Transparent polycrystalline MgAl_2O_4 spinel with submicron grains, by low temperature sintering

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Transparent, polycrystalline MgAl_2O_4 ceramics have been fabricated by sintering optimized-configuration, powder compacts formed from a material prepared by flame spray pyrolysis. Transparent parts (80% light transmission at 2 mm thickness) could be obtained after pressureless sintering in air at 1280°C/3 h, followed by hot isostatic pressing at 1320°C/3 h/200 MPa. The average grain size was 0.45 μm . Such materials exhibit property combinations suitable for transparent armor applications.

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Polycrystalline MgAl_2O_4 spinel is one of the most suitable materials for transparent armor panels strike-face fabrication.^{1)–4)} For such an application, besides a high optical real in-line transmission (RIT), a submicron grain size (GS) is desired. This is so because a fine microstructure facilitates projectile erosion by causing an optimal ceramic fragmentation pattern and increasing hardness (compared to that of large grains spinel)^{5),6)}

Most of the fabrication technologies previously developed, allow the obtainment of spinel parts exhibiting excellent optical transmission but associated with coarse microstructure.^{3),4),7),8)} Only a few workers focused on the obtainment of low grains size. For instance, remarkably fine microstructure (GS in the 1–5 μm range) was reported by Gazza and, respectively, Tsukuma.^{9),10)} Krell et al. were able to further refine, to the sub-micron region, the microstructure, and obtain, as a result, transparent spinel plates (TSP) showing improved performance in ballistic tests.^{1),5),6)} Their technology, though, is presented in the literature only in general terms, which do not allow reproduction of the results. For instance,⁶⁾ it requires the use of sintering additives, the nature and amount of which were not disclosed.

It was recently determined by us¹¹⁾ that spinel powders prepared by flame spray pyrolysis exhibit an unusually high sinterability. Transparent parts could be derived from such powders by sintering at relatively low temperature (1400°C/80 h, in air) followed by hot isostatic pressing (HIP) at 1500°C. The microstructure of the specimens was quite fine (average grains size $\overline{\text{GS}} \sim 8 \mu\text{m}$), but not at the level optimal for ballistic applications.

The objective of this work was to examine whether it is possible to further reduce the sintering temperature of FSP spinel powder compacts, by improvement of the green-body configuration, to a level at which submicron grains size can be obtained while the optical transmission is kept at $\geq 78\%$ in the visible (VIS) range.

A stoichiometric MgAl_2O_4 spinel powder (Nanocerox, Ann Arbor, MI, USA), prepared by flame spray pyrolysis, having a specific surface area $A = 30 \text{ m}^2/\text{g}$ and including as main impurities 25 ppm of Cl + 20 ppm Si + 10 ppm Ca was used. The pow-

der is made of spheroidal basic particles (individual crystallites or non-porous clusters of them) 20 to 50 nm in size, assembled in multilevel agglomerates; their morphology is illustrated in Fig. 1. The particles (agglomerates) size distribution (in ethylene glycol) has its D_{50} at 140 nm and D_{90} at 260 nm.

The powder, suspended in isopropyl alcohol (IPA), was deagglomerated by vigorous ultrasonication and pelletized (without organic additives) by the aid of a 71 mesh sieve; the pellets were spheroidized by tumbling. Disk shaped green-parts [diameter (ϕ) = 25 mm, thickness (t) = 3–8 mm] and some square plates [length (L) = 50 mm, t = 3–7 mm] have been formed by cold isostatic pressing (CIP). The pressure was raised slowly to 200 MPa, where a 10 min dwell was kept. During the gradual pressure release, dwells were kept at 140, 80 and 20 MPa. Isothermal sintering was effectuated in air (AS) at various temperatures in the 1250–1600°C range; a dwell of 3 h, at peak temperature, was kept. The final densification stage was performed by the aid of an in-house made hot isostatic press, under Ar, at pressures in the 150–220 MPa range and various temperatures in the 1300 to 1500°C range (3 h dwells at peak temperature).

The bulk density of the powder compacts was labeled BD_g ,

Fig. 1. Ultimate particles size, morphology and aggregation pattern of the FSP powder. TEM.

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that reached after AS was labeled BD_f , and that after HIPing – BD_H . It was determined by the Archimedes method. The raw materials and sintered specimens phase composition was checked by XRD (model APD 2000 of ItalStructures, Riva del Garda, Italy), while powders morphology and dense disks microstructure were examined by TEM (model TECNAI G^2 , T-20, of FEI, Eindhoven, NL). The average grain size, $\overline{\text{GS}}$, was measured by the mean linear intercept method (TEM pictures), using the approximation $\text{GS} = 1.5 X$, where X is the mean intercept (ASTM E-112088). The powder particles size distribution (dispersion in ethylene glycol) was measured with a laser scattering based sizer (model LM20, NanoSight, Salisbury, UK), while the pores size distribution (green body strengthened by heating at $850^\circ\text{C}/3\text{ h}$) was measured by mercury intrusion (model Macropore 120 porosimeter, Carlo Erba, Torino, Italy). The RIT was measured by the aid of a spectrometer (model JASCO V-570, Nihon Burko Co., Tokyo, Japan). In order to eliminate the scattered component of the light beam, a $4 \times 4\text{ mm}$ slit was located between the specimen and detector, as recommended by Dericioglu et al.¹²⁾

In our previous work,¹¹⁾ an FSP powder sintering material having $A = 60\text{ m}^2/\text{g}$ was used. It was deagglomerated by dispersing in water, and parts were formed by rapid CIPing. The replacement of that FSP powder with the new grade used here, which has $A = 30\text{ m}^2/\text{g}$, and the modification of the powder processing and forming procedure, had a significant effect on the green-body configuration. The BD_g was raised to 2.10 g/cm^3 (59%TD) from 1.93 g/cm^3 in.¹¹⁾ The average pore size, as illustrated in Fig. 2, is also very low; the average pore radius is of $\sim 25\text{ nm}$.

Fig. 2. Pores size distribution of green compacts, as measured by mercury intrusion. A – The FSP powder, B – The reference SCR-30 powder.

Fig. 3. Sintering shrinkage and BD_f (3 h dwell at peak temperature) of specimens heated in air. Shrinkage values on left side vertical axis (curve A), BD_f values on right hand vertical axis (curve a).

The quite narrow pores size distribution also indicates that the largest pores – i.e., the interagglomerate voids – are not much bigger than the intraagglomerate pores. For comparison, the pores size distribution of a green-body formed from another nano-powder (grade SCR-30 of Baikowski, France) – processed and pressed in the same way as the FSP material of interest here – is also given in Fig. 2. The SCR-30 powder (surface area of $30\text{ m}^2/\text{g}$, ultimate particles of 30 to 70 nm) is used worldwide by most of the teams engaged in research on, or production of, transparent spinel.

The improvements in the FSP powder based green-body configuration (pore size lowering and density increase) had a dramatic effect on its sinterability.

In Fig. 3 the shrinkage of a green specimen subjected to relatively fast heating ($5^\circ\text{C}/\text{min}$) in a dilatometer's furnace is shown for the RT– 1620°C range. The evolution of the BD_f (1240 – 1500°C) of disks densified by isothermal sintering, is also shown in Fig. 3. As the figure shows, the BD_f of the sintered specimens gets very close to TD (3.578 g/cm^3) at temperatures as low as 1370 – 1400°C . To attain a similar level of densification required firing at $1400^\circ\text{C}/80\text{ h}$ when green parts, derived from powder dispersed in water¹¹⁾ were subjected to AS. At a thickness $t \leq 2\text{ mm}$ the disks sintered here at $1400^\circ\text{C}/3\text{ h}$, in air, exhibit considerable optical transmission, even before HIPing (RIT $\approx 50\%$ at $\lambda = 750\text{ nm}$), as curve “c” of Fig. 4 and specimen “b” of Fig. 5 illustrate. In previous work similar levels of transmission could be attained,

Fig. 4. In-line transmission curve (250–1750 nm domain) of polished spinel discs. (a) AS $1280^\circ\text{C}/3\text{ h}$ + HIP $1320^\circ\text{C}/3\text{ h}$; $t = 2\text{ mm}$, (b) AS $1280^\circ\text{C}/3\text{ h}$ + HIP $1320^\circ\text{C}/3\text{ h}$; $t = 3.5\text{ mm}$, (c) AS $1370^\circ\text{C}/3\text{ h}$ (no HIP); $t = 2\text{ mm}$.

Fig. 5. Illustration of spinel parts (disks and plate) level of transparency in different stages of densification. (a) AS $1280^\circ\text{C}/3\text{ h}$, (b) AS $1400^\circ\text{C}/3\text{ h}$, (c) AS $1280^\circ\text{C}/3\text{ h}$ + HIP $1320^\circ\text{C}/3\text{ h}$, (d) AS $1320^\circ\text{C}/3\text{ h}$ + HIP $1320^\circ\text{C}/3\text{ h}$ (disk to background distance = 20 mm).

by pressureless sintering, only at temperatures in the 1800 to 1850°C range (special atmospheres).^{13,14)}

The transmission level attained after the AS stage, while demonstrating the high sinterability of the FSP powder, is not high enough for the intended application. In order to further reduce the residual porosity, under the 0.01 vol% required for good transmission,⁶⁾ the use of HIPing proved necessary. It was determined that disks which attained after AS a BD_f of at least 97.5%TD (attainable at 1280°C), could be made highly transparent by HIPing at temperatures $\geq 1320^\circ\text{C}$. Such specimens are illustrated in Fig. 5, while their RIT curves (250–1750 nm domain) are given in Fig. 4. The transmittance level attained after HIPing was not dependent on the value of BD_f (as long as it was $\geq 97.5\%$ TD). The quite low temperatures necessary for both the AS and HIP sintering stages allowed one to maintain a very fine grains size (GS $\sim 0.45\ \mu\text{m}$) as Fig. 6 illustrates.

The results described above indicate that improvement of green-bodies configuration, formed from a spinel powder prepared by the FSP technique, is able to markedly enhance sinterability. Such green-bodies can be densified to a level ensuring

Fig. 6. Microstructure of spinel disk (AS 1280°C/3 h + HIP 1320°C/3 h). TEM.

high optical transparency (RIT $\sim 80\%$ at $t = 2\ \text{mm}$) by AS at 1280°C/3 h, followed by HIPing at 1320°C/3 h. The average grain size of the HIPed parts is $0.45\ \mu\text{m}$; such a microstructure is optimal for plates intended for armor applications. A similar transmission/GS combination was previously obtained only by Krell et al.,⁶⁾ but with the aid of sintering additives.

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