PROCESSING AND PROPERTIES OF FINE-GRAINED TRANSPARENT $MgAl_2O_4$ CERAMICS

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Transparent fine-grained $MgAl_2O_4$ ceramics was prepared from nanometre-sized powder without any sintering additives. Ceramic green bodies were prepared by cold isostatic pressing and then pressureless presintered at temperatures of 1550-1600°C to achieve closed porosity. Presintered samples were subsequently hot isostatically pressed (HIPed) at 1500°C and 200 MPa for 1 hour. The final density as well as the transparency of HIPed samples was affected by presintering densities. The highest final density (~100% t.d.) and highest in-line transmission (60.2% for sample thickness 1.1 mm and λ = 632.8 nm) were obtained for samples presintered to the lowest density value still guaranteeing a structure with closed porosity (~94% t.d.). The HIPed samples had an average grain size of 1 μm and hardness HV = 13.0 GPa.

INTRODUCTION

Polycrystalline magnesium aluminate spinel ($Al_2O_3 \cdot MgO$) is one of the most promising optically transparent ceramics that exhibits a unique combination of optical and mechanical properties. Its advantage consists in the optically isotropic cubic structure, so that light scattering at grain boundaries is less critical than with optically anisotropic systems. To be optically transparent, spinel has to be "only" impurity-free and pore-free. The elimination of large and stable pores can be achieved with significant grain growth [1], therefore spinel ceramics are sintered at high temperatures [2-5]. To improve the poor sinterability of spinel ceramics, sintering additives (LiF, CaO, B_2O_3) are often used [6-8]. These processing conditions lead to a coarse microstructure with large grains (tens to hundreds microns), and the use of sintering additives can result in grain boundaries with impurities and second phases [9, 10]. Coarse-grained transparent spinel ceramics can be utilized in optical devices (infrared windows and missile domes) but are less suitable for transparent armour. Coarsening of the microstructure deteriorate mechanical properties (e.g. hardness), which are closely connected to the ballistic resistance [11]. In transparent armour optical transparency and fine microstructure have to meet together. However, reports on successful processing of fine-grained transparent spinel ceramics prepared without sintering additives are very rare [12, 13].

The aim of this work was to prepare transparent fine-grained spinel ceramics starting from nanometre-sized powder without sintering additives. Cold isostatic pressing, pressureless presintering and hot isostatic pressing (HIPing) were the techniques used for processing of spinel powder. The effect of the sintering schedule on the properties (density, hardness and optical transparency) of spinel ceramics was investigated.

EXPERIMENTAL

Commercial magnesium aluminate spinel powder (type Baikalox S30CR, Baikowski, France) was used as the raw starting material. The specific surface area of the powder was measured by nitrogen adsorption according to the BET method (ChemBet 3000, Quantachrome, USA). The green bodies in the shape of discs (dia 20 mm, height 8 mm) were prepared by cold isostatic pressing at 300 MPa. The behaviour of powder compacts during pressureless sintering up to 1550°C (heating rate 5°C/min) was studied by high-temperature dilatometry (L75/50, Linseis, Germany). Based on the evaluation of the dilatometric curve, different sintering schedules for the presintering of spinel compacts could be suggested. This pressureless presintering was performed in an air atmosphere. The presintered samples were then HIPed (ABRA Shirp, Switzerland) at 1500°C for 1 h under a pressure of 200 MPa of argon without any encapsulation. The relative density of bodies before and after HIPing was measured by Archimedes method (EN 623-2), with the value of 3.58 g/cm^3 for the theoretical density of $Al_2O_3{\cdot}MgO$ [3, 14]. The grain size was calculated using the linear intercept method (EN 623-3) on scanning electron microscopy (SEM) micrographs of polished and thermally etched samples. Real in-line transmission (RIT) of polished samples (thickness 1.1 mm) was measured with a He-Ne laser (λ = 632.8 nm), the distance of the sample to the detector was 800 mm. Vickers hardness was determined using 1 kg load applied for 15 s.

RESULTS AND DISCUSSION

The specific surface area of ceramic powder was 29 m^2/ g. The calculated particle size (assuming spherical and monosized particles) was 58 nm. As shown in Figure 1, the primary particles had a spherical shape; the particle size evaluated from the micrograph was in good agreement with the value calculated from the specific surface area. The densification curve of the green body prepared from the powder via cold isostatic pressing is given in Figure 2. Sintering schedules leading to selected sample densities are shown in the graph.

The ceramic discs were pressureless presintered according to the suggested sintering schedules to reach final densities in the range of 93-100 % t.d. This density range is considered as a closed porosity area [15]. The values of relative density, ρ_{rel}, and fraction of open pores, V_O, reached by pressureless presintering are given in Table 1.

It is evident from Table 1 and Figure 2 that the presintered density of discs was only slightly different from the density predicted by dilatometric measurement. The density of samples after HIPing is also given in Table 1. It was found that the presintered density of 94.9 % t.d. was optimum for reaching the maximal final density. Using samples of lower presintered density not all pores were closed and HIPing was not effective. With higher presintered densities the final density of HIPed samples decreased (see also Figure 3). The main reason for this behaviour could be trapping of pores in the grain interior due to extensive grain growth during excessive presintering. Such intragrain pores, trapped during presintering, remained even after the HIP [16, 17]. It can be concluded that the use of nanometre-sized spinel powder made it possible to sinter spinel ceramics at low temperature to full density without sintering additives. To utilise the large sintering activity of nanoparticles profitably, an appropriate temperature-pressure sintering schedule has to be chosen.

The final density of the samples strongly influenced the optical properties. The real in-line transmission increased with increasing final density (see Table 1 and Figure 3). Differences in transparency of discs are demonstrated in Figure 4.

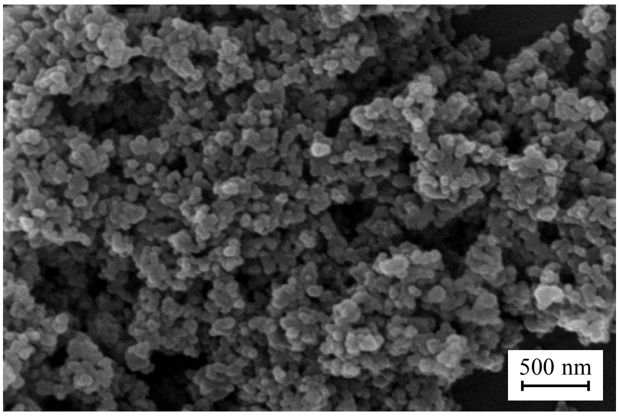

Figure 1. SEM micrograph of spinel powder.

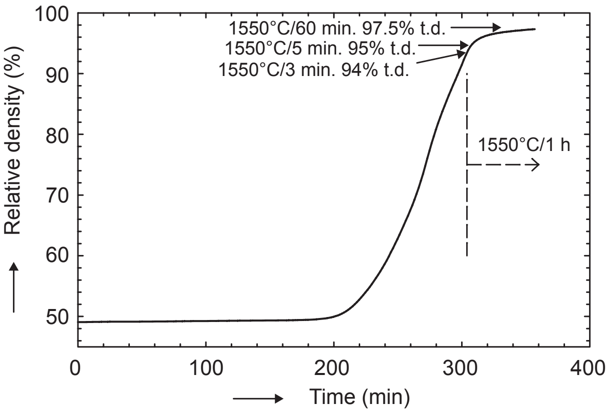

Figure 2. Sintering kinetics of spinel compacts. The beginning of the isothermal hold at 1550°C is marked.

Table 1. Relative density of pressureless presintered and HIPed samples and real in-line transmission of HIPed samples

Pressureless sintering (°C)/(min)	ρ_{rel} (%)	V_O (%)	HIP (°C)/(min)/(MPa)	ρ_{rel} (%)	s/n (%) /(-)	RIT (%)	s/n* (%)/(-)
1550/3	93.5	0.1	1500/60/200	99.80	0.03/6	42.8#	30.6/35
1550/5	94.9	0	1500/60/200	100.00	0.02/9	60.2	6.7/39
1550/60	97.9	0	1500/60/200	99.95	0.03/9	37.9	1.9/36
1600/120	99.5	0	1500/60/200	99.88	0.04/9	7.3	1.3/34

* *s* is standard deviation and n is number of measurements

\# RIT values vary significantly (from 0.2 to 70 %) with the position of the measurement

Similar results were described in [3] - the optical transparencies of spinel ceramics increased with decreasing presintering temperature. These authors did not discuss the effect of residual porosity on transparency, they identified the main reason of lower transparency to be the presence of microcracks. The amount of microcracks depended on the grain size. However, in [3] HIPing was performed at a much higher temperature (1800°C), which resulted in large grain size from 170 to 370 μm. As shown in Figure 5, the size of spinel grains was in our case about two orders of magnitude smaller due to the lower HIP temperature and microcracking was efficiently avoided. The sample presintered at 1550°C for 5 min and HIPed at 1500°C and 200 MPa for 1 hour had an average grain size of 1 μm. The grain size distribution was rather broad, however, the biggest grains did not exceed 5 μm. This fine microstructure resulted in a slightly higher hardness *HV* = 13.0 GPa in comparison to the hardness *HV* = 12.0 GPa experimentally determined for commercially available transparent spinel ceramics (Laser Optex, China) with grain size from 20 to 300 μm.

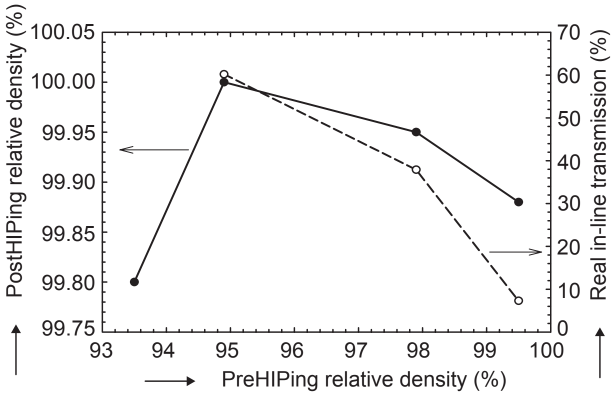

Figure 3. The dependence of final densities and RIT values of HIPed samples on the sample density before HIPing.

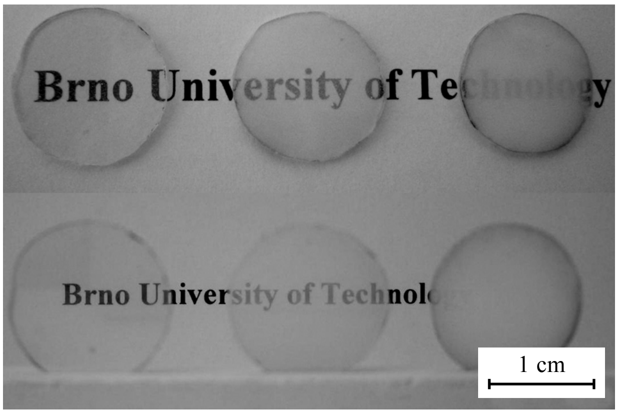

Figure 4. The optical transparency of spinel ceramics (thickness 1.1mm) prepared with different presintered densities (from left: 94.9, 97.9 and 99.5 %t.d.). In the upper image the samples are lying immediately on the sheet of paper bearing the text; in the lower one they are 5 cm above it.

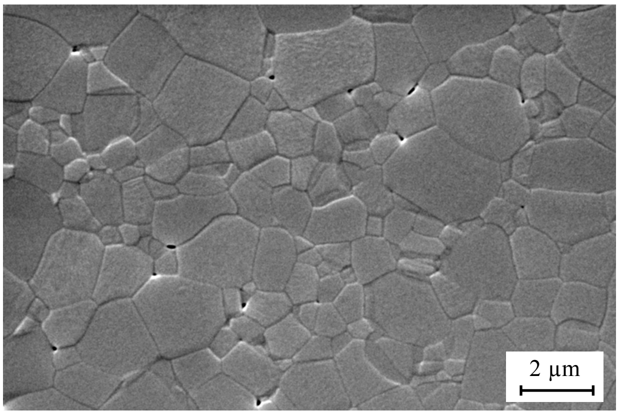

Figure 5. SEM microphotograph showing the structure of the HIPed sample pressureless presintered at 1550°C/5 min.

CONCLUSIONS

Transparent spinel ceramics were prepared from nanometre-sized powder without sintering additives via cold isostatic pressing and pressureless presintering followed by HIPing. It was found that the presintering density influenced the final relative density of HIPed samples and thus their transparency. Ceramic discs presintered to the lowest density value still guaranteeing the structure with closed porosity (94.9 % t.d.) could be hot isostatically pressed at 1500°C and 200 MPa to full density with an average grain size of 1 μm, real in-line transmission of 60% and Vickers hardness of 13 GPa.

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PŘÍPRAVA A VLASTNOSTI JEMNOZRNNÉ TRANSPARENTNÍ $MgAl_2O_4$ KERAMIKY

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V článku je popsána příprava transparentní jemnozrnné $MgAl_2O_4$ keramiky připravené z nanometrového prášku bez přítomnosti slinovacích aditiv. Keramická tělesa připravená izostatickým lisováním za studena byla beztlakým slinováním při teplotách 1550-1600°C předslinuta do fáze uzavřené pórovitosti a poté HIPována 1 hodinu při teplotě 1500°C a tlaku 200 MPa. Konečná hustota a transparentnost vzorků byly ovlivněny hustotou těles před HIPováním. Nejvyšší konečnou relativní hustotu (~100%t.h.) a nejvyšší hodnotu přímočaré optické propustnosti (60,2% pro λ = 632,8 nm a při tloušťce vzorku 1,1mm) dosáhl vzorek předslinutý na nejmenší relativní hustotu, která již zaručovala uzavřenou pórovitost vzorku (~94%t.h.). HIPovaný vzorek měl průměrnou velikost zrn 1 µm a tvrdost *HV* = 13 GPa.