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Short communication

Fabrication of translucent alumina ceramics from pre-sintered bodies infiltrated with sintering additive precursor solutions

Guanwei Liu, Zhipeng Xie *, Wei Liu, Lixia Cheng, Yin Wu

State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

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Abstract

Translucent alumina ceramics were fabricated by infiltrating aqueous solutions containing sintering dopant ions ($Mg^{2+}/Y^{3+}/La^{3+}$) into pre-sintered alumina compacts and sintering in H_2 atmosphere. The improved microstructural homogeneity, finer grain size and enhanced transmission properties of infiltration processed samples over those processed by conventional ball-milling method were corroborated by experimental results. Triple doping via infiltration appears to be significantly beneficial for achieving enhanced transmission (36.3% at wavelength 800 nm for sample thickness of 0.75 mm). This study indicates that infiltration technique can be used to fabricate translucent alumina ceramics with improved performance.

Keywords: Infiltration; Doping; Optical properties; Al_2O_3

1. Introduction

Alumina ceramics can be made translucent or transparent provided that the residual porosity can be effectively eliminated.[1] Defects like pores with comparable size to visible light, can act as the scattering center of light, thus leading to the deterioration of transparency.[2,3] Therefore the forming and sintering techniques have to be optimized to obtain highly dense, defect-free microstructure. Although HIP and SPS techniques are capable of producing alumina ceramics with very fine microstructure and excellent optical properties, they are generally complicated and usually increase the cost of processing.[4] Therefore, although conventional coarse grained translucent polycrystalline alumina (PCA) ceramics exhibit limited transparency, they are still widely used as light-transmitting material at high temperatures and in corrosive environments due to the low cost and simplicity in processing.[3,4]

Typical fabrication process for PCA always requires the indispensable MgO dopant and high sintering temperatures (>1600 °C)[4] in H_2 atmosphere. Following such strategy, alumina grains generally underwent dramatic coarsening to sizes >20 μm. Although conventional ball-milling has been feasible to incorporate dopants in numerous applications, generally it has not been regarded as the optimal route to disperse additives in the matrix due to its low degree of homogeneity on a finer scale and incapability of effectively overcoming agglomeration.[5]

Hence, various methods like using alumina powder already doped with MgO,[3] or some other chemical methods to mix alumina powder with Mg-containing precursor in slurry[2] were developed. However, these strategies often need complicated powder processing steps, so a simplified process should be desired. Liquid precursor infiltration technique is a useful approach for processing ceramics.[6–8] Recent developments of doping ceramics via infiltration have highlighted its advantage to realize highly uniform distribution of introduced species.[9–11] Among these efforts, low-content doping of ceramics boasts the special superiority, because the dilute solutions favors complete saturation of the porous structure due to both their low viscosity and low propensity to re-distribution,[10,11] so the whole infiltration process comes closer to the "ideal" doping condition.[11,12]

Employing the idea of free volume, or absorbed volume for ideal infiltration[10,11] (which could be safely approximated to be the porosity for the slightly pre-sintered compacts), we can estimate the theoretical content of introduced dopants, as revealed by equation (3) in literature[12] or equation (1) in[11]. Based on this idea, doping ceramics with a certain content of additives is feasible. In this paper, high-purity alumina preforms were first infiltrated with dilute solutions to incorporate a calculated

* Corresponding author. Tel.: +86 10 62799031; fax: +86 10 62771160.
E-mail address: xzp@mail.tsinghua.edu.cn (Z. Xie).

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theoretical content of sintering additives ($MgO/Y_2O_3/La_2O_3$) and then sintered in H_2 atmosphere to obtain polycrystalline alumina ceramics. The microstructure and in-line transmittance was examined in comparison with those prepared following the conventional ball-milling strategy. The results demonstrate that better microstructural homogeneity and optical performance were achieved via infiltration, revealing its potential to fabricate various doped ceramic materials with enhanced properties which requires stringent composition and microstructural control.

2. Experimental procedure

Pre-sintered pure alumina preforms were made from a high purity (>99.99%) α-Alumina powder (CR20, $D_{50} = 0.35\ \mu m$, Fenghuang Finechemical Co. Ltd., Shandong, China). The powder was dry pressed at 10 MPa into pellets with a thickness of 1.00 mm and cold-isostatically pressed at 200 MPa for 1 min. Pressed pellets were pre-sintered at 1000 °C for 30 min to obtain the alumina preforms for infiltration. The pore structure of pre-sintered pellets was characterized by mercury intrusion method (Autopore 9500, Atlanta, USA). The as-prepared preforms were then immersed in infiltration solution for 1 h (This is long enough to favor as complete infiltration by referring to the reported infiltration rate constants.[7,13,14]) at ambient temperature and pressure to incorporate dopants. The solution was prepared via dissolving analytically pure $Mg(NO_3)_2{\cdot}6H_2O$ and $Y(NO_3)_3$ (Beijing Modern eastern Finechemical Co. Ltd., Beijing, China) in de-ionized water. By assuming an ideal doping process, the relationship between the theoretical doping content w of MgO and the molar concentration of solution c could be determined using the formula below:

$$\rho_{Al_2O_3} \cdot (1-\delta) \cdot w = M_{MgO} \cdot c \cdot \delta \tag{1}$$

In formula (1), $\rho_{Al_2O_3}$ is 3.98 g/cm^3, δ is the porosity of alumina preform and M_{MgO} is 40.31 g/mol. The porosity of the preform (δ) has been estimated to be 50% following a geometrical route, in which $1-\delta$ should be equal to mass divided by the preform's volume and theoretical density of alumina (3.98 g/cm^3). The required concentration for doping a certain content of Y_2O_3 or La_2O_3 could be similarly determined by modifying Eq. (1). Specimens doped with a theoretical content of dopants via infiltration were designated as follows: (500 ppm MgO: 5M; 500 ppm MgO and 500 ppm Y_2O_3: 5M5Y; 500 ppm MgO, 500 ppm Y_2O_3 and 500 ppm La_2O_3: 5M5Y5L).

For comparison, samples were also doped with the same amount of sintering additives via conventional ball-milling approach. The same pure alumina powder was mixed with dopants, alcohol and alumina balls (diameter of 5 mm). The ball-milling system consists of powders/alcohol/ball in the weight ratio 1/1/2 in a teflon container. Mg/Y/La dopants were introduced (in the form of nitrate) into the slurry and then ball milling was conducted in a planetary ball mill for 6 h (QM-3SP2, Instrument Factory of Nanjing University, China). The slurry was finally dried in oven at 80 °C and then dry pressed, isostatically pressed under the same conditions for pre-sintered specimens.[9] Samples manufactured via ball-milling approach containing the same amount of MgO, Y_2O_3 and La_2O_3 were denoted as 5M-C, 5M5Y-C, 5M5Y5L-C, respectively.

In-situ precipitation treatment was carried out immediately after infiltration following the schedule previously reported.[9] Treated pellets (including those prepared following the ball-milling approach) were finally sintered in H_2 atmosphere at 1830 °C for 2.5 h with a heating rate of 5 °C/min. Sintered specimens were polished on both surfaces using diamond abrasive to a thickness of 0.75 mm and a surface roughness of 1 μm. The in-line transmittance of polished samples was measured using UV-Visible spectrophotometer (Spectrophotometer, Hitachi-3010, Hitachi, Tokyo, Japan). The microstructures and element distribution profiles of specimens were observed under the field emission scanning electron microscope (FESEM, LEO-1530, Zeiss, Oberkochen, Germany) equipped with energy-dispersive spectroscopy (INCA EDS, Oxford Instruments, Oxfordshire, UK). A rough estimation of average grain size was carried out by measuring 100 grains from the SEM image of the as-sintered sample's surface by Image Pro software (Media Cybernetics, Inc., Bethesda, USA).

3. Results and discussion

It is generally accepted that free volume could be used to estimate the content of introduced species, and better accuracy could be expected with the decreasing concentration of doping solution due to the improved rheological properties.[10,12] Based on the geometrically derived free volume and the safe assumption of complete saturation during infiltration,[11] translucent alumina samples doped with a theoretical content of sintering additive. What's more, evaporation of MgO dopants from the matrix alumina during the prolonged high-temperature heating is a widely-acknowledged problem.[4,15] So it should be further be emphasized that even the accurate introduction of an exact content of sintering additives via the conventional mechanical/chemical mixing routes is still incapable of producing a sample containing exactly the same content of dopants as in the mixing stage.[16]

Therefore, we should focus mainly on the properties and performance of the material prepared via infiltration. Fig. 1 indicates that the pore sizes of the pre-sintered pellets generally range from 30 nm to 70 nm. Fig. 2 demonstrates the microstructure of the four specimens. Much finer grain size over the ball-milling specimen 5M-C (∼30 μm) has been observed for 5 M, revealing the advantage of enhanced microstructural homogeneity of infiltration technique. It can be readily discovered from Fig. 2(a) that 5 M has an average grain size of <10 μm, and the approximate measurement with the software Image Pro reveals that the grain size of 5 M is about $6.0 \pm 2.3\ \mu m$, which to our best knowledge, is finer than that of any other pressurelessly sintered translucent alumina ceramics (generally 20–30 μm or even coarser). The above results again corroborate the claim that infiltration treatment leads to a more uniform distribution of introduced species and hence a finer final microstructure,[9] which generally features in a lower propensity to the occurrence of defects. Therefore it is reasonable that infiltration treatment results in enhanced optical properties (Fig. 3). It has also been

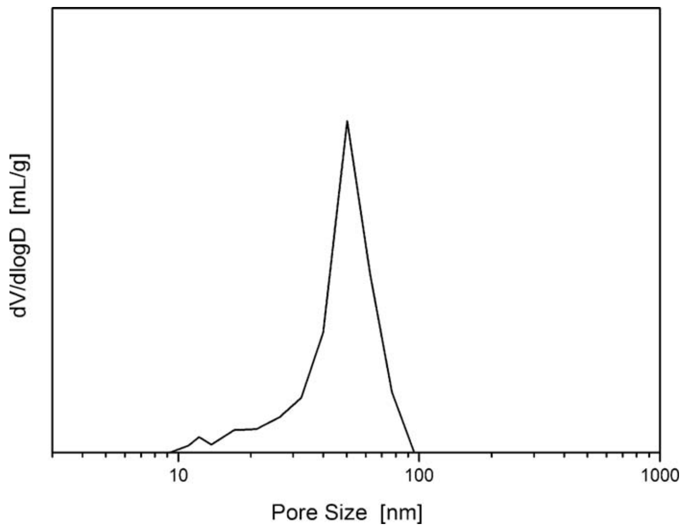

Fig. 1. Pore-size distribution of the pre-sintered alumina compact.

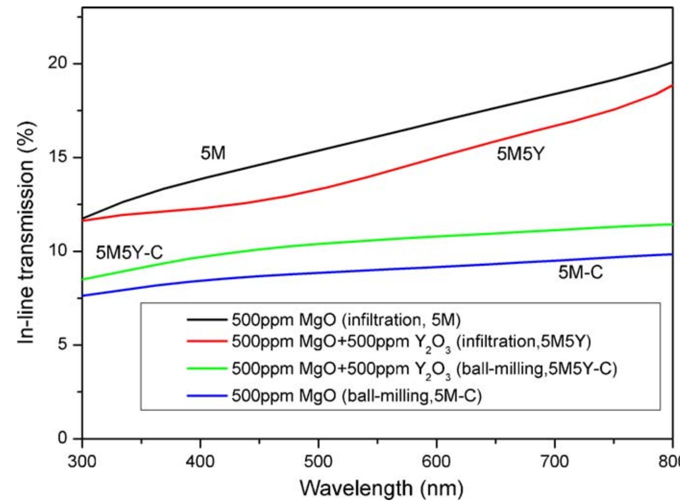

Fig. 3. In-line transmission of the prepared Mg/Y doped translucent ceramic samples.

reported that microstructural and transmittance stability of this type of materials at elevated temperatures was a concern.[1,17] Considering that specimen 5M underwent less coarsening when sintered at 1830 °C, infiltration routes as described by a European patent[18] and investigated here in more detail might be a promising strategy in achieving a finer microstructure and, therefore, an improved transmittance of PCA at high temperature.

The microstructures of 5M5Y and 5M5Y-C have been contrastively examined using backscattering signals, and it can be readily noticed that some grain boundary phase with brighter contrast (which can probably be associated with Y_2O_3 phase) exists in sample 5M5Y-C, while such phenomenon has been absent in 5M5Y. Fig. 4 demonstrates the X-ray mapping result of Y element in 5M5Y(a) and 5M5Y-C(b). It clearly confirms that more homogeneous distribution of Y element was achieved for infiltration prepared sample 5M5Y. The distribution profile of Y along the depth direction in 5M5Y (c) also reveals that complete infiltration and homogeneous doping were done throughout the sample.

It's generally accepted that yttrium has a very low solubility limit in α-alumina and segregates strongly to grain boundaries.[19] Due to its intrinsic advantage to realize more homogeneous distribution of exotic elements,[9] infiltration processing allows a more homogeneous partitioning of doping elements in the

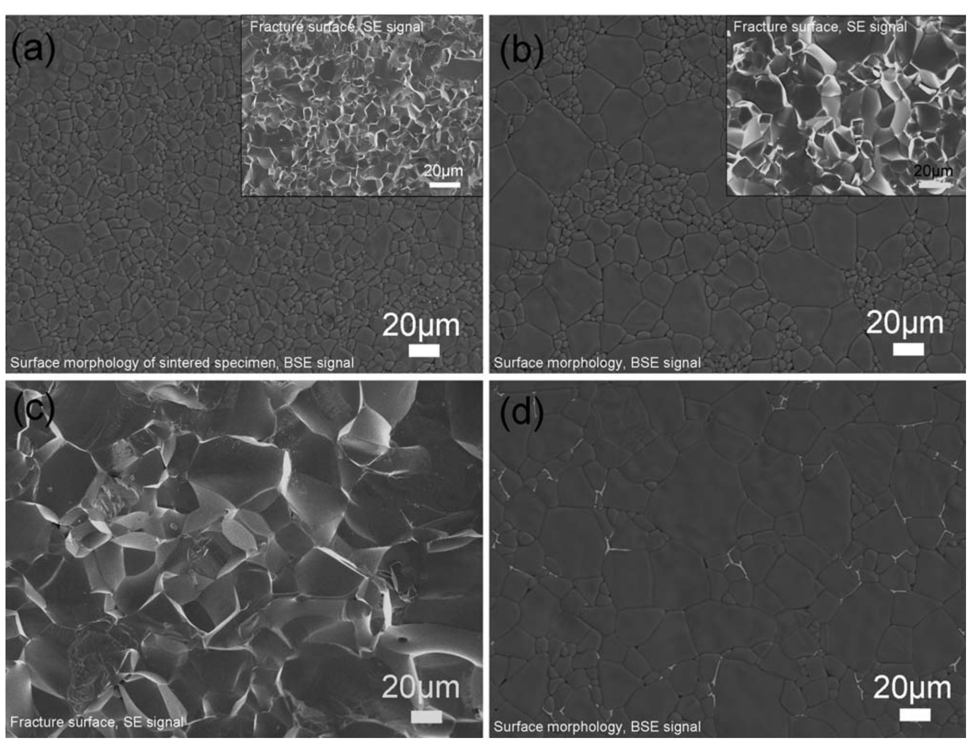

Fig. 2. Microstructure images of 5M (a), 5M5Y (b), 5M-C (c), and 5M5Y-C (d).

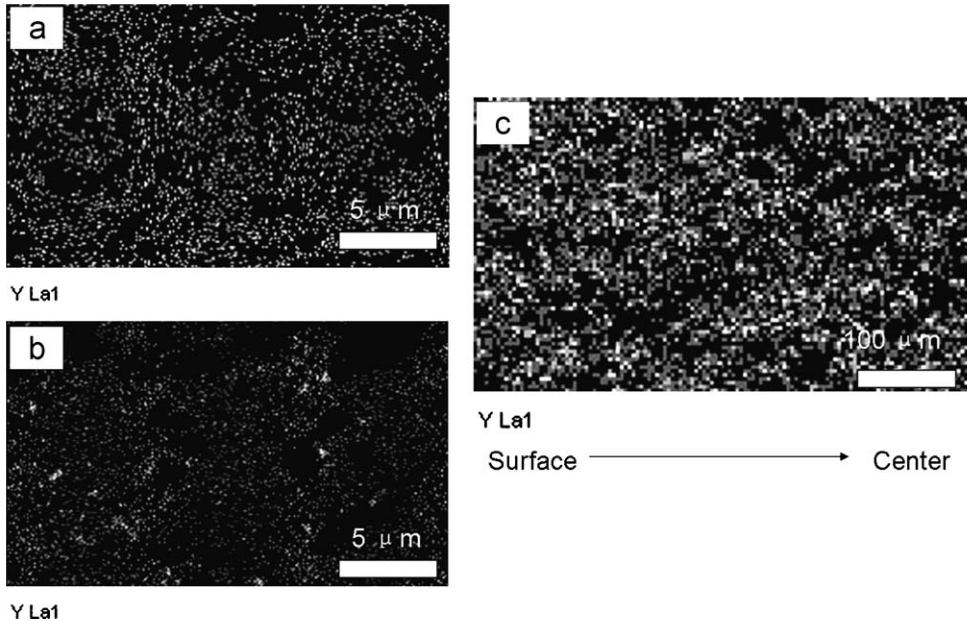

Fig. 4. X-ray mapping result of Y element in 5M5Y (a) and 5M5Y-C (b). (c) Distribution profile of Y along the depth direction in 5M5Y.

microstructure.[4] In contrast, inappropriate distribution of Y_2O_3 prior to sintering would exhibit greater tendency to segregation and the emergence of Y_2O_3 as a coarse, separate phase (as illustrated in Fig. 2(d) and Fig. 4(b)). The secondary phase in ball-milling sample 5M5Y-C would act as light-scattering center and deteriorates its optical properties, accounting for the lower in-line transmittance. The above results have confirmed the superiority of infiltration technique over conventional milling route in achieving enhanced microstructural homogeneity.

Fig. 2(b) also reveals that Y_2O_3 plays a vital role in the microstructure evolution of alumina ceramics. The grain size of sample 5 M is rather uniform, while a microstructure with obvious bi-modal feature has been confirmed for 5M5Y. Considering similar distinction has also been found between 5M-C and 5M5Y-C, we can attribute this phenomenon to the intrinsic effect of Y_2O_3 on grain boundary mobility and diffusion behavior of alumina during sintering rather than the employed infiltration technique. Although many researches have been conducted to investigate the impact of Y_2O_3 on alumina ceramics, opinions about its influence are still divided. Both densification promotion and prohibition effects have been reported.[19–21] Our study found that the incorporation of Y_2O_3 resulted in a bimodal rather than a more uniform microstructure, and the in-line transmittance data also did not reveal significantly advantageous effect for Y_2O_3 doping. Therefore, the role of Y_2O_3 addition to alumina still needs to be clarified and more work is yet to be done.

The in-line transmission of single or double doped specimens (Fig. 3) all underwent an increase with the wavelength. The infiltration processed sample 5M and 5M5Y have similar in-line transmittance, both exhibiting superior performance over their counterparts prepared via ball-milling route. Previous literature[20] has also emphasized that triple doping (Mg/Y/La) could give rise to enhanced transmission properties for translucent/transparent alumina ceramics. Therefore, we tentatively prepared the triple-doped specimen 5M5Y5L and 5M5Y5L-C, with their transmission properties and photograph demonstrated in Fig. 5. Although the ball-milling prepared sample possessed only medium in-line transmission (about 12.5% at the wavelength of 800 nm), its infiltration prepared counterpart exhibits significantly improved optical properties. Infiltration sample 5M5Y5L (left) boasts much better transparency than 5M5Y5L-C (right) as observed in the inset picture in Fig. 5. Although microstructural examinations do not reveal any significant difference between the two specimens (unshown here), such dramatic enhancement in transmission property could be directly associated with the beneficial synergistic effect of triple doping[20] and improved doping homogeneity realized via infiltration.

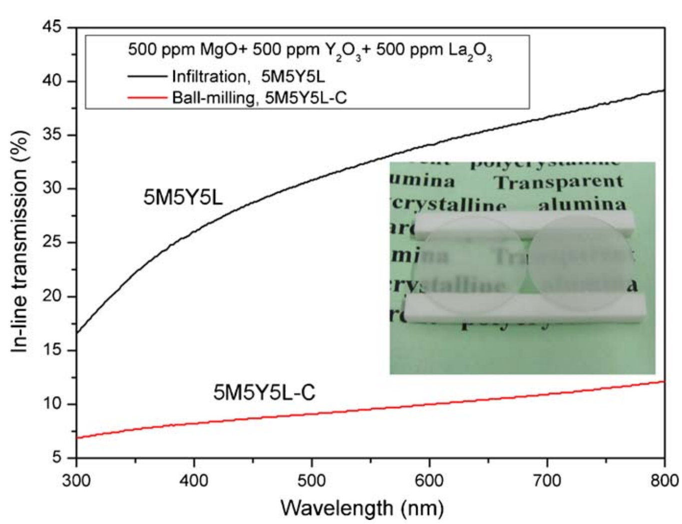

Fig. 5. In-line transmission and photograph of 5M5Y5L (left) and 5M5Y5L-C (right). The samples in the inset picture were placed 3 mm above the text.

The above optical properties data and the microstructural information give us convincing evidence that infiltration techniques could be employed to dope ceramics with a certain content of dopants, achieving enhanced microstructural uniformity and related improved transmission performance. It might be reasonably expected that such strategy could also be applied for other ceramic materials which requires delicate doping and stringent microstructural control to reach even improved properties.

4. Conclusions

Translucent alumina ceramics have been fabricated via incorporating $MgO/Y_2O_3/La_2O_3$ additives using infiltration and gelling technique and finally sintering in H_2 atmosphere. SEM and transmittance properties have confirmed infiltration technique leads to improved microstructural homogeneity and transmission properties over those processed with conventional ball-milling route. Triple doping via infiltration could result in much improved in-line transmission (36.3% at wavelength 800 nm for sample thickness of 0.75 mm). Our study reveals that infiltration technique is capable of uniformly incorporating dilute content of dopant into the matrix material and then achieving enhanced properties.

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