[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 8, No. 7 (1998)

Fabrication of Glass-Ceramic Composites by Selective Laser Sintering of Alumina-Glass Powder Blends

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알루미나와 글래스 분말의 선택적 레이저 소결에 의한 글래스-세라믹 복합재료의 제조

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(1998년 2월 9일 받음, 1998년 5월 13일 최종수정본 받음)

초 록 단사정 HBO_2 분말을 무기접착제로 이용하여 선택적 레이저 소결 기술을 적용시켜 알루미나-글래스 복합재료를 제조하였다. 만들어진 green SLS 시험편을 여러 온도에서 열처리하여 글래스-세라믹 복합재료를 얻었다. 글래스의 양이 많을수록 복합재료는 높은 밀도와 높은 굽힘강도를 보여주었다. 열처리 온도 900℃에서 복합재료는 최대 밀도와 최대 강도를 나타낸다. 이것은 글래스의 낮은 점도로 인한 좋은 유동성 때문에 글래스의 재분배가 이루어졌기에 가능하다고 생각되어진다. 그리고 기공이 많은 열처리한 SLS 시험편에 콜로이드 실리카를 주입시켜 치밀화시켰다.

Abstract Selective Laser Sintering (SLS) has been employed to fabricate alumina-glass composites using monoclinic HBO_2 as an inorganic binder. Subsequent post-thermal processing of green SLS parts at various temperatures yielded glass-ceramic composites. Composites with higher glass contents showed higher density and bend strength for all firing temperatures than those with lower glass contents. For a firing temperature of 900℃, the glass redistribution arising from a better viscous flow of the glass resulted in all of the composites exhibiting maximum density and bend strength. In addition, further densification was made through infiltration of colloidal silica into the fired, porous samples.

1. Introduction

Solid Freeform Fabrication (SFF) is an advanced manufacturing technology which generates geometrical objects directly from a three-dimensional computer image without part-specific tooling or human intervention.[1] Selective Laser Sintering (SLS) is a form of SFF and employs a focused laser beam which is controlled by a CAD data base to selectively scan a powder bed and bind loose powder, so as to make a thin layer of bonded powder. The sintered layer is lowered from the sintering plane and a new layer of the powder is spread across the surface by a counter-rotating roller. The laser scans again, resulting in sintering of the powder particles, and bonding the present layer to the underlying previous layer. The desired object is generated by laying down a number of such layers and successively sintering them.[2] The primary advantage of the SLS process is the flexibility of selecting the material systems compared to other SFF techniques.[3]

There are two kinds of intermediate binders for SLS of ceramic powders. One is to use an inorganic binder and the other is to use an organic binder, such as the Poly Methylmethacrylate (PMMA). Ammonium dihydrogen phosphate was employed as an inorganic binder for the SLS of alumina.[4] Ammonium dihydrogen phosphate has a low melting point (190℃) and forms a glassy phase around alumina particles under the laser beam. During the subsequent firing step of green SLS parts, the ammonium phosphate binder reacts with the alumina, resulting in aluminum orthophosphate ($AlPO_4$). Alumium has recently been used as a binder for the SLS of alumina.[5] Aluminum melts completely or partially under the laser beam and binds alumina particles. The subsequent heating step of the green part in air oxidizes the aluminum to alumina. Polymers have been used as an organic binder to fabricate green SLS ceramic parts.[6] The dimensional accuracy of a ceramic/polymer composite bound with polymer is excellent. However, the polymers have to be completeley removed at low temperature before further sintering at higher temperatures. This process is associated with long, careful debinding steps.

Monoclinic HBO_2 has recently been developed for use

as an inorganic binder for the SLS of alumina.[7] Due to its low viscosity and better wetting of alumina particle surfaces, one obtains better feature definition of the green SLS parts and higher bending strength of green and fired parts, compared to those made with other inorganic binders such as aluminum and ammonium phosphate. However, bend strengths and densities of the post-processed SLS parts made with alumina-monoclinic HBO_2 were still low for functional applications. Therefore, development of a new inorganic binder for SLS of alumina powder was necessarily needed.

Since alumina reacts well with zinc borosilicate glass that has a low softening point (630℃), fabrication of alumina-glass composite parts by the SLS process seemed attractive. In addition, during post-thermal processing of preform, viscous flow of glass involved glass infiltration of porous ceramic bodies, and hence it was possible to obtain fully dense ceramic parts. However, it was found experimentally that the direct use of zinc borosilicate glass as an inorganic binder for the SLS of alumina in a conventional low temperature system led to curling of the newly sintered layer, and hence a debonding between the layers. Further research to develop a glass binder for SLS of alumina will be carried out. The alternative approach is to employ monoclinic HBO_2 as an inorganic binder for the SLS of a binary alumina-glass composite system.

The selection of monoclinic HBO_2 as an inorganic binder for the SLS of an alumina-zinc borosilicate glass powder blend offers the possibility of obtaining a desired shape with alumina-glass composites. Crystalline monoclinic HBO_2 can transform completely into amorphous boron oxide during laser scanning. Densification and strengthening of the green SLS composites can occur through both the viscous flow of boron oxide and glass, as well as the reactions among alumina, glass, and boron oxide during post-thermal processing. Chemical reactions during heat treatment can lead to the formation of new crystalline phases. Thus, fabrication of glass-ceramic composites for functional application is possible by SLS and post-processing of alumina-glass-monoclinic HBO_2 powder blends.

This paper deals with the fabrication of glass-ceramic composites through the post-processing of green SLS parts that were made with alumina-zinc borosilicate glass composite and monoclinic HBO_2 as an intermediate binder. Two kinds of post-processing are employed; (i) simple heat treatment, and (ii) colloidal silica infiltration followed by high temperature firing. The effects of materials and processing parameters on the physical and mechanical properties of the final glass-ceramic parts are described in this paper.

2. Materials and Experimental procedure

High purity, electronic grade, 15 ㎛ diameter, aluminum oxide powder provided by Norton Materials Corporation and 60 mesh (250 ㎛) 99 % boron oxide powder from Johnson Mathey were the starting materials. The above boron oxide powder was further ground using a Szegvari attritor system and sieved to less than 75 ㎛.

Zinc borosilicate glass powder (400 mesh) was provided by the Transene Company. The range in chemical composition of the glass is shown in table 1. The softening point of this glass is around 630℃ and the true density is between 2 and 3 g/cm^3. Most of the particle size is less than 10 ㎛ and particle shape is irregular as revealed by Scanning Electron Microscope (SEM) micrograph.

Table. 1. Chemical composition of zinc borosilicate glass.

Component	Concentration(wt.%)
ZnO	<60%
B_2O_3	<40%
Amorphous SiO_2	<20%

Zinc borosilicate glass powder was isothermally heat treated at 600℃, 700℃, 800℃, and 900℃ for 6 hours to investigate the crystallization behavior. In addition, Differential Thermal Analysis (DTA) was carried out on zinc borosilicate glass powder to determine its crystallization temperatures. In this experiment, the alumina crucible containing the glass powder was heated from room temperature up to 1000℃ with a heating rate of 10℃/min and pure alumina was used as a reference material.

Alumina and glass powders were mixed in the ratio of 1:1, 7:3, and 9:1 by weight. Each powder mixture was blended with B_2O_3 in the ratio of 3:1 by weight (25 wt.% B_2O_3). The pre-baking-out procedure to transform B_2O_3 to Monoclinic HBO_2 was previously described in the SLS of an alumina-boron oxide system.[7] Baked-out powder blends were immediately sintered in a SLS system at the University of Texas at Austin. Test specimens having a retangular cross section with dimensions 0.025m × 0.00625m × 0.076m (1″ × 0.25″ × 3″) were fabricated in an inert nitrogen environment using the operational parameters listed in Table 2. The green SLS parts were subsequently heat treated at various temperatures ranging from 600℃ to 1200℃ with an interval

Table 2. SLS operational parameters.

Laser Power (W)	Bed Temperature (℃)	Scan Spacing (㎛)	Layer Thickness(㎛) 25~30 layers	Scan Speed (m/sec)
15	80	125	200~250	0.56

of 100℃ in order to study the densification and crystallization behavior.

Test bars made from alumina and glass powder blend having a weight ratio of 7:3, followed by firing at 700 ℃ for 6 hours, were infiltrated with Ludox colloidal silica, grade TM, provided by Dupon Corporation. The silica content of this colloid is 50 wt.% and the average particle diameter is 22 nm. The test bars were partially immersed in a shallow pool of colloid, which could be drawn up to the top surface. When the top surface of the coupons was completely wet, the infiltration was complete. The infiltrated preforms were dried for a few hours in air at room temperature, and then heated to 120℃ for several hours in a drying oven. After saturation through a sequence of infiltrations and drying, the samples were further heated to 800℃~1100℃ for 10 hours to decompose the infiltrant, and densify the composites.

The strengths of green parts, infilitrated ones and samples fired at various temperatures for 6 hours were measured by a 3-point bend test using an Instron Instrument with a constant displacement rate. For each experimental condition five specimens were prepared and tested. Densities were obtained by use of sample dimensions and mass. Identification of phases and microstructural evolution at every step of processing was carried out by X-ray diffraction analysis and SEM.

3. Results and Discussion

The glass powder was found to be amorphous up to a firing temperature of 600℃, which is just below the softening point. Conversion of the amorphous phase to crystalline phases occurs for firing temperatures above 700℃ (Figure 1). A crystalline zinc borate ($ZnO \cdot B_2O_3$) phase was found at 700℃, whereas willemite ($SiO_2 \cdot 2ZnO$) and zinc borate ($ZnO \cdot B_2O_3$) phases were found at 800℃.

Differential Thermal Analysis (DTA) plot for zinc borosilicate glass powder were obtained at a heating rate of 10℃/min (Figure 2). It shows two exothermic peaks and one endothermic peak. The first strong exothermic peak at about 740℃ corresponds to the crystallization of zinc borate ($ZnO \cdot B_2O_3$). The second exothermic peak at around 820℃ is due to the crystallization of willemite ($SiO_2 \cdot 2ZnO$). The endothermic peak at around 980℃ is possibly due to the melting of zinc borate ($ZnO \cdot B_2O_3$), which is close to the reported melting point (970℃) of zinc borate ($ZnO \cdot B_2O_3$).

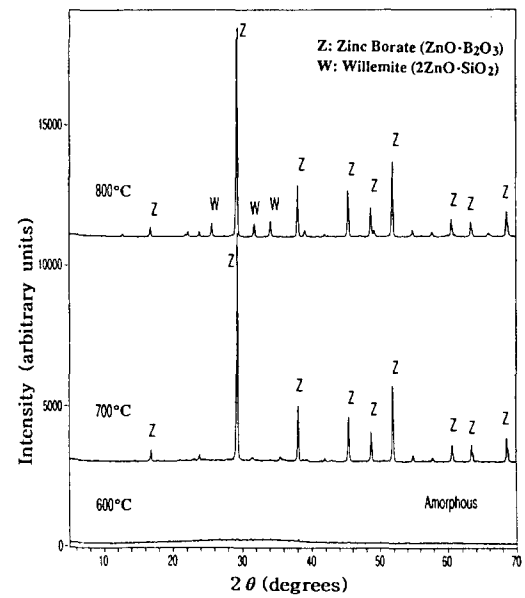

Fig. 1. X-ray diffraction patterns showing the crystallization of zinc borosilicate glass at firing temperatures T ≥ 700℃.

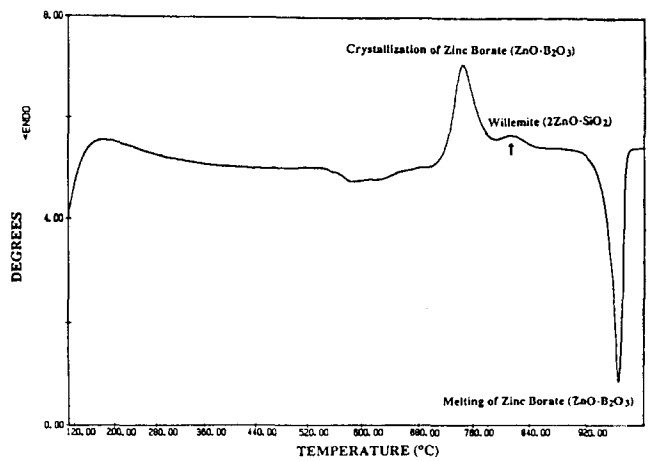

Fig. 2. DTA plot of zinc borosilicate glass.

It was found that the glass content plays an important role on the density and bend strength of the post-thermal processed SLS parts that were obtained with alumina-glass composite powder systems using monoclinic HBO_2 as a binder. Composites with higher glass content show higher density and bend strength for all firing temperatures than those with lower glass content (Figure 3). Since the true density of glass is lower than that of alumina, one would expect that the incorpora-

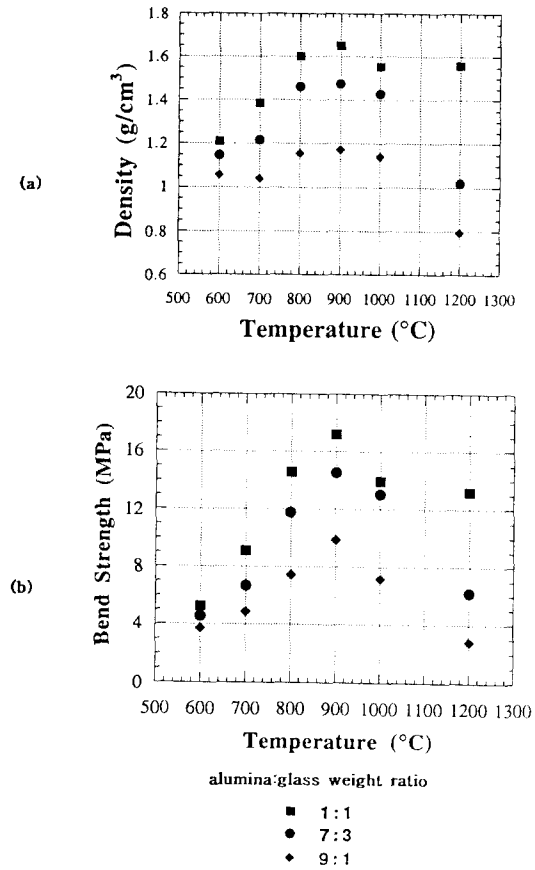

Fig. 3. Effect of firing temperature on (a) densification and (b) bend strength of SLS alumina-glass composites.

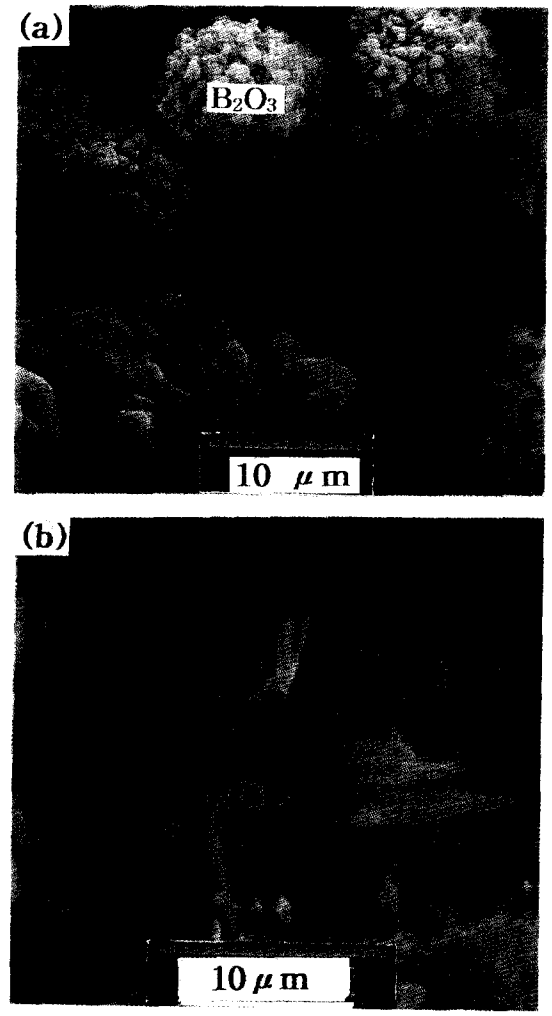

Fig. 4. Fracture surface of SLS alumina-glass composites (1:1 by weight ratio) after post-thermal processing: (a) 600℃ (b) 1200℃.

tion of glass into the alumina-monoclinic HBO_2 system can reduce the apparent density of composites if the weight ratio of the monoclinic HBO_2 remains contant. However, the experimental observation is quite opposite. It appears that densification is strongly dependent on the viscous flow of glass and reactions among glass, alumina, and boron oxide, which in turn depends on the amount of glass present in the system.

The effects of firing temperature on densification and mechanical properties were investigated. The data in Figure 3, show that there is no significant increase in density and bend strength for the firing temperature of 600℃ compared with the density (0.8g/cm³) and the bend strength (1 MPa) of the green parts. This is because only melting (m.p. 450℃) and flowing of boron oxide can contribute to the densification at that temperature. However, even at 600℃, the redistribution of boron oxide is not complete as seen in Figure 4 (a). Figure 4 (a), which shows the fracture surface of test bars fired at 600℃, reveals the presence of isolated clusters of boron oxide. Thus, it appears that the viscosity of boron oxide at 600℃ is still too high for melt infiltration into the porous SLS preform. The X-ray diffraction pattern for the SLS preform recorded after firing at 600℃ (Figure 5) shows the presence of alumina and crystalline boron oxide with a broad amorphous background, which implies that there is no reaction between either alumina and boron oxide or glass and boron oxide.

The X-ray diffraction pattern for the composite heated at 700℃ (Figure 5) indicates that a new crystalline phase, zinc borate ($ZnO \cdot B_2O_3$), was formed, while alumina remained unreacted. Zinc oxide, one of the glass components, reacted with boron oxide at 700℃ to form zinc borate ($ZnO \cdot B_2O_3$). Isolated clusters of boron oxide can no longer be observed at the fracture surface of a test bar fired at 700℃. Thus, the flow of molten boron oxide, having a low enough viscosity, begins to cause densification. Since the softening point of glass is 640℃, it is also expected that the viscous flow of glass will aid not only densification, but reaction. Therefore, composites with alumina and glass in the ratio of 1:1 by weight show rapid densification at the

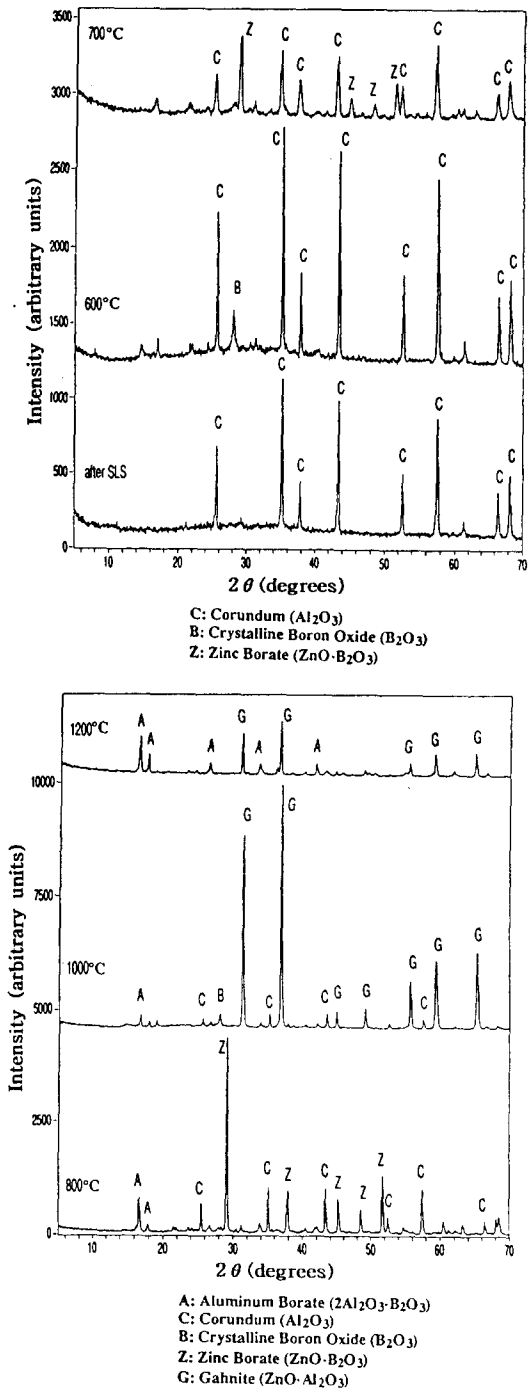

Fig. 5. X-ray diffraction patterns of alumina-glass composites (1:1 by weight ratio) after firing at various temperatures.

firing temperature of 700℃ compared to the lower glass content composites. For a firing temperature of 800℃, all three composites with various glass contents show significant increases in density and bend strength. X-ray diffraction patterns show the formation of aluminum borate ($2Al_2O_3 \cdot B_2O_3$) and gahnite ($ZnO \cdot Al_2O_3$) (Figure 5). The phases found for a firing temperature of 900℃ are the same as those formed at 800 ℃. All composites show maximum density and bend strength for the firing temperature of 900℃. Density increases from about 1.1 g/cm^3 for samples fabricated with alumina-25 wt.% boron oxide (without incorporation of glass) to about 1.65 g/cm^3 for samples made with alumina and glass in the ratio of 1:1 by weight. The bend strength of the composite with alumina and glass (ratio of 1:1 by weight) is also twice as high as that of a part without incorporation of glass. This densification is due to the glass redistribution arising from a better viscous flow of glass at this firing temperature. However, bend strength (15 MPa) of the heat treated parts are quite lower compared to the mean bend strength (70-130 MPa) of commercial SiO_2-Al_2O_3-ZnO glass-ceramic systems.[8]

For a firing temperature of 1000℃, zinc borate ($ZnO \cdot B_2O_3$) completely disappears and gahnite ($ZnO \cdot Al_2O_3$) is dominant, while aluminum borate ($2Al_2O_3 \cdot B_2O_3$) is still present. There is a slight decrease in density and bend strength for the firing temperature of 1000℃. The amount of aluminum borate ($2Al_2O_3 \cdot B_2O_3$) in the composie obtained for a firing temperature of 1200℃ increases a lot compared to that in the composite heated at 1000℃. Figure 4 (b) shows a whisker-structure morphology of aluminum borate ($2Al_2O_3 \cdot B_2O_3$). All composites show a decrease in density and bend strength for a firing temperature of 1200℃. This phenomenon could be explained by an increase in porosity arising from the evaporation of some glass and boron oxide. In addition, incorporation of a larger amount of glass into the alumina-boron oxide composite system suppresses the formation of aluminum borate, $9Al_2O_3 \cdot 2B_2O_3$, at 1200℃ due to the insufficient amount of alumina to react with $2Al_2O_3 \cdot B_2O_3$. In contrast, composites with alumina and glass (ratio of 9:1 by weight), after firing at 1200℃, results in a mixture of aluminum borate $9Al_2O_3 \cdot 2B_2O_3$ and $2Al_2O_3 \cdot B_2O_3$. In the absence of glass, the post-thermal processing at 1200℃ of an alumina-monoclinic HBO_2 system yields a single phase aluminum borate ($9Al_2O_3 \cdot 2B_2O_3$) as discussed in previous work.[9]

Figure 6 illustrates the effects of firing temperature on the density and the bend strength of alumina-glass composites infiltrated with colloidal silica. The densities of infiltrated parts are at least 0.2 g/cm^3 higher than those parts heat treated without infiltration. Similarly, the bend strengths of infiltrated test bars are at least 3 -5 MPa higher than those heat treated parts. However, the gain in density and bend strength after infiltration was less than expected. This appeared to be due to an inability of the infiltrant to react with the matrix during the firing step. X-ray diffraction patterns of the in-

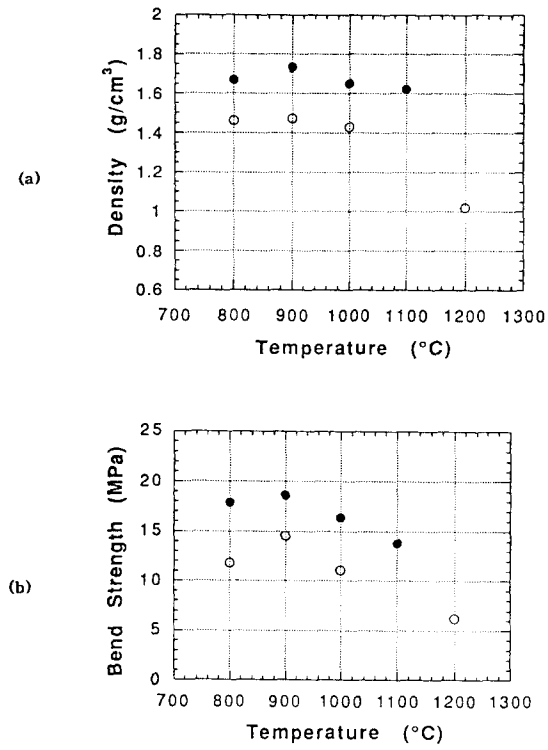

Fig. 6. Effect of silica infiltration on (a) densification (b) bend strength of alumina-glass composites (7:3 by weight ratio). The open and closed symbols refer, respectively, to uninfiltrated and infiltrated parts.

filtrated samples at firing temperatures of 800℃ ~ 1100 ℃ showed a broad amorphous background in addition to crystalline phases, suggesting the presence of unreacted infiltrant. It seemed that the heat treatment temperatures were too low for the reaction between alumina and infiltrated silica. It was concluded that the amorphous silica, which simply filled up the voids, did not contribute significantly to the increase in density and bend strength.

4. Conclusions

Glass-ceramic composites have been made successfully by post-thermal processing of green parts fabricated by laser processing of ternary alumina-zinc borosilicate glass-monoclinic HBO_2 powder blends. It was demonstrated that the incorporation of zinc borosilicate glass into alumina-monoclinic HBO_2 powder blends for the SLS process was an effective way to improve density and bend strength of SLS parts. The maximum density and bend strength of the composites were obtained at a firing temperature of 900℃. The density and the bend strength of the composites increased with increasing glass content. The infiltration of colloidal silica into the composites did not cause any significant increase in density and bend strength.

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