Journal of the Korean Ceramic Society
Vol. 40, No. 12, pp. 1159~1164, 2003.

Processing of Porous Ceramics with a Cellular Structure Using Polymer Beads

Jung-Soo Ha and Chang-Sam Kim*,†

School of Advanced Materials Engineering, Andong National University, Kyungbuk 760-749, Korea
**Multifunctional Ceramics Research Center, Korea Institute of Science and Technology, Seoul 130-650, Korea*
(Received August 1, 2003; Accepted September 16, 2003)

ABSTRACT

Two processing routes (i.e., the gel casting and polymer preform routes) using polymer beads were studied to fabricate porous ceramics with a cellular structure. The gel casting route, comprising the gel casting of a ceramic slurry mixed with polymer beads, was found to be inadequate to produce porous ceramic bodies with a interconnected pore structure, due to complete coating of the slurry on the polymer beads, which left just isolated pores in the final sintered bodies. The polymer preform route, involving the infiltration of a polymer beads preform with the ceramic slurry, successfully produced porous ceramics with a highly interconnected network of spherical pores. The pore size of 250–300 μm was demonstrated and the porosity ranged from 82 to 86%. This process is advantageous to control the pore size because it is determined by the sizes of polymer beads used. Another feature is the avoidance of hollow skeleton, giving a high strength.

Key words **: *Porous ceramics, Cellular structure, Polymer beads, Ceramic slurry, Gel casting, Infiltration, Polymer preform***

1. Introduction

Porous ceramics have been found to be essential for a variety of technical applications such as thermal insulators, filters, catalyst supports, gas sensors, and bone graft substitutes.[1] The pore size and shape, porosity, and mechanical properties should be tailored to meet requirements for each application. For bone graft substitutes, large interconnected pores with a minimum size of 100 μm are required for tissue ingrowth and vascularisation.[2,3] Such a large pore structure (i.e., a cellular structure) inevitably degrades the strength of the materials. Therefore the precise control of pore size and shape, and porosity is important in attaining optimum strength.

As the processing methods for porous ceramics with a cellular structure, there are two most common methods, which are the replication of polymer foams by impregnation with ceramic slurries (i.e., the *polymeric-sponge method*), and the foaming of ceramic slurries (i.e., the *foaming method*).[4-6] The first method uses a polyurethane foam, which is immersed into a ceramic slurry. After removing the excess slurry, the resultant structure is fired to burn out the polyurethane foam and then sintered to get a rigid porous ceramic replicating the polymer foam. The main disadvantage of this method is large flaws and hollow skeleton due to polymer elimination, resulting in inferior mechanical properties.[5] The second method involves the evolution of a gaseous species in a ceramic slurry to foam it. Foams are usually produced either by mechanical frothing or by the injection of gases, and are stabilized by a surfactant. A foamed slurry is set, dried, and fired to leave a porous ceramic. For setting the slurry, various ways can be used, such as drying or freeze-drying of the solvent, intrinsically gelling compositions (e.g., sol-gel), the addition of gelling agents (e.g., cellulose derivatives or alginates), and the in situ polymerization of monomers.[5,6] This method is a simple and inexpensive route to make porous ceramics with dense skeleton, giving optimized strength. However, the main disadvantage is the difficulty in controlling the pore size due to the formation of pores by the gas foaming.

In the present work, two processing routes using polymer beads were studied with an aim to develop a fabrication process for porous ceramics with a cellular structure, which can provide controlled pore sizes as well as optimum strength. The first route, named the *gel casting route*, comprised the gel casting of a ceramic slurry mixed with polymer beads with selected sizes. The second route, named the *polymer preform route*, comprised the infiltration of a ceramic slurry into a polymer preform made of the polymer beads. The results of these approaches are presented.

Corresponding author : Chang-Sam Kim
E-mail : cskim@kist.re.kr
Tel : +82-2-958-5483 Fax : +82-2-958-5489

2. Experimental Procedure

2.1. Gel Casting Route

Gel casting[7,8] is a novel forming technique originally

developed to produce dense bodies with complex shapes. In this technique, a ceramic slurry containing organic monomers is cast into a mold and set by the in situ polymerization of the monomers. Compared with conventional ceramic forming methods, the advantages of gel casting are smaller amounts of organic binders, high strength of green bodies allowing superior machinability, and less firing shrinkages due to high green densities. Although both aqueous and nonaqueous solvents can be used, aqueous systems are preferred because the conventional slip casting technique can be utilized and environmental pollution attributed to the use of organic solvents can be avoided. In the aqueous system, acrylamide (AM) and methylenebisacrylamide (MBAM) are normally used to make monomer solutions.

For the preparation of ceramic slurries, an α-Al_2O_3 powder (AKP-30, Sumitomo Chemical Co., Japan) with a mean particle size of 0.3 μm was used and dispersed in aqueous monomer solutions with Darvan C (R.T. Vanderbilt Co., Inc., Norwalk, CT, USA). The monomer solutions were prepared using AM, $C_2H_3CONH_2$ and MBAM, $(C_2H_3CONH)_2CH_2$. For the free-radical polymerization reaction of the monomers, ammonium persulfate, $(NH_4)_2S_2O_8$ and N,N,N',N'-tetramethylethylenediamine (TEMED), $C_6H_{16}N_2$ were used as an initiator and a catalyst, respectively. All these chemicals were obtained from Sigma Chemical Co., St. Louis, MO, USA. As the pore forming agent, polymethylmethacrylate (PMMA) beads (IH830, LG Chemical Co., Korea) with average diameter of 300 μm were used. A scanning electron micrograph showing their spherical shapes and sizes is given in Fig. 1.

The monomers were dissolved in deionized water to make the premix solution with a composition of 14.0 wt% AM, 0.6 wt% MBAM, and 85.4 wt% water, which is one of the representative compositions of monomer solution suggested in the literature.[8] Ammonium persulfate was also dissolved in deionized water to make the initiator solution with a concentration of 1 wt%. The slurries were prepared by ball-milling the alumina powder in the monomer solution with

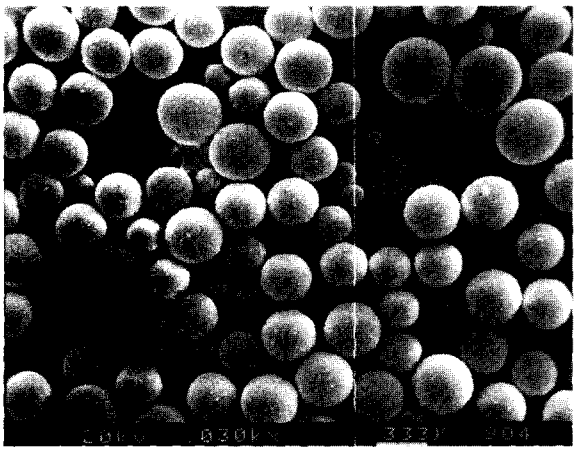


Fig. 1. Scanning electron micrograph of the PMMA beads used, showing their size and shape.

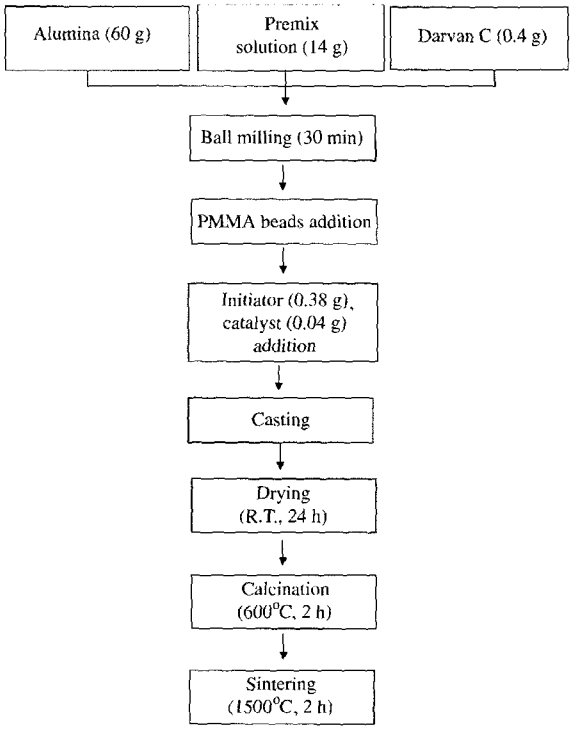


Fig. 2. Flow diagram of the gel casting route.

Darvan C for 30 min, and then the PMMA beads were mixed into the slurries by stirring for 3 min. Subsequently the initiator solution and the catalyst were added to induce setting of the slurries. The addition of the initiator solution was varied to be 10, 15, and 20 wt%. The slurries were poured into paper cups and their temperature changes were measured with time. After complete setting, the demolded bodies were dried at room temperature for 24 h and heated to 600°C with 1°C/min in air using an electric furnace to burn out the PMMA beads. The resulting bodies were sintered at 1500°C for 2 h in air. Fig. 2 shows the flow diagram of the experimental procedure. The sintered samples were cut and their microstructures were observed by a Scanning Electron Microscope (SEM).

2.2. Polymer Preform Route

This route was devised in order to increase the interconnection between pores, in which polymer beads which will form pores were warm-pressed to form a preform, and it was infiltrated with a ceramic slurry. The characteristics of this route are the utilization of the conventional slip casting technique, and the ease in controlling the pore size with the avoidance of hollow skeleton unlike the foaming and polymeric-sponge methods.

The same PMMA beads as in the gel casting route were used. Figs. 3 and 4 show the flow diagram of the experimental procedure and a schematic representation of the process, respectively. A mold with diameter of 16 mm was heated to 150°C with a rubber heater. The PMMA beads were loaded into the mold and uniaxially pressed to give green densities

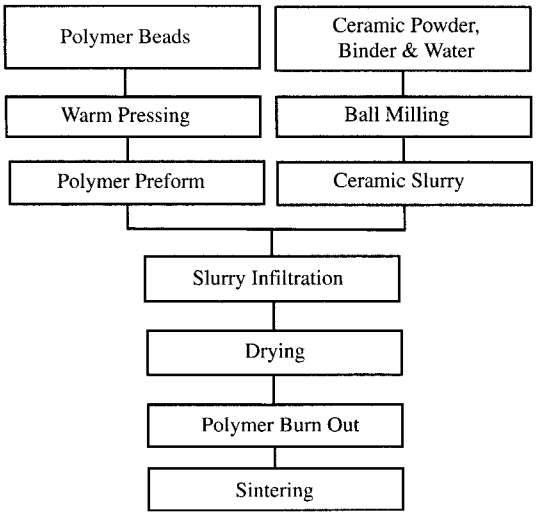


Fig. 3. Flow diagram of the polymer preform route.

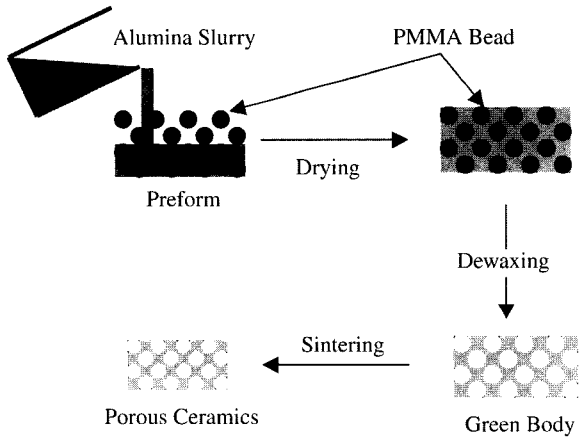


Fig. 4. Schematic of the process of polymer preform route.

of 65–76%. Slurries containing 70 wt% alumina were prepared using the same alumina powder as in the gel casting route by ball milling with a mixture of water and ethyl alcohol in a polyethylene bottle for 4 h. Darvan C and PVA were used as a dispersant and a binder, respectively. The addition of alcohol was to increase the wettability of the slurries on the surfaces of the PMMA preform. The addition was varied to be 0, 10, 20, 30, 50, and 100 wt% in order to find the optimum amount by measuring the wetting angles. The PMMA preforms were loaded into an apparatus as schematically shown in Fig. 5 and infiltrated with the slurries. The infiltrated preforms were dried at 70°C for 24 h and heated to 600°C at 1°C/min to burn out the PMMA and binder. Finally they were sintered at 1500, 1550, or 1600°C.

The dimension and weight of the sintered samples were measured to determine their firing shrinkages and relative densities by using the following equations.

Firing shrinkage = $(L_0 - L)/L_0$
L_0: the length of PMMA preform
L : the length of sintered body,

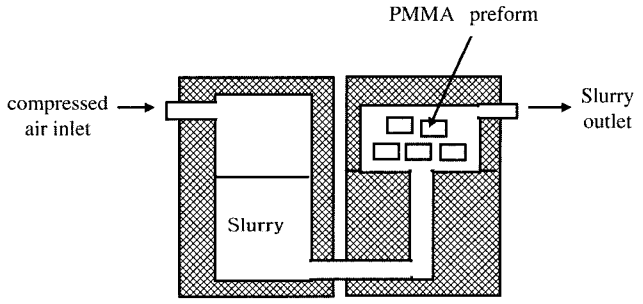


Fig. 5. Schematic of the apparatus for infiltrating a ceramic slurry into the polymer preform.

$Ds = \{W/(A \times H \times 3.99)\} \times 100$
Ds : the relative density of sintered body (%)
W : the weight of sintered body
A : the average value of the areas of bottom and top surfaces (cm^2)
H : the height of sintered body (cm)

The compressive strength of the sintered samples was measured with five specimens for each sintering temperature. Teflon plates with a thickness 0.5 mm were placed onto the top and bottom surfaces for the tests. Fracture loads were measured at a crosshead speed 1 mm/min, and the compressive strength was determined using the following equation.

$S = W/A$
S : compressive strength (MPa)
W : fracture load (N)
A : the average value of the areas of bottom and top surfaces (mm^2)

SEM analyses were performed on the PMMA preforms to observe the exterior and interior features and also on the sintered bodies for fracture and polished surfaces.

3. Results and Discussion

3.1. Gel Casting Route

According to the literature on the gel casting of alumina,[8] the polymerization reaction of the slurries begins with 1 wt% addition of the initiator solution, and the slurry temperature rises to about 70°C due to the exothermic nature of the reaction. However, in the present study, the polymerization reaction was not initiated by the same amount probably due to the presence of PMMA beads in the slurries, amounting 60 vol%. Therefore the addition of the initiator solution was increased to 10, 15 or 20 wt%, and the temperature change of the slurries was measured and the results are given in Fig. 6. With 10 wt% addition, the temperature was about 30°C for 8 min lapse, but it decreased thereafter. The slurry surface was not set in this case. With 15 wt% addition, the slurry temperature rose to the maximum of 40°C for 12 min lapse, and its surface was set. With 20 wt% addi-

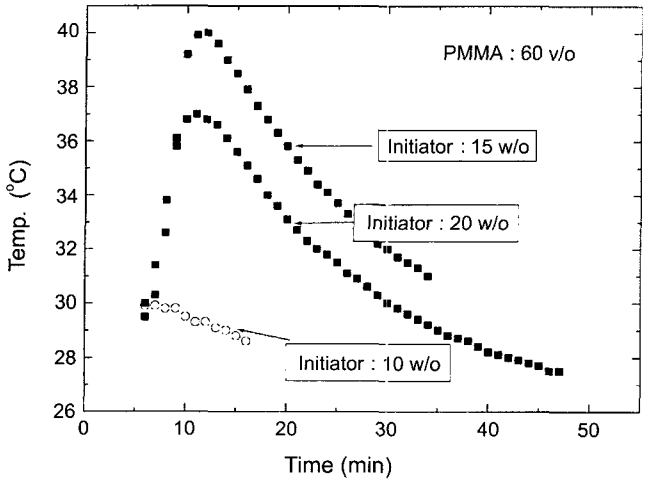


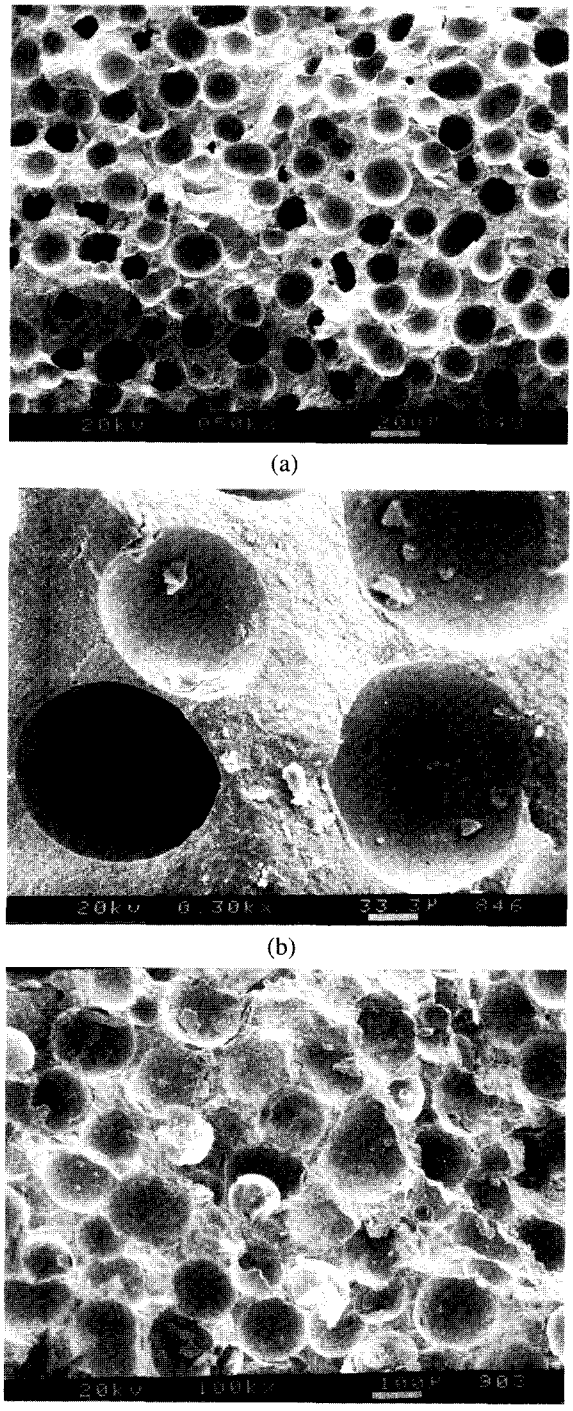
Fig. 6. Change of the temperature of the slurries containing 60 vol% PMMA beads as a function of time.

tion, the temperature rose up to 37°C, which was lower than in the case of 15 wt% addition.

The green bodies containing 30 and 60 vol% PMMA beads were calcined at 600°C and then sintered at 1500°C for 2 h. Fig. 7 shows the SEM observations of these samples. It can be seen that in the sintered sample with 30 vol% PMMA beads, the pores formed with maintaining the originally spherical shapes of the beads and their sizes were between 100 and 300 μm. They were mostly closed pores with no interconnection. The sample with 60 vol% beads also showed mostly isolated pores and thus no permeability. This is because the setting of the alumina slurries occurred with completely coating the PMMA beads. It seems that the achievement of interconnection between pores will be still difficult even though the addition of PMMA beads is increased more.

3.2. Polymer Preform Route

Fig. 8 shows the SEM observation of the polymer preforms prepared by uniaxially warm-pressing PMMA beads in a steel mold at 150°C. It can be seen that the spherical beads were interconnected maintaining the original shape with an average diameter of 300 μm. The porosity was controlled by controlling the volumes of formed preforms. The interconnection sizes were dependent on the sizes of adjacent beads. Therefore it is suggested that the size uniformity of the PMMA beads significantly affect the interconnection sizes as well as the pore sizes. Fig. 9 shows the fracture surface of a preform reheated at 190°C after warm pressing, observed by SEM. Before the heat treatment, the beads were bonded weakly and the fracture surfaces were like smooth plane. However, after the heat treatment, it was rough and had more surface area. This is because the strong bonds between beads caused the fracture to occur inside the beads rather than at the interface between them. Due to such strong bonds, the original shapes of heat-treated preforms were not damaged by infiltrating the slurries at a high pressure or by pressing them



(a)

(b)

(c)

Fig. 7. Scanning electron micrographs of porous alumina bodies produced by the gel casting route with porosity of (a) and (b) 30%, and (c) 60%.

mechanically.

Fig. 10 is the result of the contact angle measurements of alumina slurries on PMMA as a function of the addition of ethyl alcohol. The angles abruptly decreased with increasing the alcohol addition, indicating the wettability increased greatly. The alcohol addition affects not only the slurry infil-

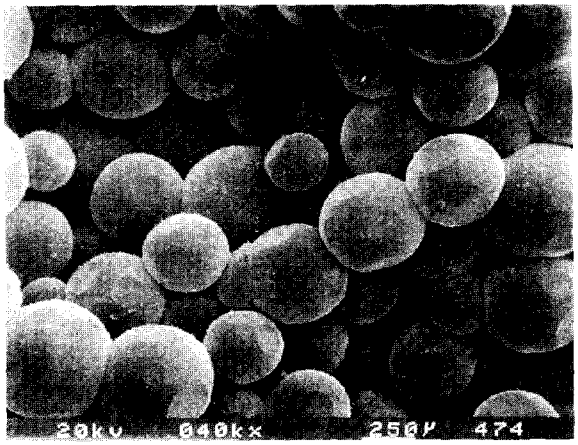


Fig. 8. Scanning electron micrograph of the PMMA preform prepared by warm pressing.

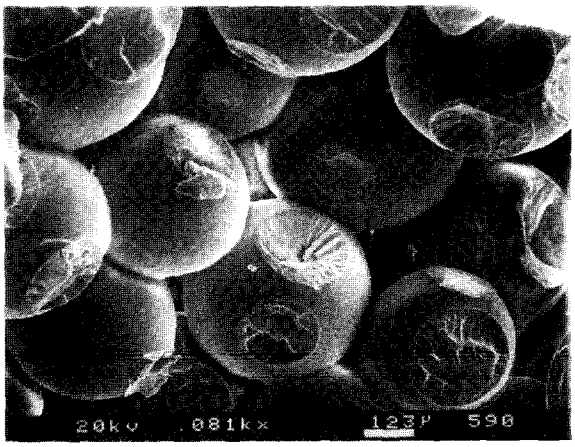


Fig. 9. Fracture surface of the PMMA preform heat-treated after warm pressing.

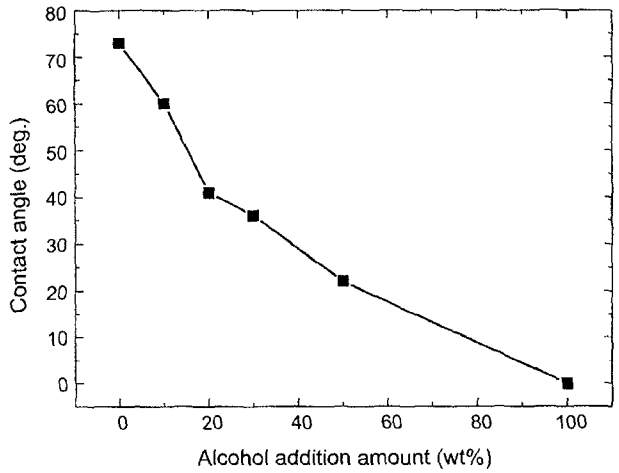


Fig. 10. Change of the contact angle of alumina slurry on PMMA plates as a function of the amount of ethyl alcohol.

trating behavior but also shape maintenance after the infiltration and crack formation. Hence a minimum addition allowing a proper infiltrating property is required and the optimum amount for the alumina slurries were 10 to 20 wt%.

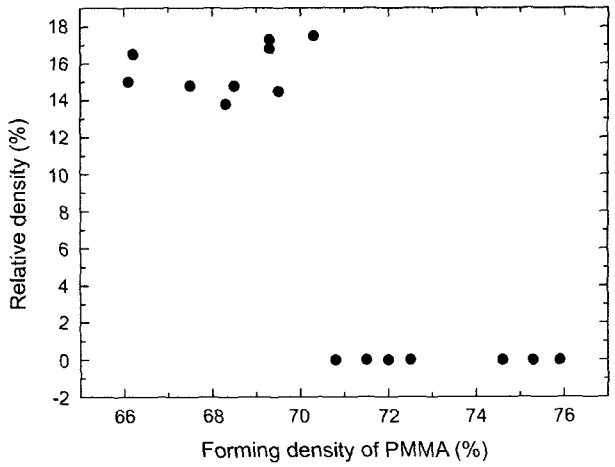


Fig. 11. Relative density of the sintered body as a function of the forming density of the PMMA preform.

The relative densities of porous sintered bodies are given in Fig. 11 as a function of the relative densities of preforms. When the preform densities were 66 to 70%, the densities of sintered bodies were 14 to 18%, giving total porosities of 82 to 86%. When the preform densities were 71% or higher, sintered bodies could not be produced because the bodies after calcination were so weak that they collapsed by itself or when picked up by hand. In the preforms infiltrated with alumina slurries, the difference in the thermal expansion coefficients of two components are very large. The expansion coefficient of alumina is 7×10^{-6}/°C and that of PMMA is 90×10^{-6}/°C. Thus, when the relative density of a PMMA preform are high, the thermal expansion of PMMA becomes so large that it causes the alumina component forming skeletons to collapse during calcination. Therefore, the preforms used in the present study were fabricated with controlling their relative densities to be about 70% constantly.

The relative densities, firing shrinkages, and compressive strengths of porous sintered bodies were investigated with varying the sintering temperature. The relative densities were found to be 18% with no change with the sintering temperature. They seemed to just vary with the compacted densities of the PMMA preforms. The shrinkages were about 17% irrespective of the sintering temperature. As shown in Fig. 12, the compressive strength was 3.4 MPa when sintered at 1550°C for 2 h. It was higher than those obtained for 1500°C (3.1 MPa) and 1600°C (2.5 MPa), indicating the sintering temperature 1550°C was optimum. This strength is higher than those of commercial products produced using the polymeric-sponge method, which are reportedly no greater than 0.8 MPa.[9]

Fig. 13 shows the SEM observations of the fracture and polished surfaces of porous sintered bodies. It can be seen that the PMMA beads were removed by undergoing the calcination and sintering steps, leaving spherical pores. As expected from the interconnected structure of the preforms, the structure of sintered bodies consisted of large spherical

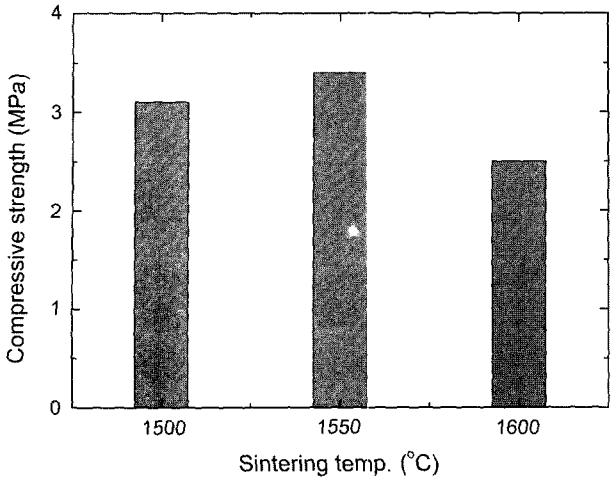
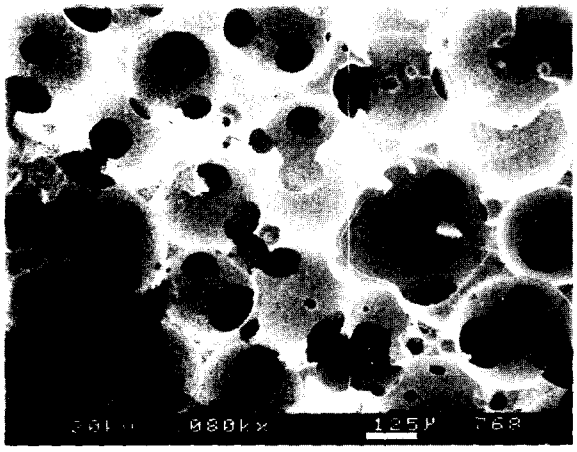
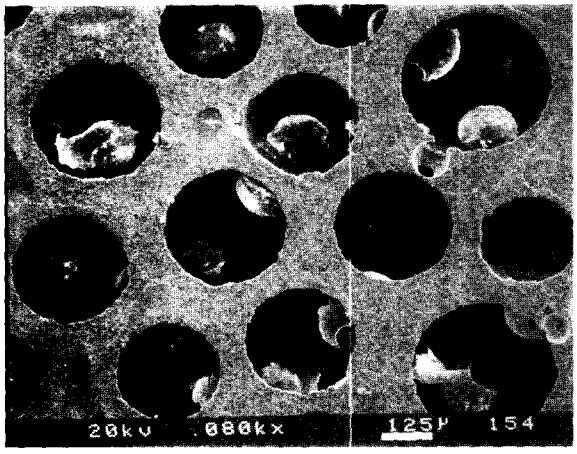


Fig. 12. Variation of the compressive strength of the ceramic porous body with increasing the sintering temperature.



(a)



(b)

Fig. 13. Scanning electron micrographs of the sintered body produced by the polymer preform route; (a) fracture surface and (b) polished cross-section.

pores (250–300 μm in diameter) and so called windows which are the interconnections between pores. The number of windows observed for one large pore on fracture surfaces was about 8 to 12 although it varied with the pore size. The overall structural feature was similar to the cellular structure of porous bodies produced by the foaming method.

4. Conclusions

The gel casting route was found to be inadequate to produce porous ceramic bodies with a interconnected pore structure, due to complete coating of the alumina slurries on the PMMA beads, which left just isolated pores in the final sintered bodies. The polymer preform route successfully produced porous ceramics with interconnected pores, in which the pore size can be controlled as desired by controlling the sizes of polymer beads used. It was demonstrated that the porosity could be controlled to range from 82 to 86%. The characteristics of this process are the use of the conventional ceramic slurry technique to make porous bodies of a variety of materials, and the ease in controlling the pore size, and the avoidance of hollow skeleton giving high strength.

REFERENCES

1. K. Ishizaki, S. Komarneni, and M. Nanko, "Porous Materials : Process Technology and Applications," p. 181, Kluwer Academic Publishers, Dordrecht/Boston/London, 1998.
2. L. L. Hench, "Bioceramics," *J. Am. Ceram. Soc.*, **81** [7] 1705-28 (1998).
3. A. R. Boccaccini, J. A. Roether, and L. L. Hench, "A Composite Approach to Tissue Engineering," *Ceram. Eng. Sci. Proc.*, **23** [4] 805-16 (2002).
4. J. Saggio-Woyansky, C. E. Scott, and W. P. Minnear, "Processing of Porous Ceramics," *Am. Ceram. Soc. Bull.*, **71** [11] 1674-82 (1992).
5. P. Sepulveda, "Gelcasting Foams for Porous Ceramics," *Am. Ceram. Soc. Bull.*, **76** [10] 61-5 (1997).
6. P. Sepulveda and J. G. P. Binner, "Processing of Cellular Ceramics by Foaming and in Situ Polymerisation of Organic Monomers," *J. Eur. Ceram. Soc.*, **19** 2059-66 (1999).
7. O. O. Omatete, M. A. Janney, R. A. Strehlow, "Gelcasting-a New Ceramic Forming Process," *Am. Ceram. Soc. Bull.*, **70** [10] 1641-49 (1991).
8. A. C. Young, O. O. Omatete, M. A. Janney, P. A. Menchhofer, "Gelcasting of Alumina," *J. Am. Ceram. Soc.*, **74** [3] 612-18 (1991).
9. F. F. Lange and K. T. Miller, "Open-cell, Low Density Ceramics Fabricated from Reticulated Polymer Substrates," *J. Am. Ceram. Soc.*, **70** [4] 827-31 (1987).