

## Phase metastability of nanosized $\alpha$ - $\text{Al}_2\text{O}_3$ crystallites

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### Abstract

The reversal of the  $\alpha$ - to  $\theta$ - $\text{Al}_2\text{O}_3$  phase transformation and the induced microstructure evolution of boehmite-derived discrete nanosized  $\alpha$ -crystallites are examined. Three categories of  $\alpha$ -crystallites smaller than 100 nm were examined and found to have similar behavior: (1) pre-existing  $\alpha$ -crystallites, (2)  $\alpha$ -crystallites formed in situ during the calcination of  $\theta$ -crystallites of sizes near the critical size, 25 nm, and (3)  $\alpha$ -crystallites formed in situ by the thermal treatment of as-received  $\theta$ -crystallites. The  $\alpha$ -crystallite may transform back to the  $\theta$ -phase above 800 °C. The backwards  $\theta$ -crystallite may also re-transform to the  $\alpha$ -phase again. Because of the density difference between  $\alpha$ - and  $\theta$ - $\text{Al}_2\text{O}_3$ , the strain involved in the volume expansion and shrinkage during the phase transition eventually results in the formation of a twinned and/or mosaic structure for the  $\theta$ - and  $\alpha$ -crystallites. A strain release model representing the microstructure evolution of the  $\alpha$ - to  $\theta$ -phase and the  $\theta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transformation is proposed.

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### 1. Introduction

The nucleation and growth mechanism has been considered the elementary procedure for forming a new phase particle.<sup>1–3</sup> During the procedure, a critical size is required to form the nucleus of the new phase. As the nucleus continues to grow, exceeding the size at which the particle is thermodynamically stable; the volume energy,  $V\Delta G_v$  grows larger than the surface energy,  $S\Delta\gamma$  (the total free energy change,  $\Delta Gr$ , becomes negative, where  $\Delta Gr = S\Delta\gamma + V\Delta G_v \leq 0$ ). If the particles cannot grow past this threshold and meet the requirement  $\Delta Gr \leq 0$ , then the particles may shrink and disappear. However, in a solid-state system, the phase shrinking-and-disappearing phenomena may not occur, especially in a new phase that resulted from a phase transformation. Though it is seldom reported, it is more likely that, the shrinking-and-disappearing phenomena can be substituted by a phase transformation back to the antecedent phase.<sup>4–6</sup>

$\alpha$ - $\text{Al}_2\text{O}_3$  has long been one of the most widely used industrial ceramics because of its combination of physicochemical

properties such as high wear resistance, high melting point, and good thermal, chemical, and mechanical stability. However, its brittle nature limits its use in the manufacture of advanced materials and therefore imposes the limitations of its applications. Phase purity and crystallite size of the starting materials play a very important role in the fabrication of dense and fine-grained alumina ceramics and provide a pathway for overcoming the disadvantages.<sup>7</sup> Previous studies indicated that the transition  $\text{Al}_2\text{O}_3$  phase coupled with the high activation energy for nucleating  $\alpha$ - $\text{Al}_2\text{O}_3$  would greatly impede efforts to process dense  $\alpha$ - $\text{Al}_2\text{O}_3$  with a controlled grain size, especially for submicrometer materials.<sup>8</sup> The nanosized  $\alpha$ - $\text{Al}_2\text{O}_3$  powder currently found on the market can be composed of more than 95% of  $\alpha$ -phase  $\text{Al}_2\text{O}_3$  crystallites. However, these crystallites are generally approximately 150–200 nm in size and are characterized by a vermicular-growth structure. Each crystallite is a single crystal but with an outward shape formed by connecting two or more  $\alpha$ - $\text{Al}_2\text{O}_3$  crystallites with diameters of approximately 100 nm.<sup>9–11</sup> The vermicular microstructures occurring in the green compacts will inhibit further densification of alumina ceramics. Likewise, nanosized discrete  $\alpha$ - $\text{Al}_2\text{O}_3$  powder is of a lower  $\alpha$ -phase purity, though it can be composed of  $\alpha$ -crystallites free of vermicular-growths and is smaller than 100 nm. In other words, there is no high phase-pure discrete  $\alpha$ - $\text{Al}_2\text{O}_3$  crystallite powder less than

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Table 1  
The specification of commercial ultrafine  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallite powder available on the market.

Manufacturer	Product	$\alpha$ -Phase fraction (wt%)	BET (m <sup>2</sup> /g)	Average particles size (nm)
Taimei	TM-DAR	>99	13.2	190
	CR30F	80	26	400
Baikowski	CR10	98	8	450
	SPA-0.5		7.5	600
Sumitomo	AKP-3000	>99	4–8	400–700

TAIMEI Chemical Co., Ltd., Japan.

Baikowski Malakoff Inc., USA.

Sasol North American Inc., USA.

Sumitomo Chemical Co., Ltd., Japan.

100 nm in diameter available on the market at present (Table 1). In previous studies, both in the literature<sup>8</sup> and in experiences from research, it was found that nanosized high phase-pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallite powder was not easily obtained by thermal treatment of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> crystallites (crystallite size  $\leq 20$  nm) through  $\theta$ - to  $\alpha$ -phase transformation. It was not until very recently that fabrication of such powders through core–shell techniques using boehmite (AlOOH) as the starting material was reported to be possible.<sup>12</sup> The  $\alpha$ -phase Al<sub>2</sub>O<sub>3</sub> particle was obtained through the nucleation and growth mechanism,<sup>9–18</sup> which may either be thermodynamically metastable<sup>19–22</sup> or stay at the state of an unfinished phase transformation if the crystallite is smaller than the dimension needed to make the volume energy,  $V\Delta G_v$ , larger than surface energy,  $S\Delta\gamma$ . Recent studies<sup>19</sup> show that  $\Delta Gr$  of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites smaller than 100 nm could be greater than 0 and the crystallites could behave as thermodynamically metastable. Thus, the nanosized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites would experience phase transformation reversal, backwards to the antecedent  $\theta$ -phase if appropriate treatments were employed. The phase transformation reversal phenomena may be one of the major reasons why there is no high phase-pure discrete  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallite powder less than 100 nm in diameter available on the market.

Based on the concepts mentioned above, this study demonstrates the thermodynamic stability of boehmite-derived discrete  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites smaller than 100 nm in diameter. It attempts to describe the phase transformation reversal phenomena through XRD examinations, as well as microstructure evolution, which occurs to Al<sub>2</sub>O<sub>3</sub> crystallites when induced by density differences during the backward  $\alpha$ - to  $\theta$ - and the followed forward  $\theta$ - to  $\alpha$ -phase transformations. The densities of  $\theta$ - and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are 3.65 and 3.98 g/cm<sup>3</sup>, respectively,<sup>23</sup> allowing the occurrence of backward ( $\alpha$ - to  $\theta$ -Al<sub>2</sub>O<sub>3</sub>) and forward ( $\theta$ - to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) phase transitions to result in an 8.3% volume expansion and a 9.0% volume reduction to the Al<sub>2</sub>O<sub>3</sub> crystallites, respectively. Thus, it is possible to find the necessary information from the variation in volume,<sup>24</sup> especially for the microstructures exhibited by the larger Al<sub>2</sub>O<sub>3</sub> crystallites, using TEM techniques.

Boehmite-derived discrete  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites smaller than 100 nm were used as the examination sample. The  $\alpha$ -crystallite was obtained by thermal treatment of the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> crystallite (crystallite size  $\leq 20$  nm) through the  $\theta$ - to  $\alpha$ -phase transformation.<sup>25–27</sup> Previous studies have demonstrated that there is a critical crystallite size ( $d_{c\alpha} = \sim 17$  nm, XRD-Scherrer

formula on (012) <sub>$\alpha$</sub> ) for phase transformation<sup>16–18</sup> and that there can be a size limit of approximately 100 nm for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to be present as discrete particles.<sup>9,12,19,28</sup> Thus,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders with crystallites ranging from 20 to 100 nm in size were presumed to consist of metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles.<sup>19</sup> Furthermore, thermodynamically, the newly formed  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites that stay at the stage of crystal growth may behave as metastable. Clearly, both would transform back to the  $\theta$ -phase and thus should be examined. This study indicates that the phase transformation reversal phenomena may be one of the major reasons why it is not easy to obtain high phase-pure discrete  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallite powder of less than 100 nm in diameter through  $\theta$ - to  $\alpha$ -phase transformation.

## 2. Experimental

### 2.1. Sample preparations

Two categories of examination samples were used in this study.

- (1) Samples for examining occurrence of the  $\alpha$ - to  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase transformation: To observe the possible phase transformation reversal, a two-stage thermal treatment was employed. Firstly, commercial  $\theta$ -Al<sub>2</sub>O<sub>3</sub> powder (Ceralox Co., USA, Table 2) was heated at 1200 °C for 60 s in a tube furnace to intentionally produce approximately 30 wt% of incipient  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites less than 100 nm in size. Thus, the powder system was composed of  $\alpha$ - and two kinds of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> crystallites of different sizes: (1)  $\theta$ -Al<sub>2</sub>O<sub>3</sub> crystallites approximately 25 nm in size, the critical size of phase transformation<sup>16–18</sup> and (2) substantial amounts of the remainder  $\theta$ -Al<sub>2</sub>O<sub>3</sub> crystallites less than 25 nm in size. The possibility of reversal of the  $\alpha$ - to  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase transformation was then tested using the  $\alpha$ - +  $\theta$ -Al<sub>2</sub>O<sub>3</sub> crystallite powder. After heating at 1200 °C, to prevent the incipient nanosized  $\alpha$ -crystallites from growing, the powders ( $\alpha$ - +  $\theta$ -Al<sub>2</sub>O<sub>3</sub>) were subsequently moved from positions at 1200 °C to positions at 700–1000 °C in the tube furnace and then thermally treated for various durations. Particles at temperatures above 1000 °C were abandoned because of vermicular growth. It is apparent that the  $\alpha$ -crystallites represent pre-existing crystallites that are subject to phase-transforming

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