Engineering Science and Technology, an International Journal 17 (2014) 2–7

Contents lists available at ScienceDirect

Engineering Science and Technology, an International Journal

journal homepage: http://ees.elsevier.com/jestch/default.asp

Sintering and microstructural investigation of gamma–alpha alumina powders

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ARTICLE INFO

Article history:
Received 29 December 2013
Received in revised form
7 February 2014
Accepted 11 February 2014
Available online 26 March 2014

Keywords:
Alpha–gamma
Alumina
Phases
Densification
Sintering

ABSTRACT

Sintering behaviors of commercially available alumina powders were investigated using constant-heating rate dilatometric experiments. Each powder had different proportion of alpha/gamma alumina. Densification behaviors of powders were studied up to 1600 °C with three different heating rates of 1, 3.3 and 6.6 °C/min. Compacts of different gamma content alumina powders exhibited systematic anomalous second peaks in the densification rate curves at certain heating rates and temperatures. At 3.3 °C/min heating rate experiments, densification curves of 10% gamma phase alumina powder compacts reached a plateau after 1450 °C, and did not increase any further at higher temperatures. This phenomenon was double checked to understand powder behavior during sintering. 10% gamma phase alumina powder compacts showed the highest density for each heating rate. It reached 94% theoretical density with 1 °C/min heating rate. But 20% gamma phase alumina powder compacts had the finest grain size of about 1.40 μm. Final density and porosity of compacts were also tested by image analysis and the results were coherent with Archimedes results.

1. Introduction

Alpha alumina (α-Al_2O_3) has unique mechanical, electrical, and optical properties therefore it is utilized in many areas of modern industry. Properties of ceramic materials are governed by their microstructures. To obtain superior microstructures, refining α-Al_2O_3 processing technique is of great interest. Transition alumina phases have recently attracted much attention because of their intrinsically nanocrystalline nature and because they can be synthesized by a variety of techniques [1]. Gamma alumina (γ-Al_2O_3) is the most common transition alumina phase. When γ-Al_2O_3 is heated, it undergoes a series of polymorphic transformations from a highly disordered cubic close packed lattice to the more ordered cubic close packed θ-Al_2O_3. When heated to $\approx$1200 °C, θ-Al_2O_3 undergoes a reconstructive transformation by nucleation and growth, where the oxygen atoms rearrange into a hexagonal close packed structure to form thermodynamically stable α-Al_2O_3 [1,2].

$$\gamma\text{–}Al_2O_3 \rightarrow \delta\text{–}Al_2O_3 \rightarrow \theta\text{–}Al_2O_3 \rightarrow \alpha\text{–}Al_2O_3$$

The α-Al_2O_3 phase transformation occurs by nucleation and growth. A low intrinsic nucleation density results in large spacing between nucleation events and the formation of micrometer scale, single crystal α-Al_2O_3 grains with dendritic protrusions surrounded by continuous pore channels. The resultant vermicular microstructure requires sintering temperatures >1600 °C to reach high densities [3]. To obtain dense, fine-grained α-Al_2O_3 at low temperatures, the scale of the vermicular microstructure must be minimized [4].

A number of researchers have attempted to enhance the transformation and the final microstructure of alumina ceramics by using dopants or by seeding [5–7].

The more relevant study, Kim and Kim [8] investigated the effect of phase transformation and dispersion of fine zirconia particle on densification of high purity nanocrystalline alumina. They mixed α-alumina with γ-alumina at different ratios and pressureless-sintered at different temperatures for 3 h in air atmosphere. According to their study, full densification with fine microstructure for the 10% γ-phase dispersed α-alumina specimen was achieved by the rapid transformation to α-phase and by the zirconia dispersion.

The objective of this investigation, therefore, was to compare the densification behavior by following the densification curves and following the corresponding microstructure evolution of three

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Peer review under responsibility of Karabuk University

http://dx.doi.org/10.1016/j.jestch.2014.02.001

Table 1
Chemical and physical properties of the powders [9].

		CR6	CR15		CR30	
Present phases		100% α	90% α	10% γ	80% α	20% γ
Ultimate particle size/TEM (nm)		400	350	20	300	20
Alpha crystallite size/RD (nm)		50	45	–	40	–
BET SSA (m^2/g)		6	15		26	
Chemical analysis ICP (ppm)	Fe	4	4		5	
	Na	13	13		13	
	Si	13	13		16	
	Ca	3	3		2	
	K	22	22		22	

different commercial aluminas, two of them contained some γ-Al_2O_3 phase and the last one was high purity α-Al_2O_3. We hope to elucidate the key mechanism of such gamma to alpha phase transformation assisted densification.

2. Material and methods

Three kinds of commercial grade submicron-grained alumina, one of them is 100% alpha (α) phase (CR6-Baikowski) powder and the second one is 10% gamma (γ) and 90% alpha-alumina phases (CR15-Baikowski) powder and the last one is 20% gamma and 80% alpha alumina phases (CR30F-Baikowski) powder were used. Their designations and some physical, chemical properties are shown in Table 1. These powders with gamma and alpha alumina phases are not mixtures blended by the authors but are mixed-phase commercial products directly obtained from the manufacturer.

Particle size distributions of the powders were analyzed by sedigraph method (Micrometrics Sedigraph III 5120). Specific surface areas of powders were measured by Brunauer, Emmet and Teller (BET) method (Micrometrics Gemini V). Particle morphologies of powders were investigated using SEM (SEM, Philips XL-30S FEG). The present crystalline phases were examined by X-ray diffraction (XRD, Philips X-Pert Pro). The sintering behavior of the powders were investigated by dilatometric method. The powders were uniaxially pressed at 200 MPa (ϕ:10 mm) and the compacts were sintered in the vertical dilatometer (Linseis L75V) up to 1600 °C under static air with different heating rates of 1, 3.3 and 6.6 °C/min. Final densities of the sintered compacts were measured by Archimedes' method (ASTM C373-88). Theoretical density for alumina was taken as 3.987 g/cm^3. To investigate the microstructure of the sintered compacts, specimens were cut from their center and then were polished with fine diamond suspension up to 1 μm. The polished surfaces were thermally etched at 100 °C below the sintering temperature for 1 h. The polished and thermally etched surfaces were investigated under SEM. The grain size was roughly measured from polished and thermally etched surfaces of sintered alumina ceramics.

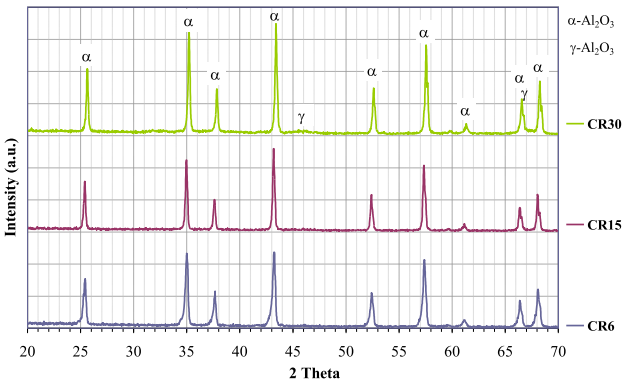

Fig. 1. XRD analysis results of the powders.

3. Results and discussion

Fig. 1 shows the XRD results of the raw powders. The peaks for the alpha phase were quite clear and sharp while those of the gamma phase were barely noticeable. The bump at 46° 2θ angle for CR30 sample is visible as this sample contains 20% gamma phase. An explanation might be that gamma alumina gives a signal of very low intensity compared to alpha alumina.

Specific surface area (SSA) of the powders was measured by the BET method. Both published and measured SSA values of the powders are given in Table 2. Published data were obtained from the producer and may change from lot to lot. Measured SSA values differed slightly from the published value, as expected.

With the sedigraph method it has been possible to investigate the particle size distributions of the powders through the granulometric curves (Fig. 2). Results are shown in Table 3 and were compared with the ones reported by the producer. The accordance between the D_{50} values obtained with this analysis and the one given by the producer were good, in fact the results were very close. It is also important to underline that a significant fraction of the powders were finer than 1 μm.

Through SEM investigation, powders morphologies and the possible agglomerations were investigated and powder particle size was roughly measured. In Fig. 3 some SEM images of the powders are shown and in Table 4 particle size results are reported.

The analyses on SEM images show some presence of soft agglomerations of the powders (Fig. 3a, c and e). At higher magnification (100 k×) γ-phase was not observed in sample CR6 (Fig. 3b). Presence of γ-phase alumina (Fig. 3d and f), as indicated by the circles and arrows, was observed in CR15 and CR30 samples. It is also possible to have a rough idea of the differences in the quantity of γ-alumina among CR15 and CR30. A particular shape of the γ-alumina powders was mainly *vermicular*.

Table 5 compares particle diameter results as obtained by different characterization techniques and the data from the producer. Important to be noticed was that there was good accordance between the results obtained with the sedigraph method and SEM images analysis, also compared to the one furnished by the powder producer.

3.1. Constant heating rates (1, 3.3 and 6.6 °C/min)

Different sets of samples were prepared to study the three different aluminas. It was decided to select three different heating regimes to analyze the sintering behavior of the powders: Constant Heating Rate (CHR) at 1 °C/min, 3.3 °C/min and 6.6 °C/min, up to 1600 °C.

Some codes are used to identify clearly the kind of powder and the heating regime used to sinter the pellet. The designation of the powders and heating rates are shown in Table 6.

Table 2
BET analysis results.

	CR6	CR15	CR30
Measured specific surface area (m^2/g)	4.0 ± 0.2	12.2 ± 0.2	21.6 ± 0.3
SSA (data from the producer) (m^2/g)	6	15	26