Phase Composition of Al₂O₃ Nanopowders Prepared by Plasma Synthesis and Heat-Treated

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Abstract—We present X-ray diffraction data for Al_2O_3 nanopowders prepared by oxidizing aluminum powder in an air plasma, followed by size separation via centrifugation and heat treatment. DOI: 10.1134/S0020168512040152

INTRODUCTION

Alumina is widely used in the production of refractory ceramics, catalysts, protective coatings, etc. Al_2O_3 preparation and processing techniques have been the subject of extensive studies for more than hundred vears now. Al₂O₃ can be prepared by many processes, including plasma synthesis, which yields Al₂O₃ nanopowders consisting of spherical particles. Despite the intense research in this area, there is currently insufficient information about the phase composition of Al_2O_3 powders prepared by different techniques and the polymorphic transformations induced by subsequent processing. The reason for this is that there are many metastable Al_2O_3 polymorphs, which form depending on the preparation technique and conditions and the nature of the starting materials. Most previous studies employed samples prepared from boehmite or gibbsite. The phase composition of Al_2O_3 prepared by plasma synthesis has been determined in a limited number of studies [1-3]. In addition, new data on Al₂O₃ polymorphism and various plasma synthesis apparatuses and procedures proposed to date have led us to redetermine the phase composition of Al_2O_3 powders prepared by this method.

The purpose of this work was to study the phase composition of Al_2O_3 nanopowders prepared by oxidizing aluminum powder in an air plasma of an arc plasma generator in a reactor with a restricted jet flow [4]. To gain insight into possible relationships between the phase composition and average particle size of alumina, the nanopowders obtained in the plasma reactor were investigated after size separation by centrifugation. In addition, we examined the effect of subsequent heat treatment on the phase composition of the synthesized Al_2O_3 nanopowders.

EXPERIMENTAL

We studied Al_2O_3 nanopowders prepared by oxidizing ASD-4 aluminum powder in an air plasma and also samples obtained through size classification and heat treatment of the nanopowders. The plasma-prepared Al_2O_3 nanopowder had a specific surface area of 26.6 m²/g and consisted of spherical particles.

The nanopowders were classified into size ranges by centrifuging aqueous suspensions (Sigma 2-16P centrifuge). The suspensions were prepared by sonication (Bandelin SONOPULS HD 3100 ultrasonic homogenizer). The samples obtained by size separation had specific surface areas of 38.4, 30, 24.4, 19.4, 15.3, and 6.7 m²/g.

The plasma-prepared Al_2O_3 was heat-treated in an electric furnace in air for 2 h at 600, 800, 1000, 1150, 1230, and 1300°C. The specific surface areas of the heat-treated powders were 25.4, 25.3, 23.4, 22.2, 10.1, and 6.1 m²/g, respectively.

The phase composition of the powders was determined by X-ray diffraction (XRD) on a Rigaku Ultima-4 X-ray diffractometer (Japan) with filtered Cu K_{α} radiation (D/teX high-speed detector, PDXL software package, PDF-2 database).

RESULTS AND DISCUSSION

Before discussing the present results, it is worth analyzing available information and ICDD (JCPDS) Powder Diffraction File data for the Al₂O₃ polymorphs. Since this study deals with Al₂O₃ powders prepared by plasma synthesis from aluminum, we will not consider phases obtained by dehydrating boehmite, gibbsite, or other oxyhydroxides.

The Al₂O₃ polymorphs (usually denoted by different Greek letters) can be divided into several groups. One group comprises the low-temperature metastable phases γ , η , and χ [5]. According to Tsybulya and Kryukova [5], these polymorphs have spinel-related structures with different octahedral and tetrahedral site occupancies. They contain stacking faults and have a cubic unit cell with an identity period of about 7.9 Å. Characteristically, their powder XRD patterns



Fig. 1. XRD pattern of the Al_2O_3 powder prepared from aluminum by plasma synthesis and annealed at 1300°C for 2 h, and schematic XRD patterns of α - and θ -Al₂O₃ (cards 46-1212 and 23-1009, respectively).

show broad diffraction peaks. The γ -phase is commonly identified using the JCPDS PDF card 10-425 (see, e.g., Rozita et al. [6]).

Another group is constituted by the high-temperature metastable phases δ , θ , and κ . Reliable XRD data for the θ -phase are presented in card 23-1009 (sp. gr. C2/m, a = 11.813 Å, b = 2.906 Å, c = 5.625 Å, $\beta = 104.10^{\circ}$ [7]). The δ -phase has been the subject of many studies, but its structure is still open to question. According to Levin and Brandon [8] and Jayaram and Levi [9], the δ -polymorph has an orthorhombic structure (sp. gr. P222 or P2₁2₁2₁, $a \approx a_{\gamma}$, $b \approx 2a_{\gamma}$, $c \approx 1.5a_{\gamma}$). Card 46-1215 describes metastable orthorhombic Al₂O₃ with smaller unit-cell parameters (a = 7.934 Å,

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b = 7.956 Å, c = 11.711 Å [3]). This phase is designated as δ*. Card 46-1215 presents data for a sample obtained by plasma-spraying α-Al₂O₃ into water. Tsybulya and Kryukova [5] described a tetragonal δ-phase obtained by annealing the γ-phase at 1513 K (card 56-1186, a = 7.9631 Å, c = 23.3975 Å).

The stable high-temperature phase is α -Al₂O₃ (corundum). The XRD data for this polymorph are presented in card 46-1212.

The transformation sequence reported by many researchers (see, e.g., Refs. [8–10]) for metastable phases obtained by heating amorphous or liquidquenched Al₂O₃ has the form $\gamma \rightarrow \delta/\theta \rightarrow \alpha$. The γ to α phase transition occurs in the temperature range



Fig. 2. XRD pattern of the Al_2O_3 powder prepared from aluminum by plasma synthesis and annealed at 1230°C for 2 h, and schematic XRD patterns of α -, θ -, and δ *- Al_2O_3 (cards 46-1212, 23-1009, and 46-1215, respectively).

from 670 to 1200°C [10]. For alumina prepared by chemical vapor deposition, the transformation sequence has the form $\kappa \rightarrow \alpha$ [8]. For all of the meta-stable Al₂O₃ polymorphs, the exact phase transition temperatures are unknown.

According to our results, the sample annealed at 1300°C contained α -Al₂O₃ (corundum) and a very small amount of θ -Al₂O₃ (Fig. 1). This indicates that heat treatment at 1300°C for 2 h is insufficient for obtaining phase-pure corundum. The sample annealed at 1230°C contained α -Al₂O₃ and significant

amounts of θ -Al₂O₃ and δ^* -Al₂O₃ (Fig. 2). The XRD patterns of the Al₂O₃ powders annealed at 1150, 1000, 800, and 600°C for 2 h are very similar to that of the asprepared powder (Fig. 3): there are a large number of diffraction peaks, many of which overlap one another. At the same time, the XRD intensities depend on annealing temperature and there is a prominent "hump" (increased background) in the angular range $2\theta = 30^\circ$ -40° for the powders that were not annealed above 600°C. The characteristic portions of the XRD patterns in Fig. 4 illustrate the annealing effect on the



Fig. 3. XRD patterns of Al_2O_3 powders prepared by plasma synthesis and then annealed for 2 h at different temperatures.



Fig. 4. Portions of the XRD patterns of Al_2O_3 powders: (a) after (1) plasma synthesis and subsequent annealing at (2) 1150, (3) 1000, (4) 800, and (5) 600°C; (b) after separation by centrifugation into size fractions with specific surface areas of (1) 38.4, (2) 30, (3) 24.4, (4) 19.4, and (5) 15.3 m²/g.

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Fig. 5. XRD patterns of the synthesized Al_2O_3 powder after separation by centrifugation into size fractions with specific surface areas of (1) 38.4, (2) 30, (3) 24.4, (4) 19.4, and (5) 15.3 m²/g.

phase composition of the Al₂O₃ powders. The major phase is δ^* -Al₂O₃, which is characterized by two overlapping diffraction peaks, similar in intensity, near 45.5° and a weaker peak near 46.5°. The percentage of the θ -phase increases with annealing temperature. The higher intensity of the smaller angle component of the peak around 45.5°, the peak near 37.3°, and the above-mentioned hump in the XRD pattern of the asprepared Al₂O₃ powder can be interpreted as evidence for the presence of the γ -phase with a cubic cell parameter of about 7.96 Å. The peak near 37.3° ($d \approx$ 2.41 Å), unrelated to δ^* -Al₂O₃, is then the strongest reflection, 311, from a cubic spinel phase. The other peaks from γ -Al₂O₃ overlap peaks from the δ^* -phase.

The XRD patterns of the Al₂O₃ size fractions with specific surface areas of 38.4, 30, 24.4, 19.4, and 15.3 m²/g (Fig. 5) differ little. The major phase is δ^* -Al₂O₃. With decreasing specific surface area, the percentage of the θ -phase increases. The XRD pattern of the powder with a specific surface area of 6.7 m²/g (Fig. 6) differs from those of the other size fractions, especially in the angular range represented in Fig. 6b. In this case, the tetragonal δ -phase prevails, which leads to a marked increase in the intensity of the higher angle component of the doublet peak around 45.5° and causes an additional peak to emerge near 43.5°. The powder with a specific surface area of 6.7 m²/g contains, in addition to δ -Al₂O₃, the δ *- and θ -phases.

The table presents XRD data for the phases identified in the Al₂O₃ powder after size separation by centrifugation (size fraction with a specific surface area of $38.4 \text{ m}^2/\text{g}$). The phases present were identified based on the data in card 46-1215 (and, accordingly, in Ref. [3]) for δ^* -Al₂O₃. The orthorhombic cell parameters were refined in space group P222 using CELREF software [11]. We obtained a = 7.933(2) Å, b = 7.965(3) Å, and c = 11.715(3) Å, in good agreement with those reported by Fargeot et al. [3]. As seen in the table, the Al₂O₃ powder with a specific surface area of 38.4 m^2/g contains a small amount of the θ -phase. Note also that 3 of the 46 diffraction peaks indicated in the table cannot be assigned to any of the phases identified. These peaks may be due to small amounts of other phases or to an increase in the unit-cell parameters of δ^* -Al₂O₃ [8, 9]. The peak corresponding to an interplanar spacing of 2.41 Å was assumed to have the Miller indices 302 and 032, which are missing in Ref. [3] and card 46-1215. As mentioned above, this peak may arise from the γ -phase (cubic spinel).



Fig. 6. (a) XRD pattern of the synthesized Al_2O_3 powder with an average specific surface area of 6.7 m²/g and (b) characteristic portion of the XRD pattern. Also shown are schematic XRD patterns of δ -, δ *-, and θ -Al₂O₃ (cards 56-1186, 46-1215, and 23-1009, respectively).

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| <i>I</i> , % | d, Å | <i>I</i> , % | hkl | d, Å | I, % | <i>d</i> , Å | <i>I</i> , % | <i>d</i> , Å | <i>I</i> , % | hkl | d, Å | I,% | <i>d</i> , Å |
|-------------------|--------|---|-------------|---|------|----------------------|--------------|---|--------------|-----------|---|-----|--------------|
| experimental data | | refined data of card 46-1215 for δ^* -Al ₂ O ₃ | | data of card 23- 1009 for θ -Al ₂ O ₃ | | experimental data | | refined data of card 46-1215 for δ^* -Al ₂ O ₃ | | | data of card 23- 1009 for θ -Al ₂ O ₃ | | |
| 4 | 7.9564 | 10 | 010 | 7.9702 | | | | | | 132 | 2.3130 | | |
| | | | $1 \ 0 \ 0$ | 7.9339 | | | 26 | 2.2810 | 50 | 223 | 2.2810 | 37 | 2.257 |
| 3 | 6.5668 | 10 | 101 | 6.5694 | | | 2 | 2.2208 | | | | | |
| | | | 011 | 6.5899 | | | 9 | 2.1615 | 10 | 115 | 2.1625 | | |
| 1 | 5.4830 | | | | 9 | 5.45 | 71 | 1.9907 | 80 | 040 | 1.9912 | 45 | 2.019 |
| 11 | 5.0610 | 50 | 111 | 5.0675 | | | 5 | 1.9900 | 80 | $4\ 0\ 0$ | 1.9832 | | |
| 2 | 4.7090 | 10 | 102 | 4.7119 | | | 43 | 1.9536 | 50 | 006 | 1.9524 | | |
| | | | 012 | 4.7186 | | | 4 | 1.8012 | 10 | 225 | 1.7995 | | |
| 4 | 4.5300 | | | | 17 | 4.535 | 2 | 1.7584 | | | | | |
| 7 | 4.0570 | 10 | 112 | 4.0554 | | | 1 | 1.7320 | | 143 | 1.7311 | | |
| 2 | 3.7461 | 5 | 201 | 3.7569 | | | 3 | 1.7004 | 5 | 422 | 1.6989 | | |
| 2 | 3.6460 | | | | | | | | | 242 | 1.7027 | | |
| 3 | 3.5510 | 5 | 210 | 3.5505 | | | 9 | 1.6156 | 10 | 144 | 1.6123 | | |
| | | | 120 | 3.5592 | | | 6 | 1.6041 | 10 | 117 | 1.6039 | | |
| 5 | 3.3960 | 10 | 211 | 3.3979 | | | | | | 226 | 1.6034 | | |
| | | | 121 | 3.4054 | | | 4 | 1.5442 | 10 | 511 | 1.5426 | 23 | 1.5426 |
| 6 | 3.2770 | 10 | 202 | 3.2842 | | | | | | 027 | 1.5428 | | |
| 4 | 3.2100 | 10 | 113 | 3.2068 | | | | | | 207 | 1.5418 | | |
| 4 | 3.0310 | 10 | 212 | 3.0362 | | | 5 | 1.5405 | | 316 | 1.5410 | | |
| 2 | 2.9200 | 5 | 004 | 2.9285 | | | 13 | 1.5114 | 10 | 152 | 1.5090 | | |
| 6 | 2.8520 | | | | 80 | 2.837 | 9 | 1.5036 | 10 | 512 | 1.5039 | | |
| 24 | 2.7864 | 50 | 023 | 2.7881 | | | 2 | 1.4872 | | 415 | 1.4871 | 26 | 1.4883 |
| 18 | 2.7288 | 50 | 221 | 2.7328 | 64 | 2.73 | 2 | 1.4615 | 10 | 335 | 1.4633 | | |
| 34 | 2.5938 | 80 | 114 | 2.5973 | | | | | | 326 | 1.4612 | 26 | 1.4526 |
| 2 | 2.5154 | | 130 | 2.5176 | | | | | | 236 | 1.4621 | | |
| | | | 310 | 2.5096 | | | 1 | 1.4347 | | 252 | 1.4332 | | |
| 55 | 2.4574 | 80 | 311 | 2.4539 | 62 | 2.444 | 12 | 1.4147 | 5 | 118 | 1.4171 | | |
| | | | 131 | 2.4614 | | | | | _ | 307 | 1.4141 | 10 | 1.4264 |
| 11 | 2.4106 | | 302 | 2.4101 | | | | | | 037 | 1.4157 | | |
| | | | 032 | 2.4181 | | | 68 | 1.4043 | 80 | 440 | 1.4052 | | |
| 5 | 2,3609 | 5 | 024 | 2.3593 | | | 100 | 1.3921 | 100 | 406 | 1.3913 | 100 | 1.3883 |
| 2 | 2.2009 | 5 | 204 | 2.3560 | | | 100 | 1.0921 | 100 | 046 | 1.3942 | 100 | 1.2002 |
| 25 | 2.3079 | 50 | 312 | 2.3068 | 46 | 2.315 | | | 200 | | | | |

Phases identified in the Al₂O₃ powder with a specific surface area of $38.4 \text{ m}^2/\text{g}$

The phase composition of the Al_2O_3 powders prepared by plasma synthesis can probably be determined more reliably by the Rietveld profile analysis method.

CONCLUSIONS

The present results on the whole agree with previous data for the metastable Al_2O_3 polymorphs forming during plasma synthesis. The synthesis conditions employed in this study and the use of aluminum as a starting material led to the formation of a mixture of metastable Al_2O_3 polymorphs, without α - Al_2O_3 . The major metastable phase in the mixture was $\delta^*-Al_2O_3$. The synthesized powder contained, in addition to the δ^* -phase, the θ -phase, tetragonal δ -phase, and, possibly, γ -phase (cubic symmetry). The percentage of $\delta^*-Al_2O_3$ in different size fractions was found to decrease with decreasing specific surface area. The powder with a specific surface area of $38.4 \text{ m}^2/\text{g}$ contained only trace levels of θ -Al₂O₃ and γ -Al₂O₃. In the powder with a specific surface area of $6.7 \text{ m}^2/\text{g}$, the tetragonal δ -phase prevailed. The annealing-induced transition to α -Al₂O₃ occurred through the θ -polymorph. A marked increase in the percentage of

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 θ -Al₂O₃ was observed even just above 600°C. The phase formation process is probably also influenced by the high-temperature annealing time.

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