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Fabrication of transparent yttria by HIP and the glass-encapsulation method

Johanne Mouzon [a,*], Alexandre Maitre [b], Lars Frisk [a], Niklas Lehto [a], Magnus Odén [a]

[a] *Division of Engineering Materials, Luleå University of Technology, SE-971 87 Luleå, Sweden*
[b] *Laboratoire Science des Procédés Céramiques et Traitements de Surface, UMR CNRS 6638, UFR Sciences et Techniques, 123 Avenue Albert Thomas, F-87060 Limoges Cedex, France*

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Abstract

This method consists of a combination of vacuum sintering at 1600 °C followed by hot isostatic pressing (HIP) at 1500 °C of a highly agglomerated commercial powder. The use of evacuated glass capsules to perform HIP treatment allowed samples that showed open porosity after vacuum sintering to be sintered to transparency. The sintering response of the investigated powder was studied by careful microstructural observations using scanning electron microscopy and optical microscopy both in reflection and transmission. The successful key of this method was to keep porosity intergranular during pre-sintering, so that it can be removed subsequently by HIP treatment. It was found that agglomerates of closely packed particles are helpful to reach that purpose, since they densify fully and leave only intergranular porosity. However, performing HIP treatment at 1625 °C was found to result in opaque samples. This was attributed to the diffusion of argon inside the capsule. Contamination at different steps of processing was also investigated by inductively coupled plasma mass spectrometry (ICP-MS).

Keywords: Yttria; Y_2O_3; Transparent; Hot isostatic pressing (HIP); Glass-encapsulation; Encapsulation

1. Introduction

Yttria is a promising optical ceramic with excellent physical and chemical properties, such as a high melting temperature (∼2430 °C), a broad range of transparency, and high corrosion resistance. Considering these properties, polycrystalline yttria ceramics has been the focus of much interest for different applications, like crucibles in the casting industry,[1] missile domes,[2] and lasers.[3,4] When used for its transparency, the advantage of polycrystalline yttria ceramics compared to single crystals lies in the fabrication process of ceramics. In fact, ceramic processing requires lower temperatures and offers a wider range of sizes and shapes for the final product.

In order to produce a transparent polycrystalline ceramics, the elimination of porosity must be fully achieved. Pressure-assisted methods like hot pressing or hot isostatic pressing (HIP) are efficient in reaching full densification of ceramics. Transparent polycrystalline yttria ceramics were successfully sintered by hot pressing without additives[5,6] or addition of LiF.[7] Ikesue et al.[8] utilized a combination of vacuum sintering with large addition of HfO_2 followed by HIP treatment to produce Nd-doped Y_2O_3.

However, these methods possess several limitations. On one hand, the shapes that can be manufactured by hot pressing are rather limited to thin pellets. On the other hand, the two-step approach consisting of vacuum sintering followed by HIP requires closed porosity in the pre-sintered samples in vacuum in order to transmit the external pressure exerted by argon during HIP. Therefore, densities >92% of theoretical density are required prior to HIP. However, at such densification level corresponding to the final stage of sintering, pores are likely to separate from grain boundaries by the occurrence of abnormal grain growth. For this reason, grain-boundary mobility must be controlled. In yttria, Th^{4+} and Hf^{4+} were shown to effectively retard grain growth by solute drag mechanism and prevent abnormal grain growth.[8,9] However, large amount of sintering additives might be detrimental for optical properties because of the presence of secondary phases or energy transfers in the case of laser applications. Other works employed tetravalent cations to enhance densification of yttria using Ti^{4+}[10] or Zr^{4+}.[11]

* Corresponding author.
E-mail address: johmou@ltu.se (J. Mouzon).

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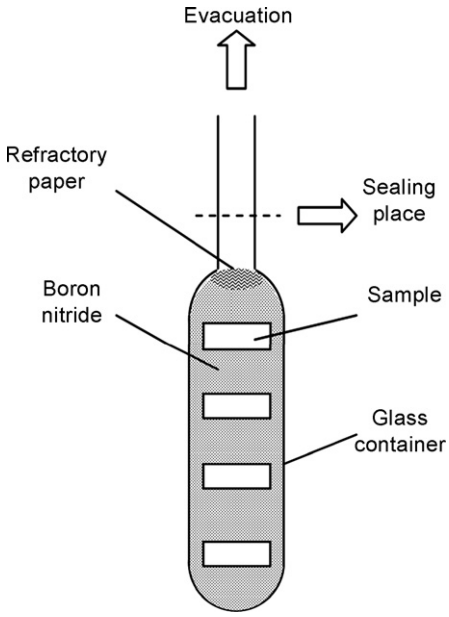

Fig. 1. Typical set-up of a glass capsule.

Moreover, most HIP equipments are equipped with graphite heating elements and shields. These latter when heated create a reducing atmosphere, which can lead to contamination and reduction of optical oxide ceramics.[12] Glass-encapsulation appears as an interesting method, to prevent such problems from occurring.

In this paper, we report on the fabrication of transparent yttria ceramics without additives by vacuum sintering to densities lower than 90% of theoretical followed by HIP treatment using the glass-encapsulation method.

2. Experimental

A commercial powder of yttria (REacton®, Alfa Aesar) with a purity of 99.99%, an average particle size below 1 μm and a BET specific area of 4.1 m^2/g was used in this work. Pellets were uniaxially pressed in a 14 mm diameter die under 10 MPa. This was followed by cold isostatic pressing at 200 MPa.

Pellets were pre-sintered at 1600 °C at a heating rate of 600 °C/h, with a holding time of 3 h, a cooling rate of 600 °C/h under rough vacuum of 10 Pa in a furnace equipped with molybdenum mesh heater.

Final densification of the samples was performed by HIP using the glass-encapsulation technique. As schematically illustrated in Fig. 1, a glass capsule was used for its ability to deform and transmit pressure at high temperatures. The capsule was made of Corning Vycor® 7913 (96% SiO_2, 3.5% B_2O_3, 0.5% Al_2O_3), whose viscosity properties are gathered in Table 1. The pre-sintered samples were placed in the glass capsule embedded in pure hexagonal boron nitride (BN) powder used as a barrier material to avoid any reaction with glass. Sealing at one end (bottom end in Fig. 1) was performed using the flame of an oxygen/hydrogen mixture (>3000 °C). The capsule was then evacuated at 700 °C for 4 h and under a vacuum of 10^{-4} mbar (10^{-2} Pa). Finally, the other end of the capsule was also sealed at the place indicated in Fig. 1.

Table 1
Viscosity properties of Corning Vycor® 7913

Strain point (°C)	890
Annealing point (°C)	1020
Softening point (°C)	1530

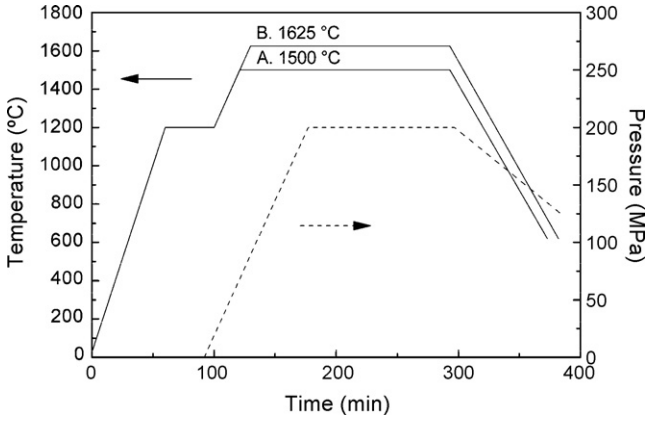

Fig. 2. Detailed regimes of the HIP treatments at 1500 °C (case A) and at 1625 °C (case B) under 200 MPa.

The HIP treatment was conducted either at 1500 °C (case A) or at 1625 °C (case B) under 200 MPa pressure. Fig. 2 shows the detailed temperature and pressure profiles employed in this study. A critical step in the glass-encapsulation technique is the heating up to the transformation point of glass. Therefore the capsules were heated up to 1200 °C in 1 h. This temperature was held for 40 min to soften glass before applying any pressure. Pressure and temperature were then raised to 200 MPa and to final temperature, respectively. Maximal pressure was held for 2 h. Temperature and pressure were let to decrease freely down to room temperature and atmospheric pressure beyond the time scale of Fig. 2.

The samples were recovered out of the capsule by machining with a diamond cutting disc and abrasive paper. Densities of the pellets were measured by the gravimetric method after the pressing and pre-sintering steps, and by the Archimedes' method after HIP. Mirror-polishing using diamond sprays down to 1/4 μm was performed on one side for the pre-sintered samples and on both sides for the HIP-treated samples. Inline transmittance was measured over the wavelength region from 200 to 1000 nm for comparison with the literature on a UV/VIS/NIR spectrophotometer (Lambda 900, PerkinElmer, MA, USA).

The microstructure after vacuum sintering and HIP treatment was observed by optical microscopy using polarised light, scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) analysis.

Inductively coupled plasma mass spectroscopy (ICP-MS) was used to assess silicon concentration before and after HIP. Bulk samples were ground and received a special silicon treatment.

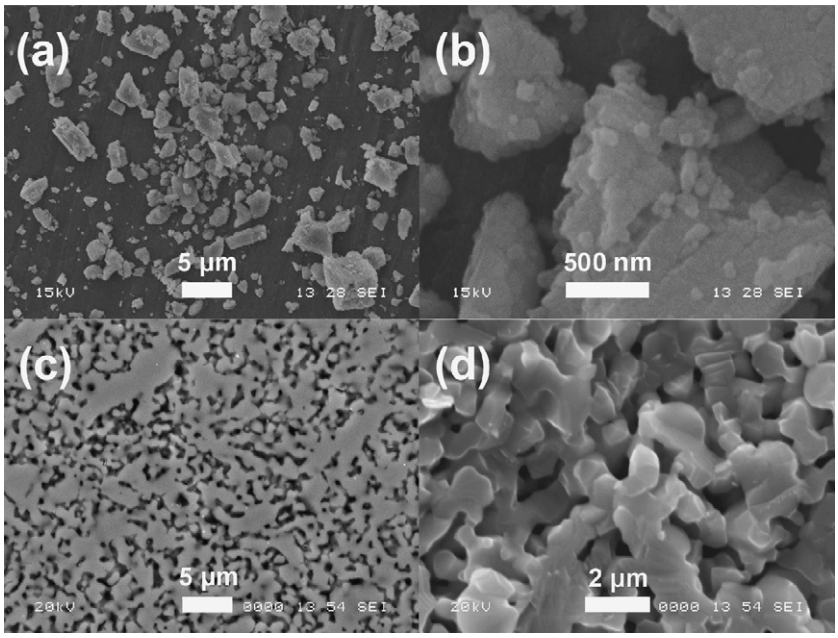

Fig. 3. (a) and (b) Scanning electron micrograph of the starting powder at different magnifications; (c) scanning electron micrograph of a polished surface after vacuum sintering and (d) scanning electron micrograph of a fracture surface after vacuum sintering.

3. Results

Fig. 3(a) and (b) shows the morphology and state of agglomeration of the REacton powder. It consists mainly in dense agglomerates of closely packed primary crystallite of 40 nm, which was confirmed by X-ray powder diffraction using the peak broadening technique. The particle size distribution ranges from a single crystallite to dense agglomerates of 5 μm. After cold isostatic pressing (CIP) at 200 MPa, green bodies with relative density of about 60% were obtained. This can be attributed to the dense character and wide size distribution of the starting powder.

Fig. 3(c) shows the typical microstructure of the REacton sample, which was pre-sintered in vacuum. By comparing Fig. 3(a) and (c), it is obvious that the hard agglomerates were left as such in the green body and that differential sintering occurred in these denser regions. Although the hardly agglomerated character of the powder prevented from achieving high pre-sintered density (83% of the theoretical density), the dense agglomerates underwent local densification, leading to the development of dense, pore-free regions, as confirmed by examination of the fracture surface in Fig. 3(d). However, differential sintering caused porosity to increase in between the dense regions. Nevertheless, residual porosity was still located at grain boundary prior to HIP.

Different results were obtained depending on the final temperature during HIP. In Fig. 4, it can be seen that the sample HIPed at 1500 °C is clear and shows transparency (Fig. 4(a)), while that HIPed at 1625 °C is mostly opaque, cracked, and with black appearance, which was found by the author to be systematically related to the presence of porosity in other samples (Fig. 4(b)).

Fig. 5 shows the transparency of the sample HIPed at 1500 °C when the sample is raised 5 mm over it. Considerable scattering can be noticed, although transparency looked acceptable when the sample lied directly on the text in Fig. 4(a). Fig. 6 shows that considerable densification and grain growth occurred during HIP, but no scattering centers could be resolved by SEM. In fact, this scattering was found to be related to defects shaped as dots and dashes observed by transmission optical microscopy, as shown in Fig. 7(a). The presence of these defects seems to indicate the presence of a secondary phase. The defects were

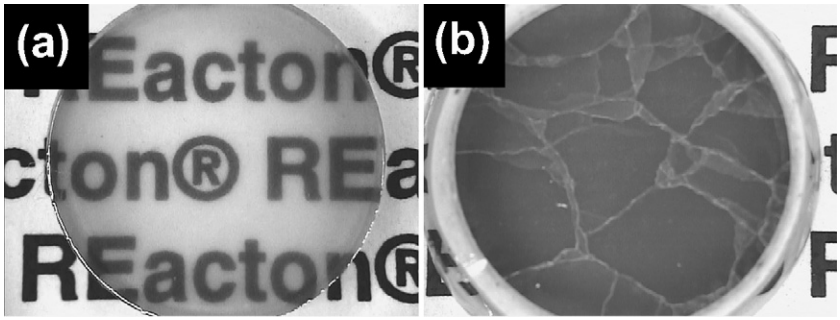

Fig. 4. Photographs of the samples after HIP treatment (a) at 1500 °C and (b) at 1625 °C.

Fig. 5. Photograph of the samples HIPed at 1500 °C when raised 5 mm over the text.

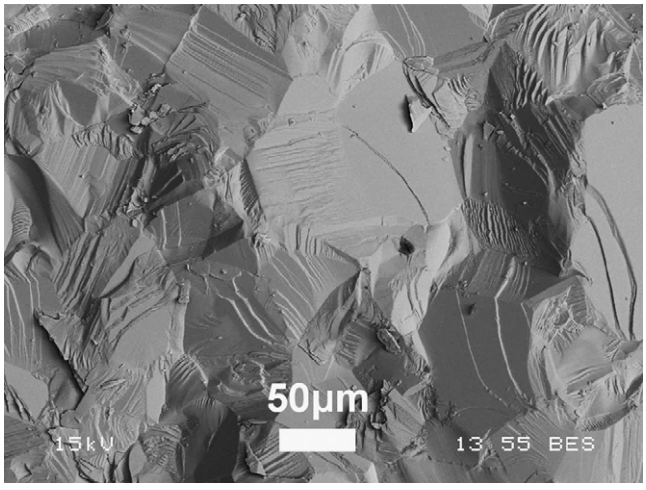

Fig. 6. Scanning electron micrograph showing fracture surface of the sample HIPed at 1500 °C.

found to be transparent by optical microscopy and being either located at grain boundary or inside grains by SEM observation. Silicon was detected in those defects by EDX analysis.

In the case of the sample HIPed at 1625 °C, Fig. 7(b) shows the presence of porosity in the middle of the grains. Considering the distances between pores (<5 μm), which is in the same order of magnitude as the grain-size after pre-sintering, pore

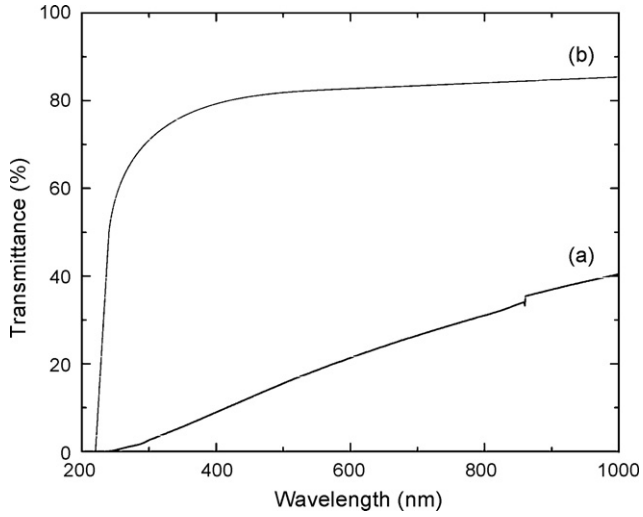

Fig. 8. Inline transmittance of: (a) 1.5-mm thick yttria ceramic HIPed at 1500 °C and (b) 0.5-mm thick single crystal of yttria.

entrapment must have occurred by pore-grain boundary separation and rapid grain growth. The micrograph also indicates the formation of pore-free zones between grain boundary and the center of the grains containing remaining porosity. These regions were formed by sacrificial grain growth, which is the removal of formerly entrapped pores when encountered by growing grain boundary.[14]

Fig. 8 compares the transmittance of the sample HIPed at 1500 °C with a 0.5-mm thick single crystal of yttria. An inline transmittance of 10% at 400 nm was found for the ceramic sample, which was 1.5-mm thick.

4. Discussion

As it was shown in Fig. 6, substantial densification and grain growth occurred during HIP in the sample treated at 1500 °C. Although the topography and distribution of the porosity was highly thermodynamically unfavourable, the HIP treatment caused the intergranular porosity to disappear. Sintering was probably reinitiated by the application of the external pressure through enhanced diffusion and possibly by plastic deformation. External pressures are known to increase densification in comparison with coarsening.[13] An applied compressive stress

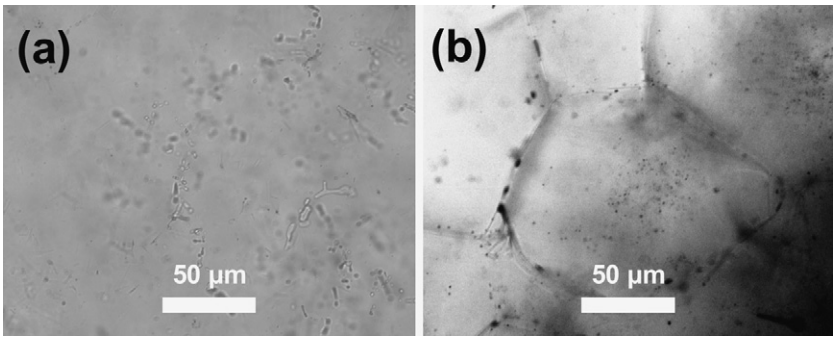

Fig. 7. Optical transmission micrographs showing: (a) defects in the sample HIPed at 1500 °C and (b) fine porosity trapped and left inside grains in the sample HIPed at 1625 °C.

Table 2
Contents in wt ppm of the main impurities in the starting powder

Powder	REacton
Si	15
Al	5
Cu	10
Fe	2
Mg	10
Ca	n.d.

decreases the concentration of vacancies at grain boundaries and hence increases mass transport by diffusion to the pores, because of the vacancy concentration gradient. Densification might also have been reinitiated by plastic deformation causing internal rearrangement and further contacts between densified regions. The fact that substantial grain growth took place during HIP can be certainly attributed to the high temperature and long dwell time, since there was no pinning effect exerted by pores to resist grain growth after removal of these latter.

Another feature of this method is the use of glass encapsulation to perform HIP treatment. It enables the transmission of external forces applied by argon gas on porous solids showing open porosity. Thus, the samples need not to be sintered to close density during vacuum sintering, as long as an evacuation of the capsules is performed before sealing. It is thereby possible to take maximum profit of the low pressure of unsoluble gases left in the pores. This low pressure provided less resistance to densification by diffusion and possibly by plastic deformation.

The silicon content of the starting powder was 15 wt ppm regime (see Table 2), thus not responsible for the presence of secondary phases throughout the sample. Pollution during vacuum sintering can be ruled out, since the authors observed the same kind of defects in other sintering atmospheres. A plausible explanation might be the infiltration of silicon dioxide from the glass capsule through the boron nitride layer into the pre-sintered sample showing open porosity. The vaporization of silicon oxide is known to occur at temperatures above 1200 °C according to the following equation:

$$SiO_2 \leftrightarrow SiO(g) + 1/2O_2(g) \quad (1)$$

However, no enrichment in silicon could be detected by ICP-MS. Concentrations both before and after HIP were found to be below 500 wt ppm, which was the detection limit of the method on bulk samples. Assuming the formation of Y_2SiO_5 as suggested by the Y:Si ratio found by EDX in the core of Si-rich inclusions, an increase in silicon content from 15 to 500 wt ppm would enable an increase in the formation of Y_2SiO_5, from 0.017 to 0.58 vol.%. This range of concentration seems to be consistent with Fig. 7(a). Therefore, silicon enrichment from the glass capsule cannot be ruled out. However, further investigation is required to understand the formation of this scattering phase and its influence on the densification process in this method.

The fact that porosity became entrapped in samples HIPed at 1625 °C, while it could be removed when treated at 1500 °C, is believed to be due to the diffusion of argon through the glass layer at temperatures over 1500 °C, but before closed porosity was reached either in the ceramic samples or in the boron nitride layer. Liu[15] showed that thin tubes of fused quartz start to become slightly permeable to argon from 900 °C. In our study, the high-temperature and high-pressure conditions might have caused considerable amount of argon to diffuse inside the capsule. Moreover, the softening point of the glass used in this study is 1530 °C as given by the manufacturer in Table 1. Softening point is defined as the temperature at which a glass fiber less than one millimeter in diameter will stretch under its own weight at a rate of one millimeter per minute when suspended vertically. Therefore, the glass capsule is likely to have become very thin at certain places while flowing down at 1625 °C.

Because of the diffusion of pressurized argon inside the capsule and through the open porosity of the samples, densification and grain growth proceeded through thermal activation only, until closed porosity was reached either in the ceramic samples or in the boron nitride layer. From this moment, pressure could be fully transmitted, but the presence of pressurized argon inside pores prevented the removal of these latter, except by sacrificial grain growth as explained above. Therefore, final density was limited to 99.5% of theoretical. Cracks probably initiated at pores during cooling.

5. Conclusion

Transparent yttria was fabricated from a highly agglomerated powder by a combination of vacuum sintering at 1600 °C followed by hot isostatic pressing using the glass-encapsulation method at 1500 °C. The use of evacuated glass capsules enabled samples that showed open porosity after vacuum sintering to be sintered to transparency. As such, porosity was still located at grain boundary and could be subsequently removed by hot isostatic pressing. The absence of pore entrapment during the densification of the dense agglomerates was attributed to the compact packing of the primary particles. However, the presence of secondary phase was responsible for residual scattering. This probably stems from the infiltration of silicon dioxide from the glass capsule. On the other hand, transparency could not be reached by performing HIP at 1625 °C. This was attributed to the diffusion of argon inside the capsule.

This study also shows the attractive side of studying the sintering behaviour of transparent ceramics, since it is possible to observe directly in the bulk the presence of defects, such as secondary phases or porosity, with a concentration less than 0.5 vol.%.

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