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Preparing bulk transparent magnesium aluminium spinel – a few tricks of the trade

Adam Witek

Institute of Ceramics and Building Materials, Department of Nanotechnology, ul. Postępu 9, 02-676 Warszawa
e-mail: a.witek@icimb.pl

Abstract

The most successful attempts for preparing transparent magnesium aluminium spinel ceramics have been conducted with using hot isostatic pressing (HIP). In this paper a list of tips and tricks useful for manufacturing bulk transparent HIPed spinel ceramics is presented. The step by step subroutine from starting material to the final product, for manufacturing transparent ceramic armours tiles and three dimensional elements is described. The green body preparation, pre-sintering parameters, HIP temperature/pressure history and discoloration parameters are released and explained in details. Master these four fundamentals, and one stands a good chance of getting $MgAl_2O_4$ ceramics with the real-inline transmission over 82% in the spectrum from visible to the mid infrared.

Keywords: Transparent ceramics, Spinel, HIP

WYTWARZANIE MASYWNEJ, PRZEZROCZYSTEJ CERAMIKI SPINELU MAGNEZOWO-GLINOWEGO – KILKA SZTUCZEK TECHNOLOGICZNYCH

Najwięcej udanych prób wytworzenia przezroczystej ceramiki spinelu magnezowo-glinowego przeprowadzono z użyciem techniki izostatycznego prasowania na gorąco (HIP). W artykule zaprezentowano listę zabiegów użytecznych przy wytwarzaniu masywnej, przezroczystej ceramiki spinelowej metodą izostatycznego prasowania na gorąco. Opisano krok po kroku postępowanie od wyjściowego materiału po produkt końcowy w przypadku wytwarzania przezroczystych, ceramicznych płytek pancerza oraz elementów trójwymiarowych. Ujawniono i objaśniono szczegółowo przygotowanie surowego wyrobu, parametry wstępnego spiekania, historię prasowania izostatycznego na gorąco w odniesieniu do temperatury i ciśnienia oraz parametry procesu odbarwiania. Mistrzowskie opanowanie tych podstaw stwarza dobrą szansę uzyskania ceramiki $MgAl_2O_4$ o realnej transmisji powyżej 82% w zakresie widma od widzialnego do podczerwieni.

Słowa kluczowe: ceramika przezroczysta, spinel, HIP

1. Introduction

Expected applications opened the quest for transparency of advanced ceramics. Transparent ceramic armours, ceramic windows and passive and active laser parts are supposed to be more reliable than their glassy or single crystals counterparts. Reliability is not only one advantage of the transparent ceramic implementation. Scaling up the single crystal growth process is hard to achieve and when successful then costly. On the other hand, for several high temperature materials even limited quality and size single crystals are not available up to date. This is the case of magnesium aluminium spinel (chemical formula - $MgAl_2O_4$) the most promising high temperature oxide material. According to J. Sanghera [1] magnesium aluminium spinel demonstrates the highest figure of merit for laser host material among cubic oxides, surpassing yttrium aluminium garnet (YAG-$Y_3Al_5O_{12}$) and yttrium oxide (Y_2O_3).

Transparent ceramic material such as the spinel offers a quantum leap in the ballistic performance over conventional glass laminated. Spinel has been shown to provide protection against armour piercing rounds at about one half the weight and thickness of conventional glass laminate [2]. Another advantage of spinel armour and/or windows is optical transmission of spinel does extend to cover the entire mid–infrared range (2-5.5 μm). This infrared optical transmission makes the transparent spinel ceramics as material of choice for high-speed infrared-guided missile domes. Future “heat seekers” missiles will require new domes that are substantially more durable than those in use today, while still retaining maximum transparency across a wide wavelength range. A long standing trade-off exists between the optical bandpass and mechanical durability within the current collection of single-phase infrared transmitting materials, forcing missile designers to compromise on the system performance. Transparent spinel ceramics may present the opportunity to engineer new materials that overcome this traditional compromise. For all aforementioned applications the ceramic spinel must be transparent demonstrating transparency close to the theoretical Fresnel limit which for the slabs of few millimetre thickness of spinel means 86.9% (for the light beam perpendicular to the surface). It has been shown that the main factor influencing beam scattering is not considered to be a grain boundary, but the residual pore. Ikesue [3] has proved that for the laser quality ceramic transparency, the absolute pore volume should be as low as 1 ppm. For the windows, transparent armours and domes, the real in line transmittance could be a little bit lower than the theoretical one, but still exceeding 80% what means that absolute volume porosity roughly estimated on the basis of Apetz and van Bruggen [4] theory should be on the level of 50 ppm. Everybody who is going to prepare transparent ceramics should be aware his product must reveal relative density above 99.999%. For such a deep densification, the special sample preparation and processing are needed. The densification rate predicted by either Nabarro-Hering or Coble creep[5], is described (at the fixed temperature) by the following formula:

$$\frac{d(\Delta\rho/\rho)}{dt} \propto \frac{\sigma_a}{G^3} \quad (1)$$

where G is the mean grain size, ρ is the relative density and σ_a is the applied pressure. Since the grain size dependence of the densification rate is proportional to G^{-3}, the plenty room for nanopowders technology is opened. Frankly speaking, the most successful attempts for preparation of transparent ceramics could be concluded as an answer for the question: how to make microstructure ceramics starting from the nanopowder?

Another opportunity for the densification during the sintering process is offered by high pressure. The pressure applied during the hot isostatic pressing (HIP) creates a significantly higher driving force for densification than pressureless sintering and should reduce densification temperatures and times, and therefore give access to finer grain–size ceramics, regardless of the densification mechanism. And this is the way we manufacture the transparent spinel ceramics.

To date only a few papers address the use of HIP for fabricating transparent spinel ceramics [6-8]. None of these papers has been addressed as a guide for manufacturing bulk transparent ceramic spinel elements and newer one [9] reporting real-inline transmission 85% (the best up to date) describes the preparing transparent samples with limited dimensions as well.

2. Step by step bulk sample preparation

Manufacturing the windows armours or three dimensional elements like domes made out of transparent spinel is more the art than the science. The devil is in the details and these details often means tricks. The set of these tricks applied in the right sequences creates technology needed for reproducibility of the transparent ceramic elements. The rough draft of this is as follows.

2.1. Green body preparing

For flat elements like windows, the first step of the forming is uniaxial pressing in dies. The best starting material is the granulated nanopowder of spinel commercially available from Baikowski, the producer catalogue description S30XW. Such a granulate should be uniaxially pressed at 100 MPa, and then isostatically pressed at 250 MPa. For the resultant samples must be placed in vacuum evacuated bags. For removing binder, we recommend annealing at 900 °C during 1 h in the ambient atmosphere. The heating rate is 3 °C per min. The same cooling rate is recommended. For the three dimensional elements like domes, the first step of the forming is cold isostatic pressing in a mould. The mould machined out of steel and hardened to the 54-56 hardness of Vickers should be polished to a maximum roughness height of 60 μm. To prevent unwelcome adhesion of the granulate to the mould, the spraying the mould with the spray of hexagonal boron nitride is strongly recommended. After the drying the BN spray, the excess of the boron nitride powder should be removed from the mould by cotton cloth polishing. The same concerns to a polyurethane jacket enveloping the mould and the granulate in the isostatic forming process. The pressurizing of the mould-jacket set, with the granulate inside, should be not higher than 120 MPa. Such formed sample, carefully removed from the mould, should be placed in a vacuum evacuated bag and cold isostatically pressed at 250 MPa. The same temperature treatment as the aforementioned one for the green body of three dimensional elements is recommended for binder removal and in one step biscuit creation. In Fig. 1, the mould and polyurethane jacket used for the dome shaping are shown.

Fig. 1. The mould and polyurethane jacket used for the dome shaping, and a green dome.

During designing the mould-jacket or dies, one should keep in mind that for the nanopowders of spinel a final sintering shrinkage is huge, and from the green body to the final sintered one is ~25%. In practice the 80 mm diameter of spinel ceramics windows we have compacted in the 107 mm diameter die.

2.2. Pre-sintering conditions

There are two ways of the hot isostatic pressing (HIP) for ceramic densification. There are so called sinter-HIP or post-sintering HIP and direct-HIP. The latter one is a method in which powder or a green compact is placed in a sealed can and pressed by using HIP, whereas in sinter-HIP (post--sintering HIP), the previously sintered (pre-sintered) sample is further pressed by using HIP without the can. For the successful post-sintering HIP process, the porosity of the previously sintered sample must be closed. The direct-HIP method applied to densification of the spinel we have reported previously [10], and in this paper, we focused on the sinter-HIP method for the manufacturing balk transparent spinel. In our approach, pre-sintering has been conducted at 1700 °C during one hour, and both ambient environment and vacuum in the furnace have been tested. Since there is no doubt when the pre-sintering is conducted in vacuum, the question about air atoms trapped in closed pores, when pre sintered in air, remains open. Let us estimate the ratio of a number of air atoms trapped in the pores to the total number of atoms in the pre-sintered spinel lattice. Assuming that the pores are closed at the temperature of pre-sintering and the air is an ideal gas one can estimate the density of air at 2000 K (closing pores abs. temp.) as:

$$\rho_{air}^{2000} = \frac{T^{room}}{T^{2000}} \rho_{air}^{room} = \frac{300[K]}{2000[K]} 1.2[kg/m^3] = 0.18[kg/m^3] \quad (2)$$

It is the density of air trapped in the pores after pre-sintering. As an effect of pre- sintering the density of the sample achieved 97% of theoretical one; it means that a mass of 3570 [kg]·0.97 = 3462.9 [kg] is in one cubic meter of pre--sintered spinel. On the other hand the mass of trapped air in the volume of one cubic meter of pre-sintered spinel ceramics is: 0.18[kg]·0.03 = 0.054[kg]. Estimating the mean atomic mass weight in the molecules of spinel as 20 (there are: one magnesium atom, two aluminium atoms and four oxygen atoms) the atomic ratio of the trapped air to the number of atoms constituting spinel ceramics in the unit volume of pre-sintered spinel could be estimated as:

$$\frac{n_{air}^{trapped}}{n_{spinel}} = \frac{0.054}{3462.9} \cdot \frac{20}{14} = 2.26 \cdot 10^{-6} \quad (3)$$

It means that the fraction of dopes introduced via pre--sintering in the air is on the level of two ppm. In the above estimation we assumed that the air consists completely of nitrogen and we completely neglected diffusion of the trapped atoms across the spinel lattice. Anyway, this ratio is small enough to make the effect of trapped atoms of air negligible from the standpoint of the further processing of spinel and their optical properties. Finally, this is why the pre-sintering environment (air or vacuum) does not make any difference on the optical properties of finally obtained bulk samples of transparent spinel ceramics. Summarizing the pre-sintering process could be conducted in a vacuum furnace with a tungsten mesh heater or in air with a superkanthal heater.

For the vacuum furnaces, we do not recommend graphite heaters for pre-sintering. In Fig. 2 we have shown the photo of the pre-sintered dome.

a)

b)

Fig. 2. The photo of the pre-sintered dome: a) upper side, b) bottom side.

2.3. Hot isostatic pressing

After the sintering has been accomplished to closed porosity, the specimens were subsequently packed in an Al_2O_3 (corundum) powder bed and HIPed. Of course the native spinel powder bed would be in advance, but a lot of spinel powder (especially for the bulk specimens) is required, and it makes all the HIP process more expensive. We HIPed our samples using an EPSI Hot Isostatic Press in a graphite furnace. This apparatus is capable to provide the temperature and pressure up to 2000 °C and 300 MPa, respectively. The pressure was applied by means by 0.99995 purity argon gas provided by Linde. In Fig. 3, the complete pressure temperature history of the HIP process is shown.

As could be seen we have started with the temperature as high as 1950 °C during the first 10 minutes, and then the temperature was decreased to 1800 °C, and kept constant during the next 110 minutes, so the all process of HIP post--sintering took two hours, excluding the heating and cooling periods. Following the temperature rising the pressure climbed up to 210 MPa for the first ten minutes, and was kept on the 200 MPa until the end of the process.

The density measured by the Archimedes method revealed the theoretical value within the experimental error. The samples were transparent but rather dark in body colour,

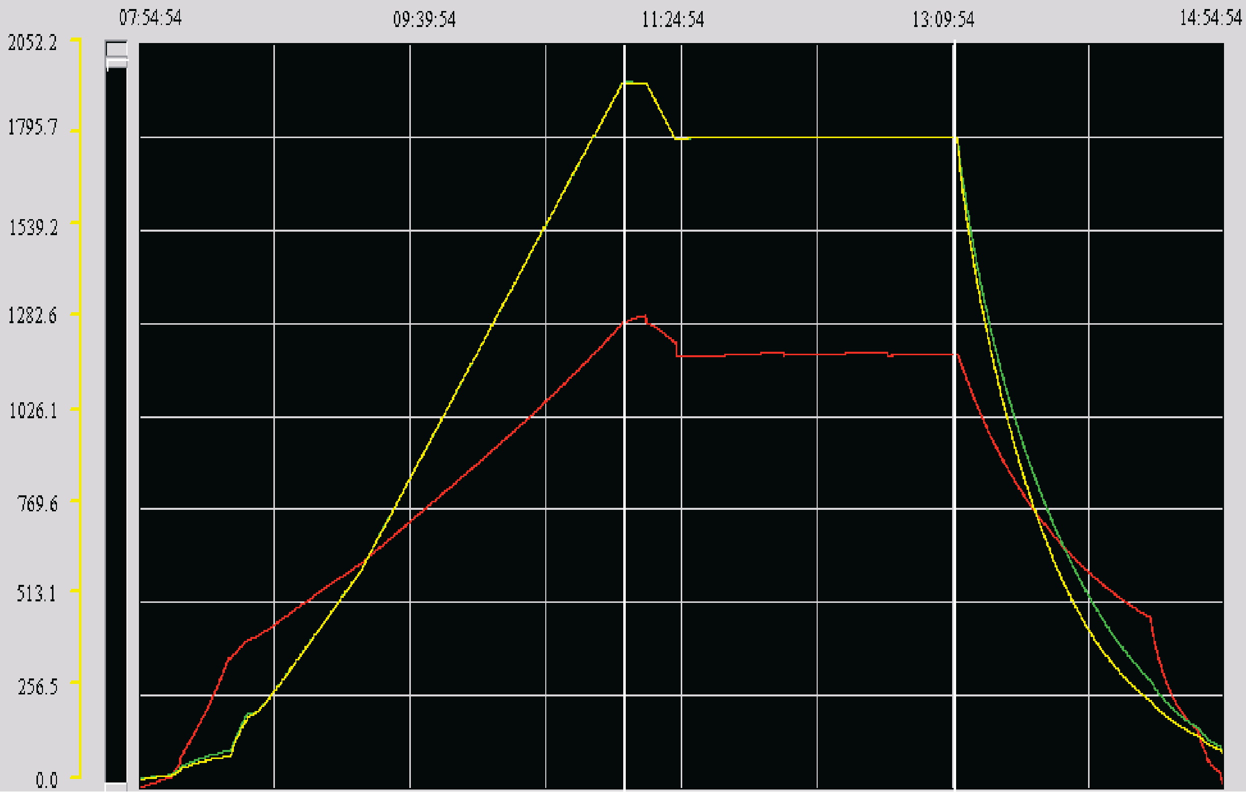
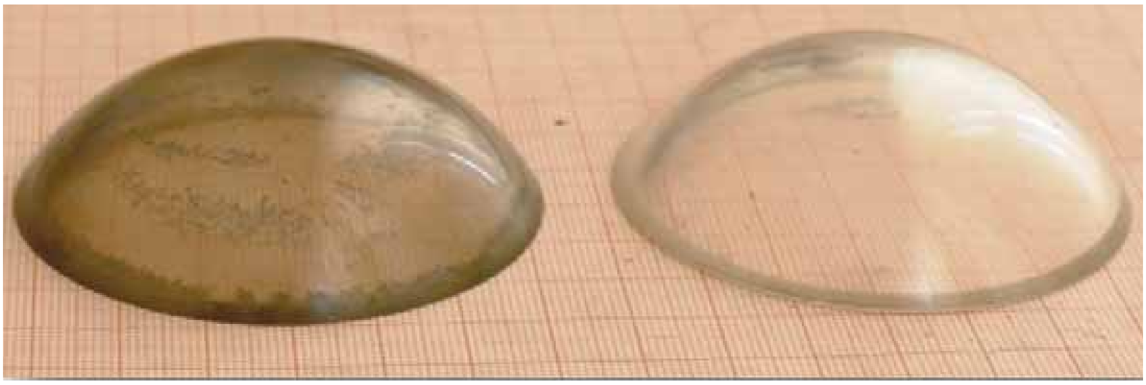


Fig. 3. The spinel transparent samples temperature and pressure HIP process history.



a) **b)**

Fig. 4. The photo of two domes: a) as-HIPed with a little bit haze caused by colour centres supposed to be generated by deficiency of the oxygen anions, b) already after the annealing in air at 1300 °C and as a result is completely colourless.

presumably having been driven slightly of stoichiometry by HIPing in the reducing environment. This environment is inevitably generated by the graphite heater of HIP. The partial protection from this reducing atmosphere provides the oxide powder bed, but this trick never give the complete balance of reducing fullerenes ejected from the graphite heater and the graphite crucible.

2.4. The final treatment

The dark colour of the just HIPed samples is probably attributed to a slight deficiency of the oxygen anions. The colourless appearance could be restored by annealing the HIPed samples in air at 1300 °C during at least 3 hours. The elevated temperature of heating like 1600 °C gives in consequence a completely opaque sample, and transparency is completely lost. On the basis of this, one can conclude that by annealing temperature limited to 1300 °C we obtained the diffusion coefficient of oxygen high enough to restore stoichiometry, low enough to prevent grain growth and, in effect, expansion of pores in the transparent spinel ceramics. So the fundamental difference between the diffusion rates for the mass transfer and oxygen diffusion restoring the stoichiometry favours this last one, what enables manufacturing, using the HIP, the fully transparent bulk spinel ceramics elements. In Fig. 4 we demonstrate two domes one as-HIPed with a little bit hazy colorization caused by colour centres supposed to be generated by deficiency of the oxygen anions. The second one is already after the annealing in air at 1300 °C and as a result is completely colourless.

The optical transmission of the transparent spinel ceramics manufactured according to the subroutine described in aforementioned steps from 2.1. to 2.4. is shown in Fig. 5.

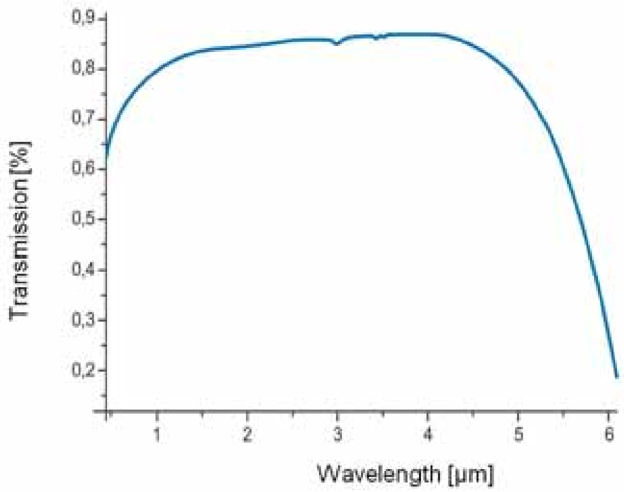


Fig. 5. Spectrum of optical transmission of colourless spinel ceramics.

This spectral dependence of transmission covers wave length from the mid-infrared to the near ultraviolet.

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References

[1] Sanghera, J.: *Ceramic laser materials,* invited lecture given in the Institute of High Pressure Research , Polish Academy of Sciences, April 2012.
[2] www.disclose.tv/action/viewvideo/8782/Spinel_Transparent_Armor_Defeats_Barret/ , 28 Jan. 2012.
[3] Ikesue, A.: Polycrystalline Nd:YAG ceramic lasers, *Optical Materials*, 19, (2002), 183-187.
[4] Apetz, R., van Bruggen, M.P.B.: Transparent alumina: A light scattering model, *J. Am. Ceram. Soc.*, 86, 3, (2003), 480-486.
[5] Helle, A.S., Esterling, K.E., Ashby, M.F.: Hot Isostatic pressing Diagrams: New Development, *Acta Metal.*, 33, 12, (1985), 2163-74.
[6] Shimada, M., Endo, T., Saito, T., Sato, T.: Fabrication of Transparent Spinel Polycrystalline Materials, *Matter. Lett.*, 28, (1996), 413-415.
[7] Gilde, G., Patel, P., Patterson, P., Blodgett, D., Duncan, D., Hahn, D.: Evaluation of Hot Pressing and Hot Isostatic Pressing Parameters on the Optical Properties of Spinel, *J. Am. Ceram. Soc.*, 88, 10, (2005), 2747-51.
[8] Tsukuma, K.: Transparent $MgAl_2O_4$ Spinel Ceramics Produced by HIP post Sintering, *J. Ceram. Soc. Jpn.*, 114, 10, (2006), 802-806.
[9] Wätzing, K., Hutzler, Th., Krell, A.: Transparent Spinel by Reactive Sintering of Different Alumina Modification with MgO, *cfi/Ber. Dt. Keram. Ges.*, 86, 6, (2009), E47-E46.
[10] Witek, A., Perkowski, K., Osuchowski, M., Witosławska, I., Tymowicz-Grzyb, P., Konopka, G., Ozięble, A.: In situ synthesis and sintering of the $MgAl_2O_4$ spinel using hot isostatic pressing", *Ceramic Materials*, 63, 3, (2011), 519-523.

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