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Ceria doped alumina by Spark Plasma Sintering for optical applications

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Abstract

Al_2O_3–CeO_2 ceramics were found to be transparent in the IR range and high-traslucent in the visible range. The surface of nanometric α-alumina particles was modified by deposition–precipitation of small fractions of ceria nanoparticles. The powders were sintered using Spark Plasma Sintering. Values of Real In-line Transmittance up to 70% in the IR-Vis range have been measured. Transparency enhancement has been attributed to Cerium oxide nanoparticles located at the grain boundaries and triple points. These particles are hindering alumina grain growth during SPS at a temperature as high as 1430 °C. This effect is found to be effective under SPS low vacuum conditions and short dwell times. The optimum ceria content was found to be 0.7 wt.%. Diffusion in Al_2O_3–CeO_2 as a function of the atmosphere has been studied in diffusion couples. The results obtained by the proposed route are discussed considering the data reported in the literature for SPS_{ed} transparent alumina.

Keywords: Optical properties; Al_2O_3; CeO_2

1. Introduction

The combination of high transparency and excellent mechanical properties such as hardness or chemical stability, makes polycrystalline transparent alumina (PTA) an interesting option in industrial and military applications such as armour parts, discharge lamps, airborne infrared sensors and laser.[1] However, obtaining large or complex shaped PTAs samples is still a challenge. The achievement of transparency in this material needs the accomplishment of mainly two requirements. Firstly, the residual porosity in the material has to be lower than 0.05 vol.%.[2] Secondly, the grain size has to be as small as possible in order to minimize the effect of the birrefringent character of alumina. In this context, the key factor to achieve these goals seems to be the control of the grain growth in order to decrease the flaw size (<100 nm) and, therefore, the volume of porosity.

The effect of the addition of small percentages of dopants such as Mg, Ti, Ca,[3–5] Zr, Y or Ln in the optical properties of alumina has been widely studied in further investigations. High transparency has been achieved using both sinter-HIP[6] and SPS[7] with MgO dopants. Despite the fact that these compounds modify the grain growth rate in alumina, it is not evident to achieve transparency due to the anisotropic character of the alumina grains. In this regard, alumina/ceria is a promising system due to its ability to change its oxidation state with oxygen partial pressure,[8] as well as the grain growth inhibition,[6] which permits to use the sintering atmosphere to control the grain growth instead of the restrictive heating rates in SPS. In the present work, the influence of CeO_x doping on the transparency of SPS_{ed} alumina compacts is investigated (CeO_x is a mixture of Ce_2O_3 and CeO_2 (according to XPS analysis approximately in a proportion of 50%), as reported in our previous work,[9] where the oxidation state of cerium has been determined for SPS_{ed} samples in vacuum by means of XPS analyses.

2. Materials and methods

Pure α-alumina (*Taimei TM-DAR*, average particle size: 170 nm, *Taimicrons*, Japan) and a ceria precursor (Cerium (III) acetate hydrated, *Sigma Aldrich*) have been used to prepare

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Table 1
Ceria content and grain sizes of the different SPS_{ed} samples.

Sample	wt.% CeO_2	Alumina grain size (μm)	Maximum calculated grain diameter Al_2O_3 (μm)	Maximum measured grain diameter Al_2O_3 (μm)
A	0	2.8 ± 0.1	6	5.7
Ace-03	0.3	0.72 ± 0.11	2.2	2
Ace-05	0.5	0.49 ± 0.03	1.3	1.3
Ace-07	0.7	0.38 ± 0.03	0.6	0.85
Ace-1	1	0.47 ± 0.02	–	1.14

alumina/ceria nanopowders. Powders with CeO_2 contents of 0.3, 0.5, 0.7 and 1 wt.% have been prepared, following the wet processing route described by the authors elsewhere.[9] Pure alumina has been sintered under the same conditions for comparison purposes. The alumina/ceria powders have been uniaxially pressed at 15 MPa and subsequently Spark Plasma Sintered in vacuum (10^{-2} mbar) at 1430 °C. The heating rate was 50 °C min^{-1}; a pressure of 80 MPa was applied after reaching the temperature of 600 °C, until the end of the process. The dwell time at the maximum temperature was 2 min. A summary of the different samples studied is presented in Table 1.

The reactivity of the Al_2O_3-CeO_2 system in pressureless sintering as a function of the atmosphere has been determined by means of diffusion couples. Al_2O_3 and CeO_2 laminates have been pressed at 200 MPa and sintered at 1600 °C in air during 2 h. Once sintered, the surface of the samples was polished down to 1 μm. The polished surfaces of alumina and ceria laminates (5 × 2x2 mm) were kept in contact under the weight of a block of alumina (20 g). The diffusion couples were heated at 1500 °C for 12 h in either argon or air. Once treated, the cross section of the samples were polished down to 1 micron and the diffusion behaviour of the different species was observed by Scanning Electron Microscopy (SEM, *Hitachi* TM3000) provided with EDX analysis (*Bruker*, *Quantax* 70).

For the measurement of the optical properties, the surfaces were polished down to 1 μm using diamond paste. The real in-line transmittance (RIT) spectra of the sintered samples were determined in the range 2.5-5 μm with a Nicolet 20 SXC FTIR spectrophotometer; for the 0.9-2.5 μm range, a Bruker IFS 66 V FTIR spectrophotometer was used; finally, in the visible range, measurements were carried out with a JASCO V-660 spectrophotometer.

The microstructure of the polished samples was observed by Field-Emission-Scanning Electron Microscopy (FE-SEM, Zeiss Ultraplus) and SEM. The samples were previously thermally etched in vacuum to activate their surfaces. For that purpose, the selected temperature was $0.7 \cdot T_s$, where T_s represents the sintering temperature of the sample. The etching time was 5 min. Grain size of alumina samples was calculated by an intercept method.[10] The crystalline phases formed in the different materials were analysed by X-ray Diffraction (Bruker D8).

2.1. Theory/calculation

For the explanation of the light scattering behaviour in the near-IR (NIR) and visible (VIS) range, a light scattering model under the approximation for polycrystalline alumina has been introduced. The model states that transmittance of well-polished dense alumina has two main scattering mechanisms: pore scattering (given by a Rayleigh approximation) and grain scattering (model by a Rayleigh-Gans-Debye expression). The first one is the classical $(a/\lambda)^4$ scattering law (being a the pore radius and λ the incident wavelength) while the second one follows a $(a/\lambda)^2$ law.[11] In a recent paper,[12] it has been shown that, not only on the maximum grain size is relevant for light scattering in anisotropic ceramics, but also the preferential orientation of their c-axis, or texture must be taken into account. The effect of texture in transparency experimentally measured on dense alumina samples with different grain size has shown very good agreement with the results of x-ray Rietveld refinements. The analytical expression for the scattering efficiency factor is

$$Q_{\mathrm{RGD}}(x,\xi) = 2x^2 \frac{\Delta n^2}{n_{av}^2}\alpha(\xi) \tag{1}$$

where Δn is the difference between the refraction index in the different axis (equals to 0.008 for α-alumina) and d is the thickness of the sample. Using these variables, a straight line is obtained for the Rayleigh–Gans–Debye approximation, its slope being proportional to the maximum grain size a_g and textural parameter $\alpha(\xi)$.

The total scattering efficiency factor is the sum of the scattering contribution of grains plus pores[11]:

$$Q = Q_R + Q_{\mathrm{RGD}} = \frac{8}{3}\left|\frac{\Delta n_{av}^2 - 1}{\Delta n_{av}^2 + 2}\right|^2 \left(\frac{2\pi a_d}{\lambda}\right)^4 + 2\left(\frac{2\pi a_g}{\lambda}\right)^2 \frac{\Delta n^2}{n_{av}^2}\alpha(\xi) \tag{2}$$

Where a_d is the deffect size and Δn_{av} the relative refractive index contrast in respect to the ceramic matrix. The relationship of the scattering efficiency factor with absorbance coefficient κ is given by:

$$\kappa = \pi a^2 Q \quad N$$
$$\kappa = \frac{3}{4}\left(f_p \frac{Q_R}{a_p} + \frac{Q_{\mathrm{RGD}}}{a_g}\right) \tag{3}$$

where N is the volume density of defects and f_p is the volume concentration of pore/inclusions. The total transmittance is therefore given by the light transmitted through a transparent samples (only affected by reflectance losses) times the factor