Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 9692–9700

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The influence of MgO, Y_2O_3 and ZrO_2 additions on densification and grain growth of submicrometre alumina sintered by SPS and HIP

Dušan Galusek[a,*], Jaroslav Sedláček[b], Jozef Chovanec[a], Monika Michálková[a]

[a]Vitrum Laugaricio – Joint Glass Center of the IIC SAS, TnU AD, and FChPT STU, Trenčín, Slovakia
[b]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

Received 17 March 2015; received in revised form 8 April 2015; accepted 8 April 2015
Available online 15 April 2015

Abstract

Spark plasma sintering followed by hot isostatic pressing was applied for preparation of polycrystalline alumina with submicron grain size. The effect of additives known to influence both densification and grain growth of alumina, such as MgO, ZrO_2 and Y_2O_3 on microstructure development was studied. In the reference undoped alumina the SPS resulted in some microstructure refinement in comparison to conventionally sintered materials. Relative density $>99\%$ was achieved at temperatures $>1200\ ^\circ C$, but high temperatures led to rapid grain growth. Addition of 500 ppm of MgO, ZrO_2 and Y_2O_3 led, under the same sintering conditions, to microstructure refinement, but inhibited densification. Doped materials with mean grain size <400 nm were prepared, but the relative density did not exceed 97.9%. Subsequent hot isostatic pressing (HIP) at 1200 and 1250 °C led to quick attainment of full density followed by rapid grain growth. The temperature of 1250 °C was required for complete densification of Y_2O_3 and ZrO_2-doped polycrystalline alumina by HIP (relative density $>99.8\%$), and resulted in fully dense opaque materials with mean grain size <500 nm.

Keywords: A. Hot isostatic pressing; A. Sintering; B. Grain size; B. Microstructure-final; D. Al_2O_3

1. Introduction

Polycrystalline alumina (PCA) with submicrometre grains (0.3–1 μm) is reported to have high hardness [1,2] good mechanical strength, [3–5] and improved wear resistance [6]. Alumina also transmits infrared radiation, and if sintered to high density (residual porosity $<0.01\%$), also visible light with possible applications in high pressure envelopes of metal halide discharge lamps [7,8], or transparent armors [9,10]. The in-line transmission in the absence of light scattering centers (pores) in birefringent materials such as alumina is expected to increase markedly if the grain size is lower than the wavelength of visible light, i.e. <340 nm [11]. Due to the lack of sufficiently fine-grained α-Al_2O_3 powders the preparation of fully dense PCAs (residual porosity $<0.01\%$) with such fine grained microstructure by conventional sintering is virtually impossible, because it requires long soaking times at high temperatures, accompanied by significant, and often abnormal, grain growth. Typically, 90% of the grain growth takes place during the final stage of sintering [12,13]. Alternatively, unconventional sintering techniques such as two stage sintering [14–17], and pressure assisted sintering techniques, such as spark plasma sintering [18], hot isostatic pressing, or sinter-HIP techniques [19] or their combinations with conventional sintering can be used, which attempt to eliminate residual porosity without excessive final-stage grain growth.

Among them, spark plasma sintering (SPS) attracts significant attention, with a reported decrease of sintering temperature and shortening of soaking times in comparison to conventional sintering. [18,20–28]. SPS seems to accelerate the processes responsible for densification and grain growth, either by self-heat generation by microscopic discharge between particles, activation of particle surfaces [21] or by electric field accelerated grain boundary diffusion and grain boundary migration [25]. It is tempting to believe that grain boundary migration requires higher

*Corresponding author.
E-mail address: dusan.galusek@tnuni.sk (D. Galusek).

http://dx.doi.org/10.1016/j.ceramint.2015.04.038
0272-8842/

temperatures and pressures than densification, and that the SPS process might, under certain conditions, result in significant microstructure refinement during sintering of alumina. Indeed, some works report on refinement of the microstructure of PCA prepared by SPS in comparison to traditional sintering, or retention of a very fine grained microstructure of PCA prepared from submicrometre powders [20,24,26]. In general, high pressure, high heating rate (>50 °C min^{-1}) and low temperatures are considered prerequisite for the retention of fine grained microstructures, although some recent works favor low heating rates, at the level of 2–8 °C min^{-1} for the preparation of fine grained and transparent PCAs [29–31] Moreover, despite the reported grain growth-retarding action of MgO in SPS–PCA [20,28], little attention has been paid until now to the influence of other known grain growth retardants, namely ZrO_2 and Y_2O_3, whose influence on the microstructure development during conventional [32–34] and two stage sintering of alumina is well documented [17,35].

Hot isostatic pressing is conventionally used for preparation of fine grained ceramics with zero residual porosity. The application of pressure reduces the sintering temperature, facilitating fast densification while simultaneously limiting the grain growth [19,36].

In the present work we report the results of the study on preparation of submicrometre PCA by SPS, and by SPS combined with HIP, with special attention paid to the influence of minor, deliberately added dopants MgO, ZrO_2 and Y_2O_3 on densification and grain growth. The results are compared to pure reference PCA densified by SPS and with the use of conventional pressureless sintering.

2. Experimental

Alumina powder (Taimicron TM-DAR, Taimei Chemicals Co., Japan) with mean particle size 150 nm and surface area 13.7 m^2 g^{-1} was used as a starting material. The reference undoped materials (denoted as A) were prepared both by conventional pressureless sintering and by SPS.

Green disks 12 mm in diameter and 6 mm thick were prepared by axial pressing in a steel die at 50 MPa followed by cold isostatic pressing at 500 MPa. These were conventionally sintered without pressure in an electrical furnace with $MoSi_2$ heating elements in air at various temperatures ranging from 1000 to 1350 °C without isothermal dwell (heating rate 10 °C/min).

For SPS 6 g of the alumina powder was filled into a graphite die with the diameter of 20 mm and spark plasma sintered in the temperature range between 1150 and 1250 °C, with heating rate 400 °C/min, pressure 150 MPa, equilibration time at maximum temperature 1 min, and subsequent isothermal dwell between 1 and 6 min.

Doped powders were prepared by mixing 100 g of the alumina powder with appropriate amounts of suitable precursors: Mg $(NO_3)_2 \cdot 6H_2O$ (p.a., Lachema Brno, Czech Republic), zirconium isopropoxide (p.a., Sigma-Aldrich), and Y_2O_3 (99.9% purity, Treibacher Industries AG, Austria) dissolved in nitric acid (p.a., Lachema Brno, Czech Republic). The mixture was homogenized in a polyethylene jar in isopropanol (pure, Sigma-Aldrich) with high purity alumina milling balls for 2 h. An aqueous solution of ammonia was then added to precipitate the respective hydroxides. The mixtures were then further homogenized for 2 h to complete the hydrolysis, and dried under continuous stirring under an infrared lamp. The powders were crushed with a pestle in an agate mortar, sieved through a 100 μm polyethylene sieve, calcined for 1 h at 800 °C in air, and sieved again to obtain a reasonably free flowing powder. The powders were filled into a graphite die with a diameter of 20 mm and spark plasma sintered at temperatures between 1150 and 1300 °C, under the same conditions as the reference material A. The specimens containing MgO, Y_2O_3 and ZrO_2 are denoted as AM, AY, and AZ, respectively. No measurable carbon contamination was observed in prepared materials as the result of the use of a carbon die during SPS.

The density of sintered pellets was measured in water using the Archimedes method. The microstructures were examined on fracture surfaces by scanning electron microscopy (Zeiss, model EVO 40HV, Carl Zeiss SMT AG, Germany). The mean grain size was determined using the linear intercept method on fracture surfaces, measuring individual intercept lengths, considering their (number-weighted) distribution, and using the correction factor of 1.56 [37]. At least 200 grains were measured in order to obtain a statistically robust set of data. In several cases sintered specimens were cut, polished and thermally etched to reveal grain boundaries. The polished cross sections were examined by SEM, and the mean grain size determined by the linear intercept method. The results were then compared to the mean grain size determined from fracture surfaces. The differences were negligible, and varied within the range of experimental error. For the sake of simplicity all results reported were obtained from the analysis of fracture surfaces.

The specimens sintered by SPS to the stage of closed porosity were cut into four parts, and each part was hot isostatically pressed at a different temperature 1050, 1100, 1150 or 1250 °C, with 3 h isothermal dwell at the maximum pressure of 150 MPa with Ar as the pressure medium. The HIP-ed specimens were characterized in the same manner as described above.

The in-line transmission in the wavelength range 400–750 nm was measured with the use of a fiber optics UV–vis-NIR spectrometer Ocean Optics S2000 (Dulven, The Netherlands) on alumina platelets with the dimensions of $5 \times 5 \times 0.5$ mm^3 with parallel faces polished to 1 μm finish.

3. Results and discussion

3.1. Spark plasma sintering

The results of the SPS experiments are summarized in Figs. 1 and 5. Fig. 1 displays the time dependence of relative density of undoped (A), Mg- (AM), Y- (AY) and Zr-doped (AZ) specimens spark plasma sintered at various temperatures in the interval between 1150 and 1300 °C. Fig. 2 shows the microstructures of undoped, Mg-, Y- and Zr-doped specimens spark plasma sintered at 1250 °C and 3 min isothermal dwell.