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Short communication

Transparent alumina ceramics densified by a combinational approach of spark plasma sintering and hot isostatic pressing

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ABSTRACT

In order to increase the in-line transmission of fine transparent alumina in visible light the grain growth during sintering of alumina ceramics was supressed using a combined densification process. This process combines presintering of a green body by spark plasma sintering with final hot isostatic pressing. The presintering by spark plasma sintering provided bodies with a substantially smaller grain size than pressureless presintering. It is shown that the fine-grained presintered microstructure could be retained during final hot isostatic pressing and alumina ceramics doped with spinel and zirconia nanoparticles in particular could be sintered to full density with only minor grain growth during final hot isostatic pressing. The novel combined densification process enhanced by the unique nanoparticle doping approach provided fully dense alumina ceramics with an average grain size of 237 nm and an in-line transmission of 76.2% at a wavelength of 632.8 nm and a sample thickness of 0.8 mm.

1. Introduction

Alumina (Al_2O_3, corundum) is one of the important birefringent transparent ceramics. High hardness, high melting point, excellent corrosive resistance, and competitive fracture toughness make transparent alumina ceramics a promising candidate for applications as transparent armors, electromagnetic windows, envelopes of high-pressure halide lamps, etc. [1]. Mechanical properties of submicrometer-grained alumina can exceed the mechanical properties of sapphire (single-crystal alumina) [2,3] and it is believed that such fine-grained alumina could replace sapphire in many optical applications.

Up to now, transparent alumina ceramics with a submicrometer-grained structure were prepared exclusively by pressure-assisted sintering processes. Pressureless presintering followed by hot isostatic pressing (PLS/HIP) and spark plasma sintering (SPS) are the two most common densification processes for the production of transparent fine-grained alumina. Recently reported values of real in-line transmission, *RIT*, (i.e. in-line transmission of light scattered at an angle $\leq 1°$) of submicrometer-grained alumina ceramics in visible light are shown in Fig. 1. The reported values are compared with the theoretical in-line transmission of non-absorbing fully dense alumina at a wavelength of 640 nm. The theoretical in-line transmission, $T_{in-line}$, of an ideally dense fine-grained alumina ceramic only depends on the grain size, d, and was calculated using the model proposed by Apetz and van Bruggen [4].

$$T_{in-line} = T_{th}\exp(-3C_{sca}t/(\pi d^3)), \quad (1)$$

where T_{th} is the total theoretical transmission limit of a body (including multiple surface reflections and neglecting the grain boundary reflections), C_{sca} is the scattering cross-section of one grain, and t is sample thickness. The scattering cross section, C_{sca}, was calculated using the Mie theory according to the numerical algorithm by Bohren and Huffman [5]. The theoretical transmission limit $T_{th} = 0.86$, refractive index $n = 1.76$, and average birefringence $\Delta n = 0.005$ were used for the calculation. As the grain size of the samples measured was represented by a mean value although the grains had a wider grain size distribution, the *RIT* values could exceed the theoretical limit that was calculated for spherical monosized grains. Nevertheless, it is evident from Fig. 1 that alumina samples prepared by pressureless presintering and hot isostatic pressing (PLS/HIP) exhibit *RIT* near or at the theoretical limit. This means that they reached almost full density and their in-line transmission was controlled by the grain size. *RIT* values from 51 to 64% at a wavelength of 640 nm have been reported by several authors [6–8] for 0.8 mm thick samples with a grain size from 470 to

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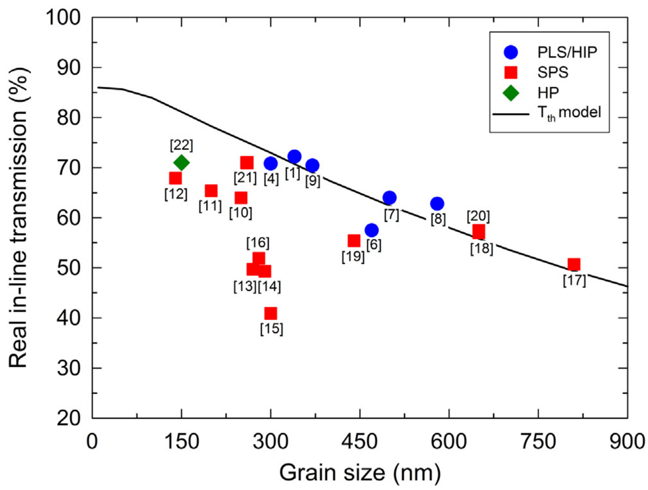

Fig. 1. Theoretical in-line transmission of dense non-absorbing polycrystalline alumina as a function of grain size at a wavelength of 640 nm and sample thickness of 0.8 mm, and an overview of recent literature data on real in-line transmission of alumina ceramics. The in-line transmission data were recalculated to a thickness of 0.8 mm. All in-line transmission values were obtained at a wavelength of 640 nm except the values from [4,10,11], which were measured at a wavelength of 645 nm and the value from [9], which was measured at a wavelength of 632.8 nm.

580 nm. The maximum transparency has up to now been achieved by Apetz and van Bruggen [4] (*RIT* = 71% at 645 nm wavelength), Krell et al. [1] (*RIT* = 72% at 640 nm wavelength) and later by Trunec et al. [9] (*RIT* = 70.4% at 632.8 nm wavelength) in 0.8 mm thick samples with a grain size of 300, 340, and 370 nm, respectively. Interestingly, the transparent alumina ceramics prepared by spark plasma sintering (SPS) can reach an even smaller grain size. Grain sizes in the range from 140 to 300 nm were obtained by SPS [10–16]. However, the transparency in the visible range was low (40–50%) as a result of some residual porosity in densified bodies (the values lie well below the theoretical limit) [13–16]. Higher in-line transmission of about 65% (at a wavelength of 640 nm and a sample thickness of 0.8 mm) was only obtained when extremely high pressure during SPS (400–500 MPa) was applied [10–12]. The *RIT* of SPS bodies sintered at pressures <100 MPa could only be improved to over 50% when the alumina powder was doped with Mg, La, Y or Zr ions [17,18] or when the powder was carefully consolidated prior to SPS instead of using a free powder [19,20]. Recently, the fabrication of highly transparent alumina samples (*RIT* = 71% at 640 nm wavelength and 0.8 mm thickness) based on SPS of a La-doped and preconsolidated nanoparticle green body has been reported [21]. Unfortunately, the considerable transparency inhomogeneity even in small samples excludes this promising method from any potential application at the moment. A similar result was also obtained using a rather rare method of hot pressing (HP) at an extremely high pressure of 7.7 GPa [22].

Despite considerable progress in the processing of polycrystalline alumina in the last decade the current in-line transmission maximum of 70–72% (at a wavelength of 640 nm and a sample thickness of 0.8 mm) is not sufficient for most applications in visible light and further improvement is desirable [1,4,9]. To improve the current in-line transmission of birefringent alumina in the visible wavelength region, grain size refinement in fully dense ceramics towards the nanometer range is inevitable [4]. The presented overview shows that the current densification processes of alumina ceramics fail to reach both small grain size (<300 nm) and full density (>99.99% t.d.). Therefore, we have proposed a combined spark plasma sintering/hot isostatic pressing densification process (the SPS/HIP method) to obtain fully dense ceramics with a grain size of below 300 nm. This process is based on the SPS warm pressing concept [23] and advantageously utilizes the nanoparticle doping approach [9]. The SPS warm pressing provides bodies in the state of closed porosity, with much finer grain size than pressureless sintering due to particle rearrangement and pore size control during low-temperature SPS sintering [23]. Moreover, Trunec et al. [9] have recently shown that an alumina powder compact doped with zirconia and spinel nanoparticles exhibits only minor grain growth during final HIP densification and that the final grain size of transparent alumina ceramics is primarily determined by the grain size of the presintered body prior to HIP densification. Based on this recent experimental findings it has been assumed that the SPS presintering of a consolidated doped alumina body combined with the final HIP densification could provide fully dense ceramics with the grain size below 300 nm and break through the present in-line transmission maximum of alumina in visible light. Therefore, the objective of the present work was to experimentally prove the proposed combined SPS/HIP densification process by preparing highly transparent alumina ceramics.

2. Experimental procedure

The Taimicron TM-DAR and TM-UF (Taimei Chemicals Co., Tokyo, Japan) alumina powders with a specific surface area of 13.8 and 21.5 $m^2 g^{-1}$, respectively, were used for the preparation of alumina green bodies by the gelcasting process. The TM-DAR and TM-UF powders were dispersed in a premix solution of monomers to obtain suspensions with a powder loading of 47.5 and 45 vol%, and a median particle size of 102 and 90 nm, respectively. All suspensions with the zirconia addition were ball-milled with zirconia balls (1 mm YTZ, Nikkato-Tosoh, Tokyo, Japan) instead of mixing. The milling was performed in a polycarbonate bottle (1000 cm^3 volume, 100 mm diameter) rotating at 125 rev min^{-1} for 24 or 48 h. The total volume charge of the plastic bottle was 220 cm^3 with a balls/powder weight ratio of 3.6. The wear of the zirconia balls remained in the suspension and acted as a zirconia nanoparticle additive. Spinel nanoparticles (Baikalox S30CR, Baikowski, Annecy, France) with a specific surface area of 29 $m^2 g^{-1}$ were added to selected suspensions prior to ball milling as a sintering additive. More details about gelcasting suspensions and their processing can be found in a previous paper [9]. The exact composition of ceramic green bodies after polymer gel burnout is given in Table 1. The ceramic green bodies were milled to a diameter of 30 mm (to exactly match the graphite SPS die) and a thickness of 4 mm, and presintered in an SPS apparatus (Dr. Sinter 2050, Sumitomo Coal Mining, Tokyo, Japan) to the stage of closed porosity at temperatures ranging from 1125 to 1200 °C (100 °C min^{-1} heating rate, 80 MPa sintering pressure, 10 min hold time at the sintering temperature). The SPS presintered bodies were then exposed to air atmosphere at 800 °C for 10 h to eliminate most of the carbon contamination coming from the SPS graphite die. Finally, the bodies were densified in a graphite-free hot isostatic press (Shirp, ABRA, Widnau, Switzerland) at temperatures ranging from 1190 to 1295 °C and at an argon pressure of 198 MPa for 3 h. The sintered bodies were ground and polished to a thickness of ca. 0.8 mm.

The density of presintered bodies was determined in water by the Archimedes method, using the value 3.987 g cm^{-3} for the theoretical density of alumina. The average grain size of presintered and sintered bodies was determined using the linear intercept method on at least three scanning electron microscopy (SEM) micrographs of polished and thermally etched samples. The linear intercept grain size was multiplied by a factor of 1.56 to yield the true grain size [24]. The real in-line transmission (*RIT*) of polished samples was measured with a non-polarized He-Ne laser (λ = 632.8 nm), the distance from the sample to the detector was 860 mm (with an opening angle of 0.5°). The real in-line transmission was mea-