th system.

After finding the average dislocation contrasts for all dislocation systems, the characteristics of corundum structure are determined using Eqs. (3)–(10).

EXPERIMENTAL

In this work, we used aluminum hydroxides with a pseudoboehmite structure and submicron (150–300 nm) and nanometer (5–14 nm) particles, obtained using proprietary alkoxy technology developed at ZAO VNIIOS NK. According to data from X-ray phase analysis, the size of CSRs was 3–5 nm for both types of hydroxides.

Corundum samples from the two types of hydroxides (below, $\mathrm{Al_2O_{3(micro)}}$ and $\mathrm{Al_2O_{3(nano)}}$) were produced by annealing in an SNOL electric furnace at 1200, 1250, and 1300°C with holding times of 2 and 6 h at the maximum temperature.

Some corundum samples produced at 1200°C with 2 h of holding were treated with radiation from a 38 W $\mathrm{CO_2}$ laser. The diameter of the laser spot on the surfaces of the treated material was 5 mm with a regular distribution of radiation intensity over the spot. Layer of powder 0.7 mm thick were treated with the laser beam without overlapping of individual passes; the scanning rate was 0.5 m min^{-1}. Single and double treatment were performed.

For purposes of analysis, we also used white electric corundum A24 samples, both as-delivered and annealed in the furnace at 1300°C with holding times of 6 and 40 h.

X-ray diffraction analysis was performed using a DRON-3 unit with CoK_α radiation. The dimensions of the horizontal and vertical forming slits were 0.5 and 6 mm, respectively, while the size of the analytical slit was 0.1 mm. The seven most intense diffraction lines (Table 2) were recorded at points spaced at intervals of 0.01° (recording time, 10–30 s). Instrumental distortions were determined by recording the lines of reference samples (quartz).

RESULTS AND DISCUSSION

The following slip systems can exist in the structure of corundum: in the basal plane, $\{0001\}\frac{1}{3}\langle 2\bar{1}\bar{1}0\rangle$; in the prismatic plane, $\{\bar{1}2\bar{1}0\}\langle 10\bar{1}0\rangle$; in the pyramidal plane, $\{10\bar{1}1\}\frac{1}{3}\langle \bar{1}101\rangle$ (this system is unlikely at temperatures below 1400°C and was not considered in this work).

According to [14, 15], most basal dislocations occur along the $\langle 10\bar{1}0\rangle$ direction, so they are logically either perfect edge (90°) or mixed (30°) dislocations. If the basal dislocations split into two according to the reaction proposed by Kronberg, a 30° dislocation will lead to one purely screw part (0°) and one 60° partial dislocation, while a 90° edge dislocation will generate two different 60° (±60°) partial dislocations. In a similar manner, the screw dislocation will split into two different 30° partial dislocations. Dislocations in the prismatic plane are defined as purely edge or purely screw [16].

A complete list of split reactions and the corresponding alphanumeric designations of partial dislocations are given in Table 1.

The values of dislocation contrasts for partial dislocations of different types are given in Table 2 along with the average (for each hkl) contrast values.

It is clear that the contributions from different dislocations to the line profile distortion are very different for each plane, and the contribution from dislocations of one of the above types normally predominates.

Our calculation procedure was validated by analyzing our samples of A24 electrocorundum. According to calculations based on the specified algorithm for electrocorundum, m = 270 nm; this means the broadening of its diffraction lines was entirely due to structural defects. Our data from analyzing the structure of dislocations are given in Table 3.

The results presented in Table 3 show that our technique allows us to estimate the density of dislocations depending on the conditions of treatment, though the reliability of the obtained values still requires verification. We may consider the procedure for determining the density of dislocations and the qualitative depen-

Table 1. Split reactions and dislocations

A	$\langle 10\bar{1}0\rangle^{\text{edge}} \rightarrow \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{edge}}}_{A1} + \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{edge}}}_{A1} + \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{edge}}}_{A1}$
B	$\langle 10\bar{1}0\rangle^{\text{screw}} \rightarrow \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{screw}}}_{B1} + \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{screw}}}_{B1} + \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{screw}}}_{B1}$
C	$\frac{1}{3}\langle 2\bar{1}\bar{1}0\rangle^{\text{edge}} \rightarrow \underbrace{\frac{1}{3}\langle 1\bar{1}00\rangle^{\text{mixed}\,(60^\circ)}}_{C1} + \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{mixed}\,(-60^\circ)}}_{C2}$
D	$\frac{1}{3}\langle 2\bar{1}\bar{1}0\rangle^{\text{mixed}\,(30^\circ)} \rightarrow \underbrace{\frac{1}{3}\langle 1\bar{1}00\rangle^{\text{screw}}}_{D1} + \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{mixed}\,(60^\circ)}}_{D2}$
E	$\frac{1}{3}\langle 2\bar{1}\bar{1}0\rangle^{\text{scred}} \rightarrow \underbrace{\frac{1}{3}\langle 1\bar{1}00\rangle^{\text{mixed}\,(30^\circ)}}_{E1} + \underbrace{\frac{1}{3}\langle 10\bar{1}0\rangle^{\text{mixed}\,(-30^\circ)}}_{E2}$

Table 2. Dislocation contrast factors for different dislocation subsystems and contrast factor $\bar{C}_{hkl}$, averaged for all dislocation systems

hkl	*I*, %	Contrast factors								$\bar{C}_{hkl}$
		A1	B1	C1	C2	D1	D2	E1	E2	
012	75	0.279	0.433	0.211	0.541	0.070	0.043	0.082	0.958	0.327
104	100	0.111	0.412	0.339	0.516	0.107	0.049	0.194	0.806	0.317
110	50	0.389	0.928	0.094	1	0.276	0.138	0.633	0.140	0.450
113	94	0	0.506	0.236	0	0.247	0.237	0.174	0.852	0.282
024	47	0.279	0.433	0.211	0.068	0.070	0.043	0.082	0.958	0.268
116	94	0.016	0.400	0.245	0.084	0.119	0.090	0.085	0.818	0.232
214	35	0.080	0.489	0.461	0.016	0.19	0.151	0.741	0.727	0.357

dence of its variations on the conditions of treatment as reliable. The scatter in the densities of pair dislocations is due to differences in the magnitude of dislocation contrasts and the clearly insufficient amount of initial data, since nine unknown parameters were calculated using seven diffraction peaks. The use of a more powerful X-ray source and the addition of new lines for analysis should yield more reliable results.

Our data from analyzing corundum produced from pseudoboehmite with different particle sizes are given in Tables 4 and 5. In those tables, m and σ are the median and dispersion of the lognormal CSR size distribution; D_{vol} is the average CSR size, nm; $\langle\rho\rangle$ is the average density of dislocations, cm^{-2}; and $\bar{s}$ denotes the root-mean-square deviation of the approximate and experimental Fourier transforms, minimized using the least squares method.

According to Table 4, the distribution maximum regularly shifts toward small CSR sizes at 1200°C and 1250°C with an increase in a holding time, while the width and asymmetry of distribution grow. Additional nonequilibrium heating (e.g., laser treatment) shifts

Table 3. Density of dislocations in the structure of electrocorundum, $\times 10^9$ cm^{-2}

Sample	Partial dislocation								$\bar{s}$
	A1	B1	C1	C2	D1	D2	E1	E2	
Initial	0.1	0.3	2.7	2.4	2.1	2.3	3.2	2.9	0.056
1300°C, 6 h	0.07	0.1	0.4	0.2	0.8	0.6	1.8	1.9	0.073
1300°C, 40 h	0.06	0.08	0.3	0.2	0.8	0.7	1.7	1.7	0.061

Table 4. Structural characteristics of $Al_2O_{3(nano)}$

Processing conditions	m, nm	σ	D_{vol}, nm	$\langle\rho\rangle$, cm^{-2}	$\bar{s}$
1200°C, 2 h	48.4	0.434	70.2	$\sim 10^5$	0.052
1200°C, 6 h	42.3	0.538	87.4	$\sim 10^5$	0.056
1250°C, 2 h	56.5	0.430	80.9	$\sim 10^5$	0.058
1250°C, 6 h	54.4	0.498	97.2	$\sim 10^5$	0.052
1300°C, 2 h	56.9	0.492	99.6	$\sim 10^4$	0.062
1300°C, 6 h	70.2	0.450	107.0	$\sim 10^4$	0.055
1200°C, 2 h + LP	47.5	0.470	77.2	$\sim 10^4$	0.081

Table 5. Structural characteristics of $Al_2O_{3(micro)}$

Processing conditions	m, nm	σ	D_{vol}, nm	$\langle\rho\rangle$, cm^{-2}	$\bar{s}$
1200°C, 2 h	49.4	0.428	70.4	$\sim 10^7$	0.150
1200°C, 6 h	57.2	0.428	81.5	$\sim 10^7$	0.111
1250°C, 2 h	54.0	0.443	80.5	$\sim 10^7$	0.081
1250°C, 6 h	58.3	0.464	92.9	$\sim 10^7$	0.090
1300°C, 2 h	63.8	0.445	95.7	$\sim 10^7$	0.102
1300°C, 6 h	75.5	0.416	103.8	$\sim 10^7$	0.097
1200°C, 2 h + single LP	56.4	0.425	79.6	$\sim 10^5$	0.110
1200°C, 2 h + double LP	49.9	0.466	80.1	$\sim 10^5$	0.105

the CSR size distribution toward lower values and increases its width and asymmetry, as does lengthening the holding time in the furnace. It should be noted that the accuracy of determining the structural characteristics of a sample after laser treatment is lower than for the initial furnace sample.

In contrast, a longer holding time at 1300°C results in a higher median value and a narrower size distribution. This is because reaching temperatures of 1200–1250°C is accompanied by a phase transition to the Al_2O_3 α-phase, while a temperature of 1300°C results in a powder baking effect.

We should note the low values of the average dislocation densities, which are far below the limit of XRD sensitivity. The values given in Table 4 are likely mathematically calculated artifacts.

The calculated average dislocation densities are somewhat higher for corundum with submicronic particle size than for $Al_2O_{3(nano)}$. However, we cannot assert unequivocally that the real density of dislocations was also higher, since the calculated values are also below the level of XRD sensitivity. The lognormal distribution parameters at different temperatures are consistent: When the temperature and/or holding time in the furnace was increased, the median distribution shifted toward higher values.

The average sizes of the CSRs of our corundum samples obtained from hydroxides with submicron and nanometer particle sizes were approximately the same under identical conditions of synthesis.

Also noteworthy are the high values of the root-mean-square deviations in the approximation of the Fourier transforms using the least squares method, which are 2–3 times greater than the analogous values for the $Al_2O_{3(nano)}$ samples. These were most likely not due to dislocations in the structure, since their calculated densities are too low for any notable presence in the diffractograms. However, the clear difference between both the properties of the corundum powders and the quality of the approximation of the diffraction lines' Fourier transforms testifies to the considerable difference between these structures. Possible reasons for this include nonsphericity of the CSRs or the presence of structural defects not considered by the above model.

To verify the hypothesis of CSR nonsphericity, instead of a dimensional Fourier transform we used formulas that simulated CSR with ellipsoids of revolution, the sizes of which along crystallographic axis c were characterized by a lognormal distribution while the aspect ratio was similar for all particles [17]. The accuracy of approximation was in this case 2–8 times worse than when CSRs were assumed to be spherical.

Unexpected defects can include twins or grain boundary defects that arise when particles are sintered. However, the active sintering of corundum is conducted at 1600°C [18]. The absence of baking in our samples was indirectly confirmed by measurements of their bulk density after shaking: the bulk density for $Al_2O_{3(micro)}$ grew slightly, from 1.1 g cm^{-3} at a treatment temperature of 1200°C (2 h) to 1.3 g cm^{-3} at 1300°C (6 h); for $Al_2O_{3(nano)}$, it grew to around 0.75 g cm^{-3} irrespective of the conditions of production.

The occurrence of specific defects could be associated with the prehistory of oxide formation. Corundum is produced from aluminum hydroxide via the initial decomposition of AlOOH (pseudoboehmite) in several stages to γ-Al_2O_3, polymorphic transformations γ-$Al_2O_3 \rightarrow \delta$-$Al_2O_3 \rightarrow \theta$-$Al_2O_3$, and finally a phase transition to α-Al_2O_3. When obtaining α-Al_2O_3 from hydroxide with nanometer particle size, grains grow due to the fusion of grain nanoparticles as early as the stage of the formation of low-temperature phases, apparently without the development of a great many defects. With $Al_2O_{3(micro)}$, the initial hydroxide particle is originally a polycrystalline agglomerate. The heating of such particles does not result in complete destruction of the agglomerate, and the structure of boundaries and boundary defects is inherited in some form. However, we cannot say that this structure is described by the dislocation structures listed in Table 1.

CONCLUSIONS

Analysis of X-ray diffraction line profiles was adapted to study the structure of corundum.

Dislocation contrast factors were calculated for the most intense diffraction lines of corundum and its basic systems of dislocation.

The structures of corundum samples with different production prehistories were analyzed.

It was found that distortions of electrocorundum diffraction lines can be interpreted as belonging to the dislocation type. The densities of variable dislocations were determined.

It was established that defects in corundum obtained via the decomposition of hydroxides are incorrectly described by the dislocation Fourier transform of profile distortions. The defect model used to study corundum microstructure must be elaborated further.

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