Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 321–326
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Novel fabrication of pressure-less sintering of translucent powder injection molded (PIM) alumina blocks

J.Y. Roh [a], J. Kwon [a], C.S. Lee [a,*], J.S. Choi [b]

[a] Division of Materials and Chemical Engineering, Hanyang Univ., Gyeonggi-do 426-791, Republic of Korea
[b] HT Co. Ltd., HBI 513, Hanyang Univ., Gyeonggi-do 426-791, Republic of Korea

Received 5 July 2010; received in revised form 30 July 2010; accepted 28 August 2010
Available online 25 September 2010

Abstract

A new method of fabricating translucent alumina brackets using powder injection molding (PIM) is reported. Alumina powder was mixed with MgO, La_2O_3, and Y_2O_3 to control grain size and porosity. The powders were mixed with a binder consisting of a mixture of paraffin wax and polyethylene in a 1:1 ratio to make feedstock for injection molding. The total amount of binder was limited to 14 wt% to minimize shrinkage and cracking after sintering. After injection molding, debinding was performed using the wicking method and samples were sintered in a vacuum at 1700 °C to achieve high density. Ultimately, translucent corundum was fabricated. The sintering additives resulted in a decrease in porosity and an improvement in translucency by promoting grain growth during pressure-less sintering. After sintering, Vickers hardness, bending strength, density, and transmittance of the fabricated parts were measured to show that those values were comparable to those of the commercially available dental brackets. Therefore, the translucent alumina block was successfully fabricated using PIM method to be potentially used as a dental bracket.

Keywords: Bracket; Powder injection molding; Sintering aids; Translucent alumina

1. Introduction

Most orthodontic appliances are made of metals, such as titanium, stainless steel, and nickel alloys, because these materials have good mechanical strength. However, metallic materials can be problematic due to their innate color and metallic allergy. Recently, the use of ceramic-based orthodontic appliances has been examined to overcome these issues. High-density, high-purity Al_2O_3 is being adopted in orthodontics because it has several beneficial properties, including excellent corrosion resistance, good biocompatibility, esthetic color, and good hardness characteristics. Single-crystal phase Al_2O_3 dental orthodontic appliances are superior to polycrystalline Al_2O_3 in terms of esthetics, discoloration, and customization. However, the use of single-crystal Al_2O_3 is limited because of its high processing cost.

This study is focused on α-Al_2O_3, and small amount of sintering additives were used as grain growth inhibitors. These additives are essential to achieve a very dense sintered body with a fine-grained microstructure [1]. Powder injection molding (PIM) technology was used to make polycrystalline alumina blocks and to reduce the machining sequences. PIM technology is an emerging technology for processing metal and ceramic parts. Mass production, cost-effective fabrication, and a near net-shape forming process for small, intricate, precise parts are possible using PIM [2]. The mixed powders were injection molded as blocks, which were debinded and sintered to obtain dense compacts of the desired material. Debinding can be done with thermal treatment, which extracts solvent or causes catalytic decomposition of the binder components. Moreover, while sintering at temperatures of 1600–1800 °C, the green body shrinks, producing a dense structure. Therefore, the sintering profile must be carefully controlled to avoid distortion and crack formation, caused by pores, resulted from extraction of the binder [3].

To be translucent, it is necessary to minimize residual pores in the ceramic body, as pores scatter light. Two methods have been used to eliminate residual pores in the fabrication of

* Corresponding author at: Rm. #312, 5th Engineering Building, Hanyang University, 1271 Sa 1-dong, Sangnok-gu, Ansan-si, Gyeonggi-do 426-791, Republic of Korea. Tel.: +82 31 400 5221; fax: +82 31 417 3701.
E-mail address: sunyonglee@hanyang.ac.kr (C.S. Lee).

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.09.011

translucent ceramics: one accelerates mass transport from particles to voids by sintering at high temperatures and by adding sintering additives and the other inhibits discontinuous grain growth, which can result in large grains with pores trapped inside. To achieve this, two sintering techniques have been developed to fabricate a translucent and dense ceramic body with a theoretical density: one technique uses high-temperature sintering with additives and the other uses pressure sintering, such as hot isostatic pressing (HIP) or hot pressing (HP), to promote diffusion. As HIP is not suitable for conventional mass production, a pressure-less sintering process using additives was studied. The fabrication of these translucent alumina blocks using PIM technology can be applied to the manufacture of orthodontic brackets.

There have been several methods introduced to produce translucent alumina blocks by controlling sintering profiles, sintering atmosphere, etc. [4–8]. In this study, unique way of fabricating translucent alumina block using PIM method was introduced and its effect of sintering additives on the translucency of alumina block was discussed.

2. Materials and methods

2.1. Powder preparation

The powders used in this study were high-purity AKP-50 alumina powder (α-Al_2O_3) with a particle size of 100–300 nm (Sumitomo Chemical, Tokyo, Japan). The amounts of magnesium oxide (MgO), yttrium (III) oxide (Y_2O_3), and lanthanum (III) oxide (La_2O_3) were varied as sintering agents to study their effects on translucency of the sintered alumina parts [9]. Table 1 shows the compositions of the ceramic parts.

The powders were mixed in ethanol using a stirring bar under infrared light for drying. Then, the powders were filtered through a 100-μm sieve. Paraffin wax and polyethylene were used as binders for feedstock fabrication. Paraffin wax softens as the temperature increases and melts at temperatures greater than 60 °C. As polyethylene softens at temperatures greater than 80 °C and becomes a liquid, a mortar and pestle were used to mix the powders to fabricate 50 g of feedstock at 120 °C. The percentage of binder to the total composition was approximately 14 wt%, which is the lowest possible percentage for mixing to minimize shrinkage during debinding and sintering, while enabling some mixing fluidity during injection molding. The paraffin wax gives fluidity to the feedstock during injection molding and the polyethylene consolidates the powders to maintain the shape of the feedstock. A 1:1 ratio of paraffin wax to polyethylene was found to be optimal. After mixing the binders and powders, injection molding was performed at a pressure of 50 bar at temperatures of 148–160 °C using Ministar VMP-43 molding equipment (ANC, Ansan, Korea).

Table 1
Powder preparation.

Sample	Additive composition	Sintering profile
A	0.25 wt% MgO	1
B	0.25 wt% MgO + 0.01 wt% La_2O_3 + 0.01 wt% Y_2O_3	
C	0.25 wt% MgO	2
D	0.25 wt% MgO + 0.01 wt% La_2O_3 + 0.01 wt% Y_2O_3	

2.2. Debinding

The injected parts must be debinded to achieve a high density of the desired material. To avoid large numbers of pores and cracks, the debinding process was carried out using the wicking method, and this was followed by the debinding profile, as shown in Fig. 1.

Wicking is a method to remove the binders after injection molding of the sample. Wicking provides Al_2O_3 bedding to surround the injection molded sample for heat treatment. As the surrounding temperature increases, the binders on the surface of the injection-molded sample melt and pores are formed. These pores enable elimination of binder inside the sample, as the powder bed is linked to the pores. Moreover, the powder bed absorbs binder vapors immediately, which prevents the pores from connecting and increasing in size [10].

2.3. Sintering

Before the main sintering, the debinded samples were presintered at 800 °C in air for 50 h. Then, high-temperature sintering was carried out using a vacuum furnace (TM-14-16; Thermonik, Tokyo, Japan) at 1700 °C for 2 h with a pressure of 2.0×10^{-5} Torr. During sintering, thermal treatment at 1300 °C to promote diffusion of MgO into the alumina grain boundaries was done to prevent the irregular grain growth. The sintering profile was adjusted to vary hold times at 1300 °C to examine the effects of MgO on grain growth, as shown in Fig. 2. The hold time for sintering profile #2 was 1 h longer than that of profile #1. 2 samples for each profile were prepared with total of 4 samples.

After sintering, the Vickers hardness and bending strength were measured using Vickers hardness tester and UTM (Universal Testing Machine), respectively. Additionally, density was measured by Archimedes' method and the structure

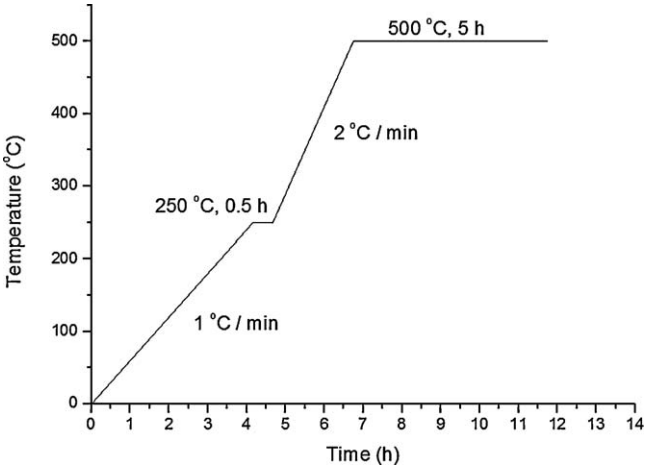

Fig. 1. Debinding profile.

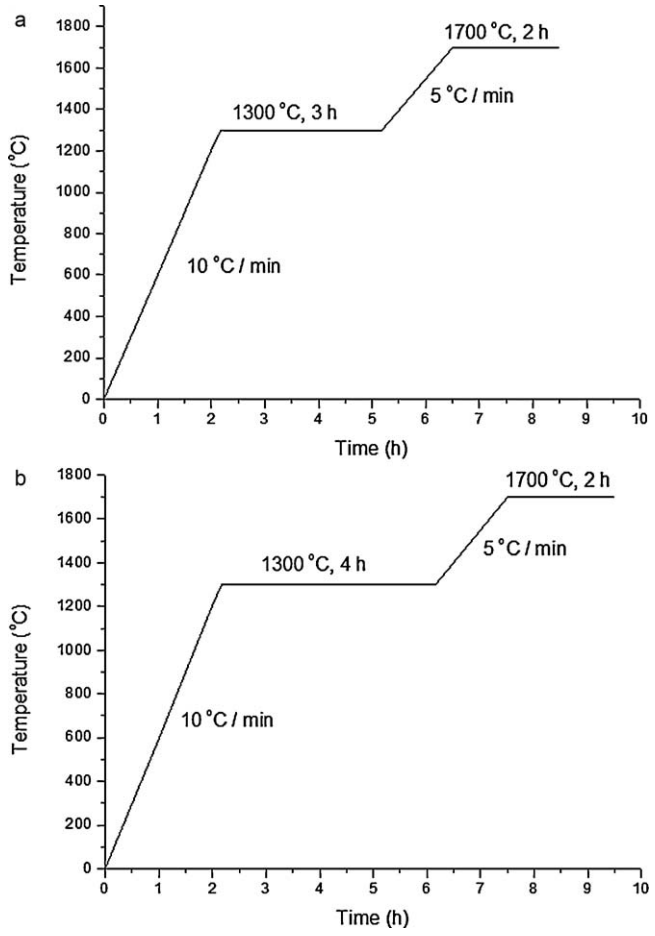

Fig. 2. (a) Sintering profiles #1 and (b) #2.

was observed using OM (Optical Microscopy) and XRD (X-ray Diffractometer).

2.4. Mechanical properties

2.4.1. Vickers hardness

To understand the effects of rare earth materials on the hardness of the alumina block, hardness of samples, A through D, were tested using Vickers hardness tester (MMT-7; Matsuzawa, Tokyo, Japan). The average of six H_v measurements at an applied load of 200 kgf was determined and the hardness values were compared to those for a commercial bracket (Clarity™; 3M Unitek, Monrovia, CA). To measure the Vickers hardness and translucency, all samples were cut to a thickness of 1.0 mm and both sides were polished for optical observation.

2.4.2. Bending strength

According to the ASTM C 1684-08, the 3-point bending strength of the samples was measured. The bending strength of the sample was calculated by Eq. (1)

$$\sigma_b = \frac{8PL}{\pi D} \quad (1)$$

Table 2
3-Point bending test condition.

Test condition	Actual
Type of the specimen	Cylindrical
Span length, L (mm)	20
Specimen diameter, D (mm)	2.5
Crosshead speed (mm/min)	0.2
Temperature (°C)	23 ± 1
Room humidity (%)	~60

where P = load at a given point on the load deflection curve (N), L = support span (mm), D = sample diameter (mm), and σ_b = bending strength (MPa). The test condition is shown in Table 2.

2.4.3. Density

Density of the sintered samples was calculated using Archimedes' method. It was compared to the theoretical density of Al_2O_3, 3.96 g/cm^3.

3. Results

3.1. Debinding result

After debinding following the debinding profile as shown in Fig. 1, the sample was white and uniformly porous, indicating that the most of the binder had been eliminated successfully, instead of being burned. Moreover, a number of small holes which were caused by extraction of the binder were observed.

3.2. Grain structure

Pre-sintering for 50 h at 800 °C is necessary for uniform grain growth of alumina [11,12] and it is efficient to eliminate pores in the samples. The sintering process was carried out after pre-sintering.

Fig. 3 shows the dramatic differences in the microstructure of parts sintered using profile #2 as shown in Fig. 2. Compared to the sample with 100% α-Al_2O_3, adding 0.05 wt% MgO in Al_2O_3 powders, the average grain size decreased from 15.0 to 5.6 μm. Therefore, sintering additives played a vital role in controlling grain size.

Fig. 4 shows an optical image of alumina blocks fabricated using different profiles specified in Table 1. The measured grain sizes of samples A and C were 5.04 and 6.48 μm, respectively, and those of samples B and D with MgO and rare earth materials additives were 12.43 and 19.98 μm, respectively. These observations indicated that increasing heat treatment time at 1300 °C by 1 h increased the grain size, as expected. Comparing the samples sintered based on profiles #1 and #2, sample D, which was sintered using profile #2, had grains with less porosity than those without rare earth additives. These observations indicated that a 1-h increase at 1300 °C with rare earth additives decreases porosity, while increasing grain size giving an optimized microstructure for translucency.

Fig. 5 presents a comparison of the translucency of the fabricated blocks. Samples with MgO additives had only

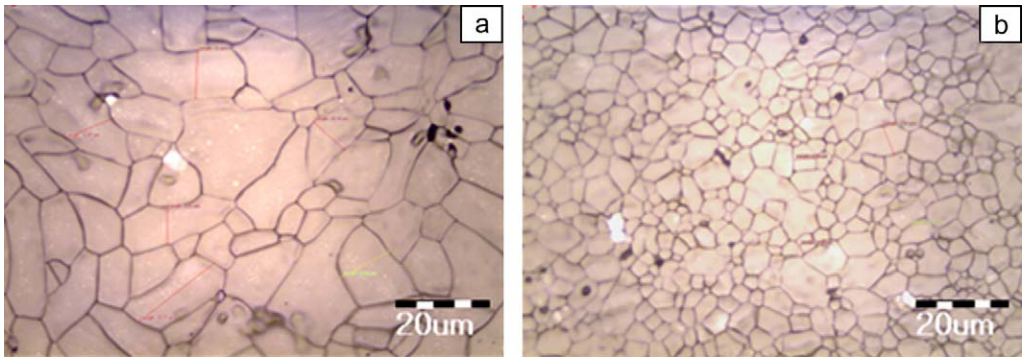

Fig. 3. Optical images of samples from profile #1: (a) 100% Al_2O_3, (b) 0.05 wt% MgO + 99.95 wt% Al_2O_3.

comparatively low translucency because decreasing grain size promotes light scattering. Accordingly, to decrease porosity and to improve the translucency, it is necessary to add both MgO and rare earth materials, as shown in samples B and D in Fig. 5. Samples B and D had the same composition, but sample D, which was sintered using profile #2, had larger grains due to the additional hour of sintering at 1300 °C and therefore, it was more translucent than that of sample C. Therefore, a 1-h increase at 1300 °C caused a dramatic increase in grain size, while reducing porosity, to give better translucency.

3.3. Mechanical properties

3.3.1. Vickers hardness

Table 3 shows the Vickers hardness values of four different samples in comparison with those of commercial products. Comparison of samples A and B, and samples C and D, indicated that the addition of the rare earth sintering additives improved the hardness in addition to the translucency. Finally, the Vickers hardness of a bracket which is commercially being used (Clarity^{TM}, 3M Unitek, USA) was determined to be 1981 H_v, which is comparable to the values for the alumina parts fabricated in this study.

3.3.2. Bending strength/density

The 3-point bending test was carried out using sample D which showed the highest translucency compared to the others and its bending strength was measured to be 264 MPa. This strength value is comparable to that of dental bracket (Clarity^{TM}) which is approximately 315 MPa [13].

Also, the density of the sample D was calculated using Archimedes' method. Compared to the theoretical density, the

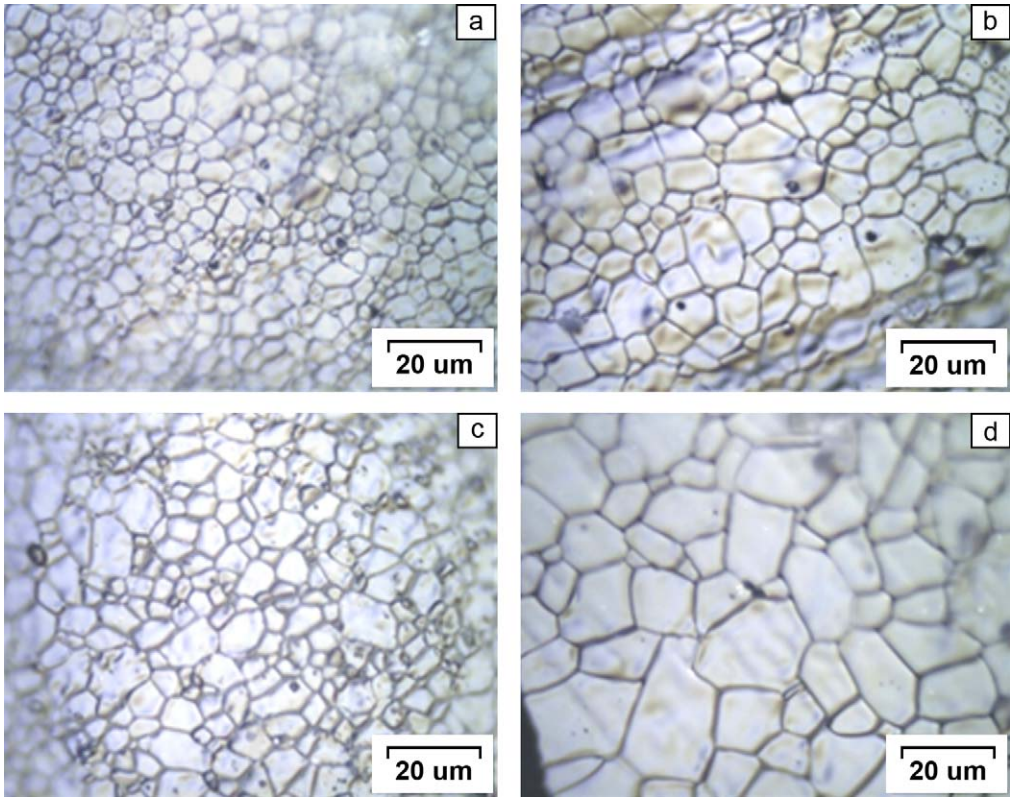

Fig. 4. Optical images of samples (a) A, (b) B, (c) C, and (d) D.

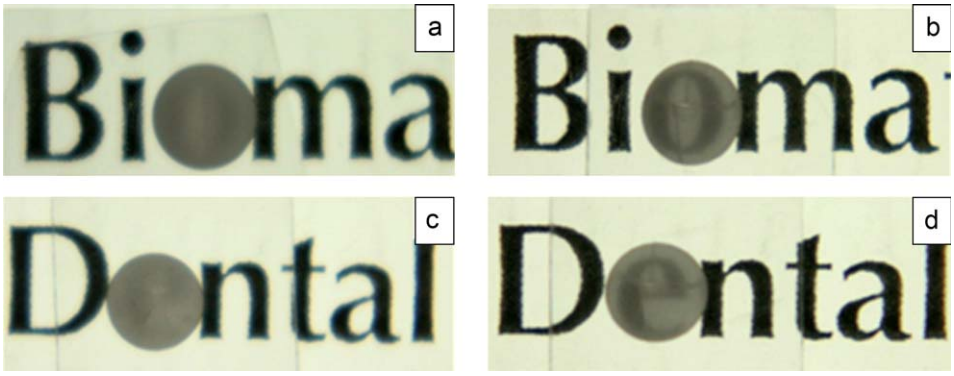

Fig. 5. Translucency comparison of samples (a) A, (b) B, (c) C, and (d) D.

Table 3
Vickers hardness of samples with different sintering profiles.

Sample	A	B	C	D	Clarity™
Vickers hardness (H_v)	1924	1959	1846	1903	1981

Table 4
Mechanical properties of the sample D and commercial bracket.

	Sample D	Clarity™
Vickers hardness (H_v)	1903	1981
Bending strength (MPa)	264	315
Density (g/cm^3)	99.50	99.90

density of the sample D was measured to be 99.50% which is close to full density. The mechanical properties of the sample D are shown in Table 4. Therefore, translucent alumina bracket using PIM method was successful to achieve high density and good mechanical properties which are comparable to those for commercially available dental brackets.

4. Discussion

In this study, the role of additives played a vital role after PIM process; MgO can be added only up to 0.25 wt% because too much MgO can be evaporated during sintering steps, contaminating the furnace and resulting in an increase in porosity [14]. The effects of MgO on increasing porosity were confirmed by comparing the microstructure of sintered pure alumina with an alumina sample with 0.05 wt% MgO, as shown in Fig. 3.

Fig. 6 shows the XRD result of the sample D which is the optimized translucent sample. As shown in the figure, the corundum phase was detected mainly. The density and the strength of corundum increase with the amount of additive. The increase in the strength is related to a decrease in the grain size which can be achieved by introducing MgO.

In addition, the amount of La_2O_3 additives is limited to 0.01 wt% because excessive La_2O_3 can adversely influence the thermal shock resistance and anticorrosion properties of alkali

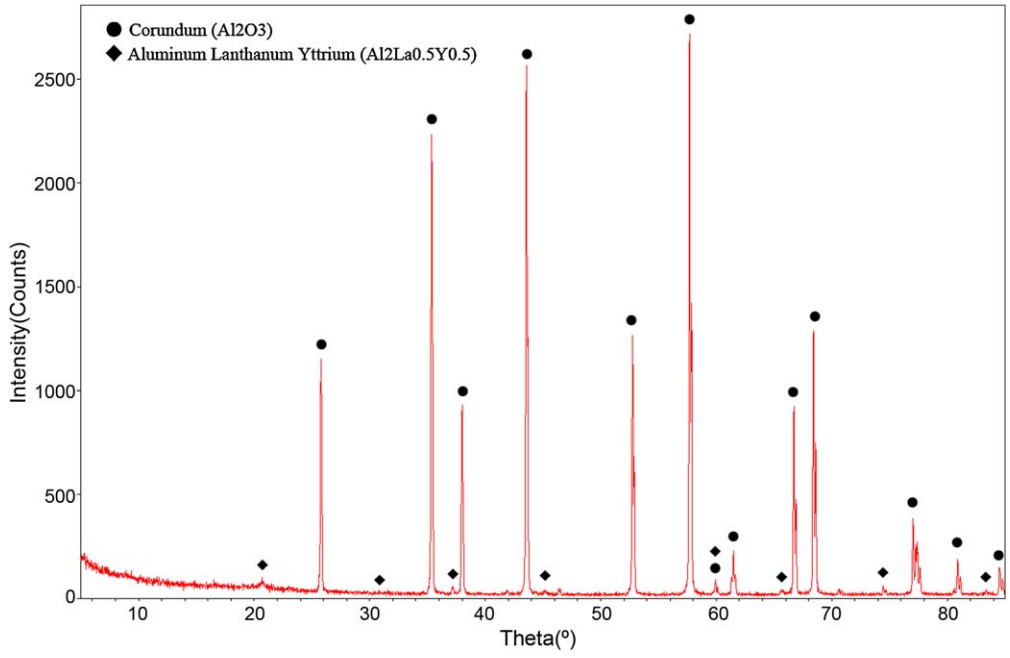

Fig. 6. XRD results of the sample D.

metals in the translucent alumina. Moreover, Y_2O_3 is limited to 0.5 wt% because too much Y_2O_3 can result in excessive acceleration of grain growth initially, making the grain growth irregular [14].

White et al. [15] reported that the shrinkage in total volume and spheroidization of grains occur during these reactions. Therefore, adding MgO prevents rapid coarsening, which can increase closed pores in the sample, and enhances the mechanical properties, while improving densification. However, the excess MgO can be volatilized at high temperatures, creating pores. Gradual sintering is crucial to minimize pore formation.

Adding rare earth materials can improve creep resistance. Rare earth materials, such as La_2O_3 and Y_2O_3, are located at the triple points of alumina grains through the sintering process. These rare earth materials prevent the excessive growth of alumina grains, while protecting against slip occurrence, resulting in improved mechanical properties [6]. Table 2 shows that the samples with rare earth additives are harder than those without rare earth additives. Moreover, as shown in Table 4, mechanical properties of the sample D, which showed the highest translucency, were comparable to those of the brackets, indicating that PIM fabrication of alumina bracket was successful.

5. Conclusion

Powder injection molding (PIM) was used to fabricate translucent alumina blocks successfully for use in dental bracket manufacture. Binders were mixed with the alumina powder to make the powders flow during injection molding and debinding was performed successfully without discoloration. The effects of adding sintering additives, such as rare earth materials and MgO, on the microstructure and translucency of the corundum were discussed. MgO, La_2O_3, and Y_2O_3 were used to eliminate pores and to accelerate the uniform growth of the alumina grains. Due to the addition of sintering additives, the sintering temperature was lowered to 1700 °C. An average grain size of 20 μm and improved translucency were obtained by adding rare earth materials with a 1-h increase in sintering at 1300 °C. Also, comparable mechanical properties and density of commercially available dental brackets were obtained. Therefore, it is possible to produce translucent dental brackets using the powder injection molding method, which is a simple and cost-effective process.

Acknowledgements

This study was supported by Small & Medium Business Administration, Korea (S0807212-E0815610-10100013) and Mid-career Researcher Program through NRF grant funded by the MEST (No. 2010-0000450).

The authors thank Shinhan Diamond Industries for supplying the powder injection molding equipment and Mr. Sung-Dong Woo and Mr. Jung-Hwan Park from HT Ltd. for supplying bracket samples.

References

[1] R. Supati, N.H. Loh, K.A. Khor, S.B. Tor, Mixing and characterization of feedstock for powder injection molding, Mater. Lett. 46 (2000) 109–114.
[2] L.L. Hench, J. Wilson, An Introduction to Bioceramics, Advanced Series in Ceramics 1, World Scientific, Singapore, 1993.
[3] L. Merz, S. Rath, V. Piotter, R. Ruprecht, J. Ritzhaupt-Kleissl, J. Hausselt, Feedstock development for micro powder injection molding, Microsyst. Technol. 8 (2002) 129–132.
[4] H.P. Cahoon, C.J. Christensen, Sintering and grain growth of alpha-alumina, JACerS 39 (2006) 337–344.
[5] R.L. Coble, Sintering alumina: effect of atmosphere, JACerS 45 (2006) 123–127.
[6] I. Ganesh, S. Bhattacharjee, B.P. Saha, R. Johnson, Y.R. Mahajan, A new sintering aid for magnesium aluminate spinel, Ceram. Int. 27 (2001) 773–779.
[7] C.W. Seo, S. Kim, S.J. Ko, S.H. Kim, K.Y. Jo, The synthesis and hydraulic properties of Calcium Sulfo Aluminate (CSA) derived from secondary refining slag, J. Kor. Inst. Met. Mater. 46 (7) (2008) 437–442.
[8] D. Lee, J. Song, N. Park, I. Shon, Properties and fabrication of 5 $Cu_{0.6}Fe_{0.4}$–Al_2O_3 composite by high frequency induction heated sintering, J. Kor. Inst. Met. Mater. 47 (11) (2009) 754–758.
[9] M. Kaneno, T. Kajihara, Polycrystalline translucent alumina sintered body, a method for producing the same and a high pressure vapor discharge lamp obtained by using said sintered body, US Patent 4373030, 1985.
[10] W.J. Tseng, C.-K. Hsu, Cracking defect and porosity evolution during thermal debinding in ceramic injection moldings, Ceram. Int. 25 (1999) 461–466.
[11] H. Yoshida, Y. Ikuhara, T. Sakuma, High-temperature creep resistance in rare earth-doped, fine-grained Al_2O_3, J. Mater. Res. 13 (1997) 2597.
[12] D.S. Kim, J. Lee, R.J. Sung, S.W. Kim, H.S. Kim, J.S. Park, Improvement of translucency in Al_2O_3 ceramics by two-step sintering technique, J. Eur. Ceram. Soc. 27 (2007) 3629–3632.
[13] A. Podesta, R. Miller, N. Heinig, Orthodontic perspectives, 3M Unitek 14 (1) (2007) 11.
[14] K. Kobayashi, M. Kaneno, Translucent alumina containing magnesia yttria and lanthanum oxide, US Patent 3905845, 1975.
[15] J. White, Review of high-temperature materials and their repercussions of the future of refractories, Bol. Soc. Esp. Soc. 11 (1972) 11–31.