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Effect of freeze-drying treatment on the optical properties of SPS-sintered alumina

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Abstract

This study looks at the influence of alumina powder processing on the preparation of transparent alumina by Spark Plasma Sintering (SPS). Zeta potential measurements were carried out on alumina suspensions in order to determine the best dispersion conditions. Stable slurries were submitted to a spray freeze drying process and their sintering behavior was compared with the corresponding non spray freeze dried powders. Transparent alumina samples were successfully prepared from alumina powders by Spark Plasma Sintering. An optical model considering pore and grain size distributions has been developed to obtain information about porosity in dense materials. It was found that the final density and, accordingly, the optical properties were improved when spray freeze dried starting powder was used.

Keywords: A. Sintering; C. Optical properties; D. Al_2O_3

1. Introduction

Transparent alumina (Al_2O_3) ceramic can be obtained either as single crystal, sapphire, or in polycrystalline form, and it is used for different applications such as IR windows [1,2], high pressure discharge lamps [3–5], coatings [6], etc. Compared with sapphire, the cost of producing polycrystalline alumina is lower, it is less time-consuming, and it is easier to produce in large size components. Homogeneous particle compaction in the green body is well-known to be a critical parameter in connection with preparing dense and defect-free ceramics with superior optical and mechanical properties [7], since transparent polycrystalline materials require high densities and low porosity ($<0.05\%$) [8].

Mixing and grinding of slurries is often the first step of ceramic processing. One of the main problems in the development of these materials is that ceramic powders tend to agglomerate due to the attractive inter-particle Van der Waals forces. The presence of these agglomerates makes it difficult to obtain a good homogeneity of the particle coordination leading to local density gradients and the resultant green compact formed is not homogeneous [9]. In order to obtain stable slurries, it is beneficial to control the dispersion of the powders, which in turn, generates homogeneously dispersed particles after drying. Changing the inter-particle forces leads to well-dispersed, weakly flocculated or strongly flocculated aqueous suspensions [10].

The drying processes applied to the starting suspensions have significant influence on the properties of the final powders. Access to a fine dispersion of nano-sized alumina powder that is subsequently dried using an appropriate procedure is one of the most important steps in obtaining well dispersed alumina powder [11]. A re-agglomeration of the powders frequently occurs when conventional drying methods are used. This implies that alternative methods of drying such as the freeze-drying process are of interest.

The freeze-drying process [12–14], involves the rapid freezing of small droplets of a well dispersed solution containing the desired components that in turn is well dispersed. The water content is subsequently removed by

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sublimation using standard freeze-drying conditions yielding highly dispersed powders [15,16].

However, not even well-prepared green bodies, free of agglomerates, ensure obtaining a transparent material and special, optimized sintering regimes are required. Conventional sintering often leads to a residual porosity or grain growth that prevents transparency in the sintered materials. In this way the strategy consists of performing pressure-less sintering, sometimes combined with doping, up to closed porosity followed by hot-isostatic post-densification.

More recently, with the development of non-conventional techniques other approaches leading to transparent materials have been implemented such as microwave sintering or Spark Plasma Sintering. The main advantage of these techniques is that very high heating rates (>100 °C/min) compared to conventional sintering can be applied. In the particular case of spark plasma sintering, also a pressure over 100 MPa can be applied during the sintering cycle, which helps reaching higher densities.

The aim of this work is to study the influence of applying the spray freeze drying process to nano-sized alumina powders on the sintering behavior using SPS and its influence on the final optical properties of the materials obtained.

2. Experimental procedure

The starting material was a commercially available alumina powder (TM-DAR, Taimei Chemicals, Japan) of 99.99% purity with an average particle size of 150 nm and a specific surface area of 14.5 $m^2\, g^{-1}$.

Nano-ZP (Malvern Instruments) was used to measure the zeta potential of alumina at different pH values. The pH of the slurries was changed by the addition of reagent-grade HNO_3 (65%, Fluka) or NH_4OH (25% NH_3 in H_2O, Fluka), in order to reach pre-determined pH levels between 4 and 12. Alumina slurries with solid contents of 50 wt% and 6 cP of viscosity approximately measured by viscometer equipment at 100 rpm (Brookfield), were prepared in distilled water at pH 4 and mixed in a ball-mill for 1 h. Droplets were formed using a conventional sprayer (with an inner diameter around 0.8 mm and a pressure around 0.3 MPa) over liquid nitrogen. The frozen solution was placed in a freeze dryer (Hetosicc Model, 1481N S1L) for 72 h. The microstructure of the powders was observed using a high-resolution scanning electron microscope, SEM (JEOL JSM-7000F).

Approximately 0.9 g of the spray freeze dried powder and of the starting powder, respectively, was put into a graphite die (12 mm diameter) and sintered in a SPS apparatus. (Dr. Sinter 2050, Syntex Inc. Japan). The samples were heated to 1400 °C at a rate of 100 °C/min with a holding time of 3 min and at a pressure of 100 MPa.

The Archimedes method does not provide values of density higher than 99.5%. For this reason in order to know the real density of the specimens a theoretical model based on that given by Apetz and Van Bruggen was used [17]. The sintered samples, each having a thickness of ~1 mm, were polished down to 0.8 mm using a finish of 1 μm prior to taking the transmittance measurements (Perkin Elmer UV/VIS/NIR Spectrometer Lambda 19).

3. Results and discussion

Grain size, absence of agglomerates and high density are important features for making transparent materials. Krell et al. [18] have shown that in order to obtain high density alumina components, it is necessary that the particle size distribution in the starting powder be as narrow as possible.

According to Fig. 1, the zeta potential of the alumina suspensions has an isoelectric point close to a pH value of 9.5. At pH lower than 6.5, the zeta potential value remains constant and is in the range of 60 mV, indicating that the original surface of the alumina particles is completely charged with positive charges and a stable suspension can be expected [19]. Rheological measurements indicated that the suspensions with small potential values contained agglomerated powder particles [20].

The microstructures by SEM of the alumina powder before and after spray freeze drying are shown in Fig. 2. After the spray freeze drying process, the particles show a spherical morphology with a narrow particle size distribution and an average particle size around 150 nm. Although the individual particle size is the same in both the raw material and the spray freeze dried powder, the former powder contains larger agglomerated particles with diameters of over 3 μm. Thus the applied spray freeze drying process allows us to prepare a well dispersed alumina powder with a narrow particle size distribution.

Typical shrinkage rate curves for the two powder samples as a function of the sintering temperature are given in Fig. 3. It is evident that when the starting powder is not agglomerated, the densification takes place in a much narrower temperature range than the agglomerated powder, which has been confirmed by previous findings [21].

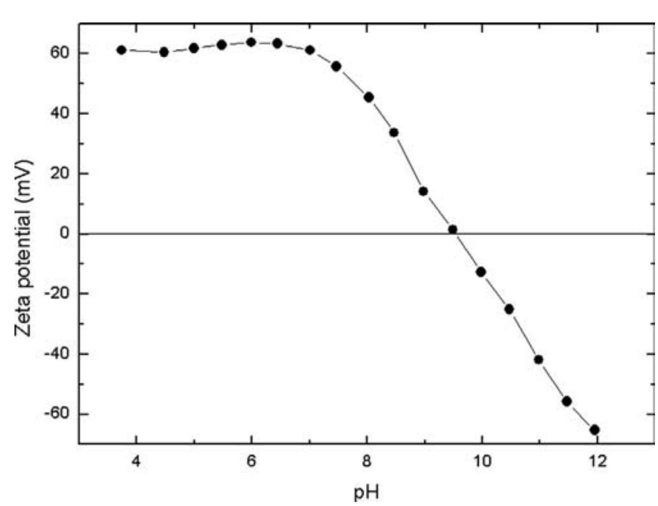

Fig. 1. Zeta potential plotted as function of pH.

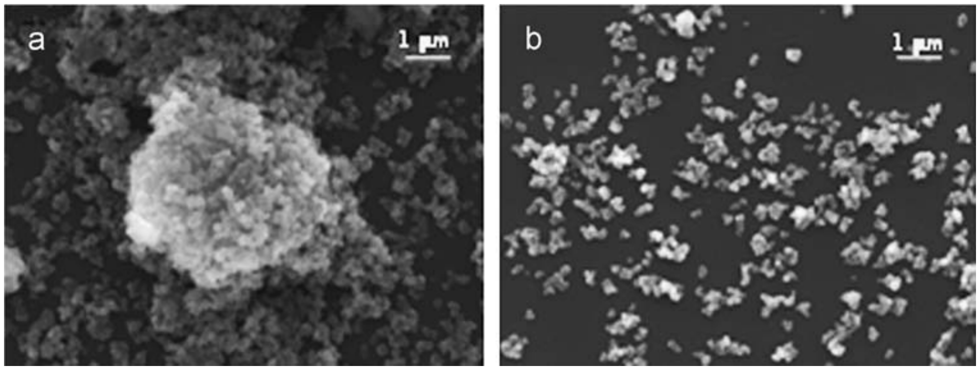

Fig. 2. Microstructure of Al_2O_3 (a) before and (b) after being spray freeze dried.

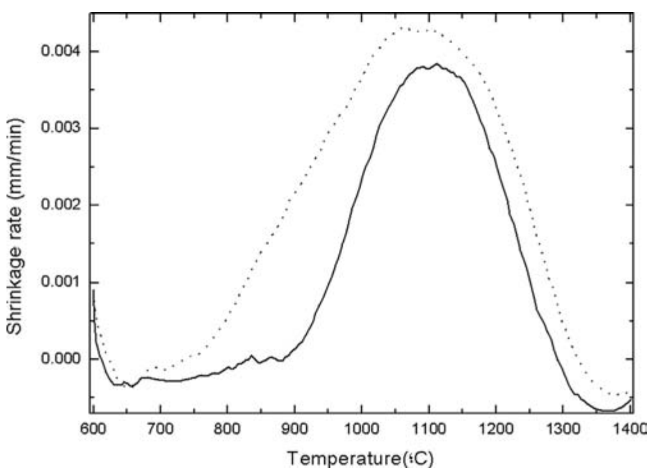

Fig. 3. Shrinkage rate vs. temperature for spray freeze dried (solid line) and not spray freeze dried (dotted line) samples.

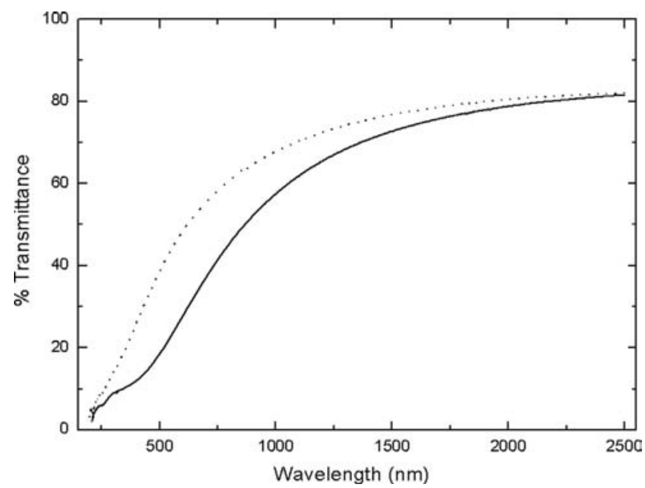

Fig. 4. Transmittance for spray freeze dried (solid line) and not processed (dotted line) alumina powders.

The initial size of the particles, size distribution, morphology, presence of aggregates and the friction resistance of particles against packing influence the packing (green body) density and the distribution of smaller and larger pores, etc. Upon heating and when a uniaxial pressure is applied the friction resistance of particles is reduced, which, in turn, may lead to the collapse of particle aggregates, yielding a denser packing of the initial particles. During the hot pressing the powders are also subjected to a radial constraint from the die wall, with the radial stress generated at the die wall being proportional to the applied pressure according to an effective Poisson's ratio, υ. This radial stress causes inter-particle shear, which, in turn causes particle rearrangement, collapse of larger pores, elimination of flaws and disruption of particle surface films. Green bodies formed from spray freeze dried powders contain less large pores than the green bodies from the non-processed powder due to the easy collapse of weak granules. The shrinkage starts at a lower temperature in the case of non-processed powder and the initial shrinkage is ascribed to the collapse of particle aggregates and larger pores. In the absence of aggregates and large pores the shrinkage rate curve for the spray freeze dried powder proves much narrower and more symmetrical than the corresponding curve for the non-processed powder.

The transmittance spectrum in the visible range for the SPSed alumina powders is shown in Fig. 4. The presence of agglomerates in the compacts creates local density variations, and partial sintering may occur between individual agglomerates and the surrounding material, creating larger pores or even cracks [22]. Accordingly, the transmittance values at 640 nm are 16% less in the case of the powder which is not spray freeze dried.

The transmittance values were normalized following the expression given in Ref. [23]. Information concerning the total porosity and its distribution in the different sintered materials was obtained according to Ref. [17] (Table 1). Average grain size and its distribution were obtained from the SEM characterization and in this case are not fitting parameters.

According to the results shown in Table 1, the spray freeze drying process is an effective method for avoiding the formation of agglomerates and yields a homogeneous grain size distribution that in turn yields a green body with an improved particle packing. This enhanced packing allows a

Table 1
Grain size, pore size and porosity for the sintered samples with and without FD.

Sample	Grain size (μm)	Pore size (nm)	Porosity (%)
Al_2O_3 without FD	0.70 ± 0.10	20 ± 6.7	0.01
Al_2O_3 with FD	0.65 ± 0.10	12 ± 4.0	0.002

reduction of 80% in porosity and 40% in the pore size, leading to samples with a larger transmittance than the non-processed ones. The transmittance value achieved with the freeze-dried powders is 52% at 640 nm, this value being remarkably better than the transmittance reported previously, 30.5% [24] and 35% [25] approximately.

4. Conclusions

Freeze-drying is an effective method of dispersion since it is possible to prevent the formation of agglomerates and produce fine and dispersed powders. Samples prepared from spray freeze dried powders show higher density values due to the fact that this method of dispersion causes a uniform distribution of particles and improves the green body package. A combination of freeze-drying and SPS sintering allows the preparation of transparent polycrystalline alumina compacts. These samples show transmittance values of around 80% in the near-IR range and 52% at 640 nm.

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