

Selective Laser Sintering of Alumina-Zinc Borosilicate Glass Composites using Monoclinic HBO₂ as a Binder

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Abstract

Selective Laser Sintering (SLS) process has been employed to fabricate alumina-glass composites using as an inorganic binder monoclinic HBO₂. Subsequent post-thermal processing of green SLS parts at various temperatures yielded glass-ceramic composites. The crystalline phases and microstructural evolution at each firing temperature were identified by X-ray diffraction analysis and Scanning Electron Microscopy. The role of glass content, firing temperature, and alumina particle size on the densification and bend strength of fired samples were studied. In addition, further densification was made through infiltration of colloidal silica into the fired, porous samples.

Introduction

Selective laser sintering (SLS) is a form of SFF technique and employs a focused laser beam which is controlled by a CAD data base to selectively scan the powder bed surface and bind the loose powder [1]. The primary advantage of SLS process is the flexibility of selection of material systems compared to other SFF techniques [2].

Monoclinic HBO₂ has been recently developed as an inorganic binder for SLS of alumina [3]. It demonstrated better green SLS parts and higher bending strength of green and fired parts due to its low viscosity and better wetting of the alumina particle surface, compared to other inorganic binders such as aluminum and ammonium phosphate [4,5].

The selection of monoclinic HBO₂ as an inorganic binder for SLS of alumina-zinc borosilicate glass powder blend provides the possibility of an alumina/glass composite in the desired shape. The crystalline monoclinic HBO₂ completely transforms into amorphous boron oxide during scanning of laser. Densification and strengthening of the green SLS composites are expected to take place through both the viscous flow of boron oxide and glass and the reactions among alumina, glass, and boron oxide during post-thermal processing. As a result of heat treatment, new crystalline phases will be incorporated into the composite body; i. e. the heat treatment of alumina/glass composites after SLS results in glass-ceramic composites. Therefore, glass-ceramic composites in the desired shape can be fabricated by SLS and post-processing of alumina-glass-monoclinic HBO₂ powder blends. The effects of the materials and processing parameters on the physical and mechanical properties of final glass-ceramic product are investigated. The ceramic-glass composite fired at 600° C for 6 hours, for easy handling, was also subjected to the Ceracon forging process in order to fabricate fully dense material. The results of the Ceracon process will be described in a separate paper in this symposium.

Materials and Experimental procedures

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

Zinc borosilicate glass (400 mesh) was provided from Transene Company. The range in chemical composition of the glass is shown in table I according to MSDS from Transene Company. The softening point of this glass is around 630°C and the true density is between 2 and 3 g/cm³. Most of the particle size is less than 10 μm and particle shape is irregular as revealed by SEM micrograph.

Table I. Chemical composition of zinc borosilicate glass

component	concentration (wt.%)
ZnO	<60%
B ₂ O ₃	<40%
Amorphous SiO ₂	<20%

Alumina and glass powders were mixed in the ratio 1:1, 7:3, and 9:1 by weight. Each powder mixture was blended with B₂O₃ in the ratio 3:1 by weight. The prebaking-out procedures to transform B₂O₃ to Monoclinic HBO₂ were described in the alumina-boron oxide system [3]. Baked-out powder blends were immediately sintered in a SLS system of the University of Texas at Austin. Test specimens with dimension of 0.076m x0.025m x0.00625m (3"x1"x0.25") were fabricated in an inert nitrogen environment using the operational parameters listed in Table II. The SLS parts were subsequently heat treated at various temperatures of 600°C, 700°C, 800°C, 900°C, 1000°C, and 1200°C in order to study the densification and crystallization behavior.

Table II. SLS operational parameters

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

Test bars made from the alumina and glass powder blend having the weight ratio 7:3 and fired at 700°C 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 according to MSDS from Dupon Corporation. 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 assumed to be near completion. The infiltrated preforms were dried for a few hours in air at room temperature and then heated to 120°C in a drying oven for several hours. After saturation through a sequence of infiltrations and drying, the samples were further heated to 800°C-1100°C for 10 hours to decompose the infiltrant, and densify the composite.

The strengths of green parts, infiltrated parts and parts fired at various temperatures for 6 hours were measured by 3-point bend test using an Instron constant displacement rate machine. Density was obtained by direct measurement of dimension and mass. Identification of phases and microstructural evolution at every step of processing was carried out by x-ray diffraction analysis and SEM.

Results and Discussion

It is found that the glass content play an important role on the increase of density and bend strength of the alumina-monoclinic HBO_2 SLS composite during post-thermal processing. Composites with higher glass contents show higher density and bend strength for the all the firing temperatures in comparison to the composites with lower glass contents. Since the true density of glass is lower than that of alumina, it is anticipated that the incorporation of glass into the alumina-monoclinic HBO_2 system reduces the apparent density of composites if the weight ratio of the monoclinic HBO_2 remains constant. However, the experimental observation was quite opposite. Therefore, it can be concluded 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 effect of firing temperature on densification and mechanical properties were investigated. According to figure 1, there is no significant increase of density and bend strength for the firing temperature 600°C compared to the density (0.8 g/cm^3) and the bend strength (1 MPa) of the green parts. This is because only melting and flowing of boron oxide (m. p. 450°C) contributes to the densification at 600°C . Even at that temperature, the redistribution of boron oxide is not complete as is shown in figure 2 (a). In figure 2 (a) which represents the fracture surface of test bars fired at 600°C , isolated clusters of boron oxide are revealed by SEM. Thus, it is speculated that the viscosity of boron oxide at 600°C is still too high for melt infiltration into the porous SLS preform. XRD pattern at 600°C (Figure 3) shows the presence of alumina and crystalline boron oxide and an amorphous broad peak, which implies that there are no reactions between either alumina and boron oxide or glass and boron oxide.

The XRD patterns for the firing temperature 700°C (Figure 3), indicates the formation of a new crystalline phase zinc borate $\text{ZnO}\cdot\text{B}_2\text{O}_3$, while alumina still remains unreacted. It is obvious that glass starts to decompose and zinc oxide, one of the glass components, react with boron oxide to form zinc borate $\text{ZnO}\cdot\text{B}_2\text{O}_3$. Isolated clusters of boron oxide cannot be observed any more at the fracture surface of test bar fired at 700°C . Therefore, the main densification results from the flowing of melt boron oxide whose viscosity is low enough. Since the softening point of glass is 640°C , it is also expected that the viscous flow of glass will aid not only densification but also the reaction. Thus, composites with alumina and glass ratio 1:1 by weight shows rapid densification at firing temperature 700°C compared to the lower glass content composites. At firing temperature 800°C , all three composites with various glass contents show significant increase of density and bend strength. XRD pattern shows the formation of aluminum borate $2\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ and gahnite $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ (Figure 3). The phases found for firing temperature 900°C are same as those present at 800°C . At this temperature, all composites show maximum density and bend strength. This densification is due to the glass redistribution arising from a better viscous flow of glass.

For the firing temperature 1000°C , zinc borate $\text{ZnO}\cdot\text{B}_2\text{O}_3$ completely disappears and gahnite $\text{ZnO}\cdot\text{Al}_2\text{O}_3$ becomes dominant, while aluminum borate $2\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ still exists. There is a slight decrease of density and bend strength for 1000°C . For the firing temperature 1200°C , aluminum borate $2\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ increases a lot compared to that for 1000°C . Figure 2 (b) shows the whisker structure morphology of aluminum borate $2\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$. All composites show a larger decrease in density and bend strength for 1200°C . This phenomenon could be due to the increase in porosity arising from the evaporation of some glass and boron oxide. In addition, it is found that incorporation of a higher amount of glass into alumina-boron oxide composite system suppresses the formation of aluminum borate $9\text{Al}_2\text{O}_3\cdot 2\text{B}_2\text{O}_3$ at 1200°C due to insufficient alumina to react with $2\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$. In contrast, composites with alumina and glass ratio 9:1 by weight fired at 1200°C produces a mixture of aluminum borate $9\text{Al}_2\text{O}_3\cdot 2\text{B}_2\text{O}_3$ and $2\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$. In the

absence of glass, the post-thermal processing at 1200°C of alumina-monoclinic HBO₂ system yields single phase aluminum borate 9Al₂O₃·2B₂O₃.

The effect of alumina particle size on densification is shown in Figure 4. For this investigation, small quantity of high purity, electronic grade 25 μm which is the biggest particle size in that grade was provided as a sample from Norton Materials Corporation. A larger alumina particle (25 μm) contributes to rapid densification at low firing temperature due to a reduced glass redistribution distance associated with a better packing of glass particles around the alumina particles. In addition, it gives higher density for the composite for the firing temperature 900°C than that for the composites fabricated with the 15 μm alumina particle.

Figure 5 illustrates the effect of firing temperature on the bend strength of alumina-glass composites infiltrated with the colloidal silica. The bend strength of infiltrated test bar shows at least 3-5 MPa higher than those of simple heat treated samples. However, the gain of bend strength after infiltration is less than expected. This is associated with the infiltrant behavior during the firing step. XRD patterns of infiltrated samples for firing temperature 800°C-1100°C shows a broad amorphous peak in addition to the crystalline phases. This suggests that the infiltrant may remain unreacted with the matrix materials. It is concluded that the amorphous silica, which simply fills up the voids, does not contribute to the significant increase of bend strength.

Summary

Glass-ceramic composites were successfully synthesized by post-thermal processing of green parts fabricated by laser processing of ternary alumina-zinc borosilicate glass-monoclinic HBO₂ powder blends. It was demonstrated that the incorporation of zinc borosilicate glass into alumina-monoclinic HBO₂ powder blend for SLS application is an effective way to improve density and bend strength of SLS part. The maximum density and bend strength of the composite was obtained for firing temperature of 900°C. The density of the composite increases with higher glass content and increasing alumina particle size. The infiltration of colloidal silica into the composite does not contribute significantly to the increase of bend strength.

Acknowledgments

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References

1. D. L. Bourell, H. L. Marcus, J. W. Barlow, and J. J. Beaman, "Selective laser sintering of metals and ceramics," *The International Journal of Powder Metallurgy*, 28(4), 369, 1992.
2. D. Kochan, "Solid Freeform Manufacturing," *Manufacturing Research and Technology* 19, Elsevier, New York, 1993.
3. Insup Lee, A. Manthiram, and H. L. Marcus, "Selective Laser Sintering of Alumina-Boron Oxide Composites," *Proceedings of the Solid Freeform Fabrication Symposium*, Austin, Texas, August 8-10, 339, 1994.
4. P. Kamatchi Subramannian, Guisheng Zong, and H. L. Marcus, "Selective Laser Sintering of Ceramic Composites," *Proceedings of the Solid Freeform Fabrication Symposium*, Austin, Texas, August 3-5, 63, 1992.
5. U. Lakshminarayn, and H. L. Marcus, "An experimental study of relationship between microstructure and mechanical properties of a ceramic composites fabricated by selective laser sintering," *Proceedings of the Solid Freeform Fabrication Symposium*, Austin, Texas, August 3-5, 44, 1992.

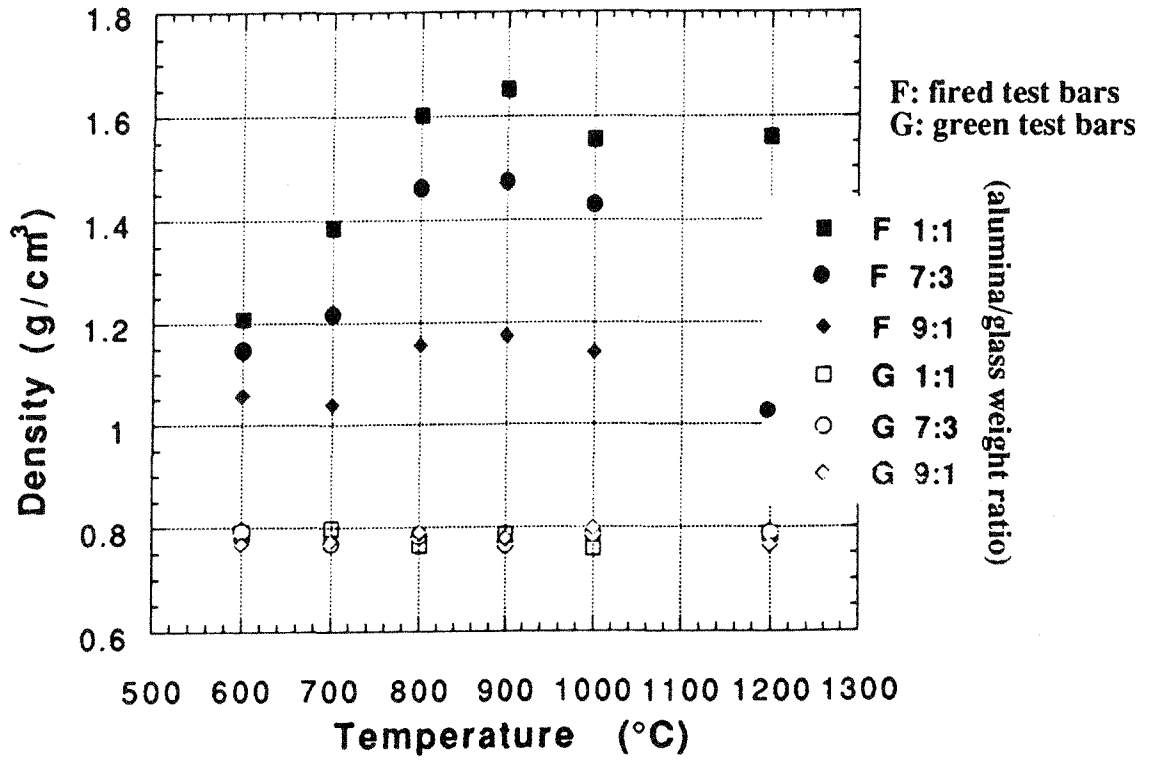


Figure 1 (a) Effect of firing temperature on densification of SLS alumina/glass composite parts.

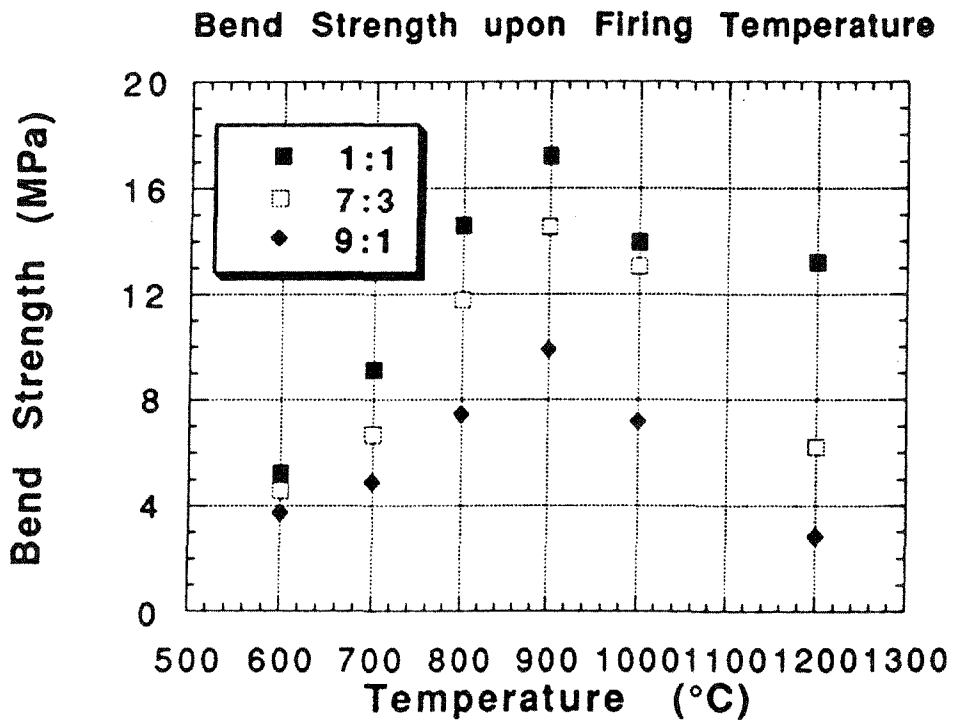
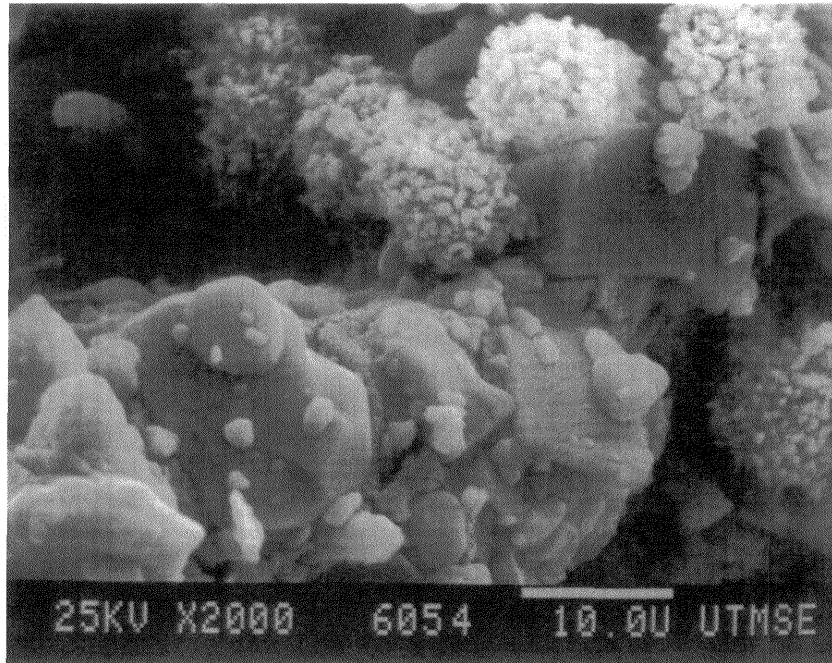
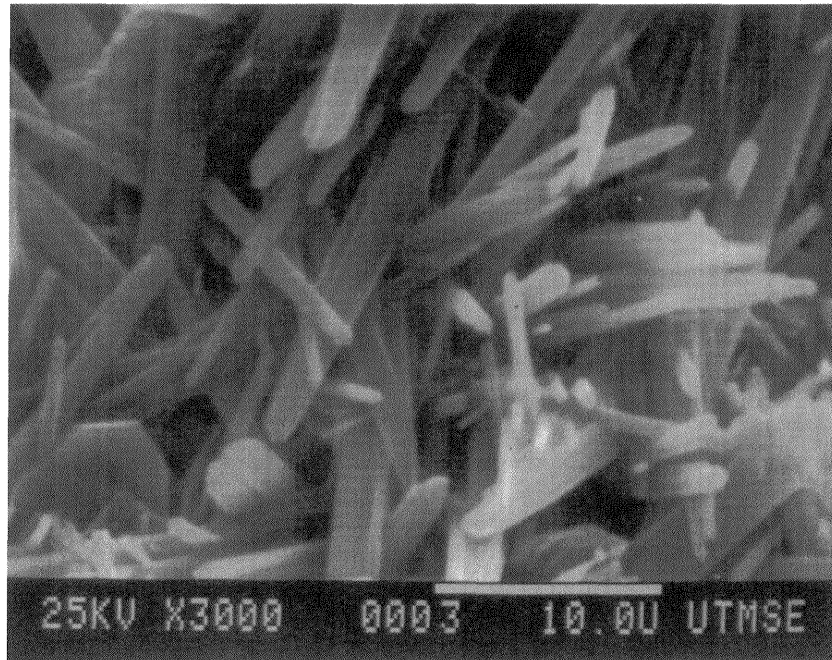


Figure 1 (b) Effect of firing temperature on bend strength of SLS alumina/glass composite parts.

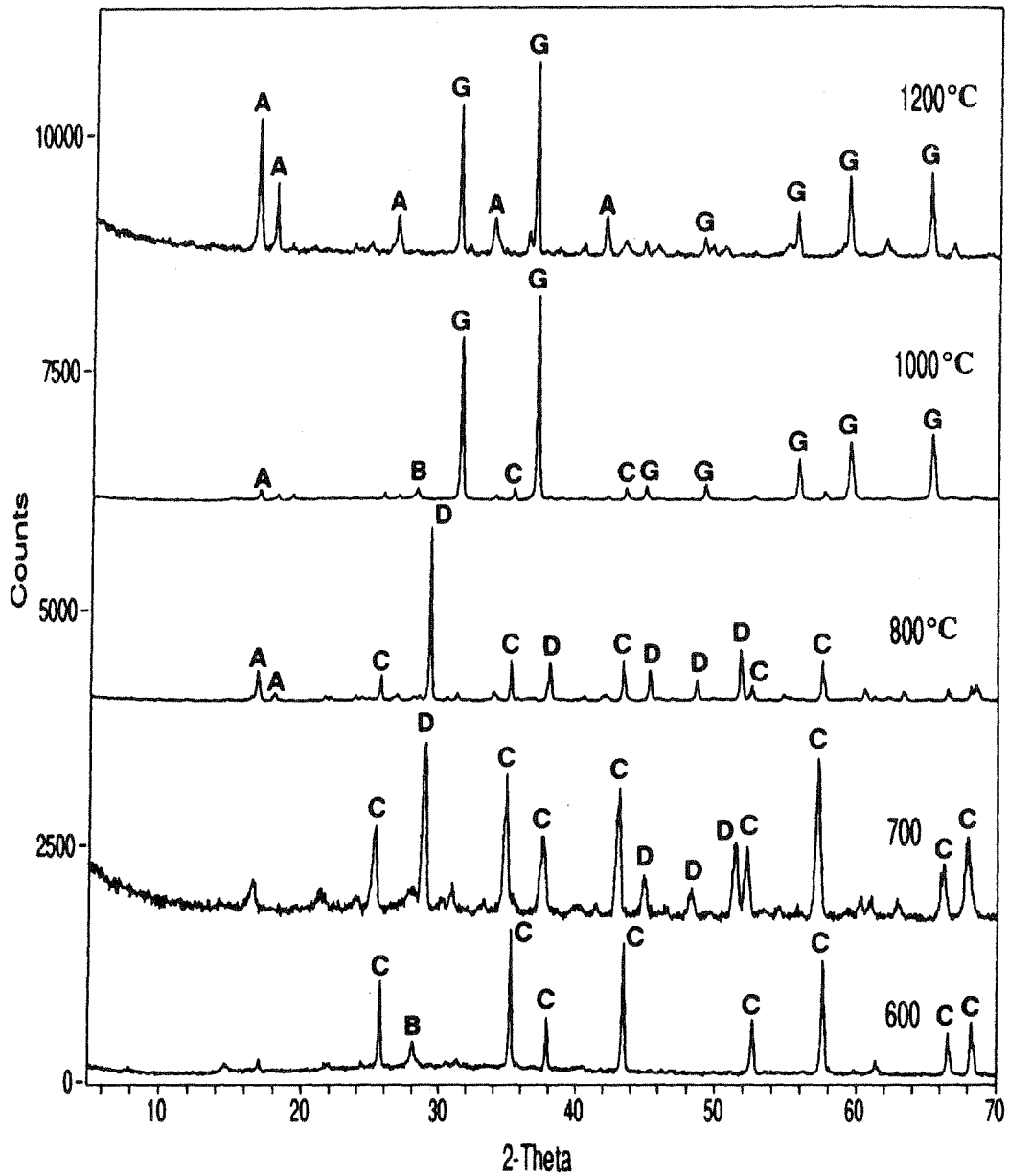


(a) 600°C



(b) 1200°C

Figure 2. Fracture surface of SLS alumina/glass composite (1:1 by weight ratio) after post-thermal processing.



- A:** Aluminum Borate($2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$)
- B:** Crystalline Boron Oxide(B_2O_3)
- C:** Corundum(Al_2O_3)
- D:** Zinc Borate($\text{ZnO} \cdot \text{B}_2\text{O}_3$)
- G:** Gahnite($\text{ZnO} \cdot \text{Al}_2\text{O}_3$)

Figure 3. X-ray diffraction patterns of alumina/glass composites (1:1 by weight ratio) after firing at various temperatures.

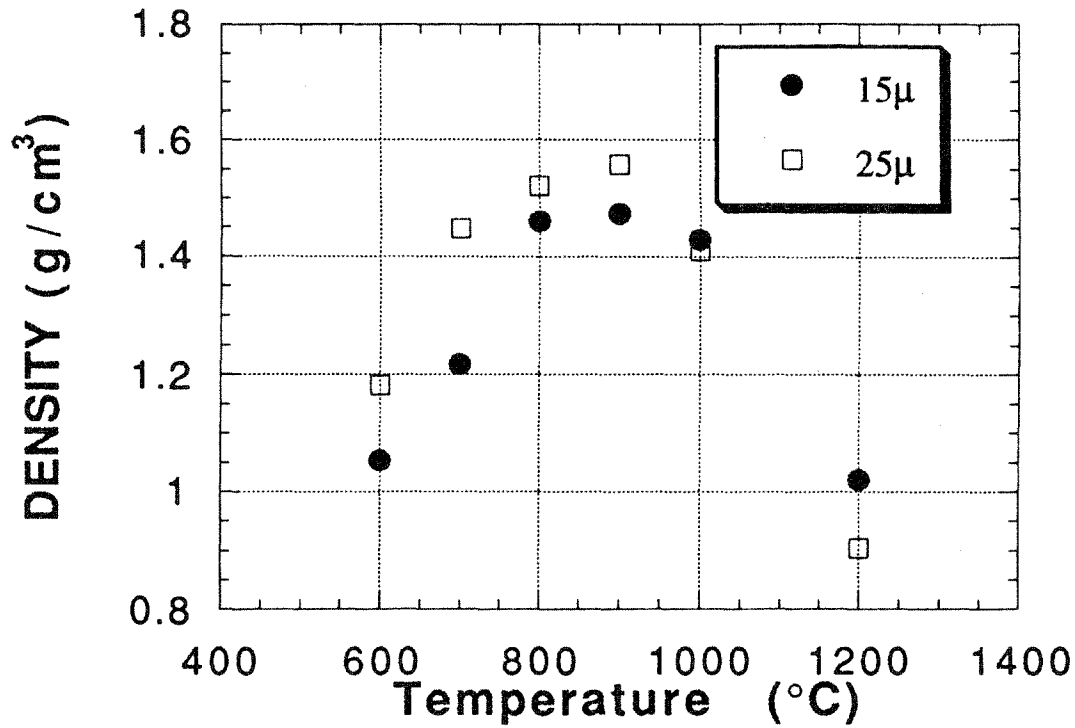


Figure 4. Effect of alumina particle size on densification of alumina/glass (7:3 by weight ratio) with firing temperatures.

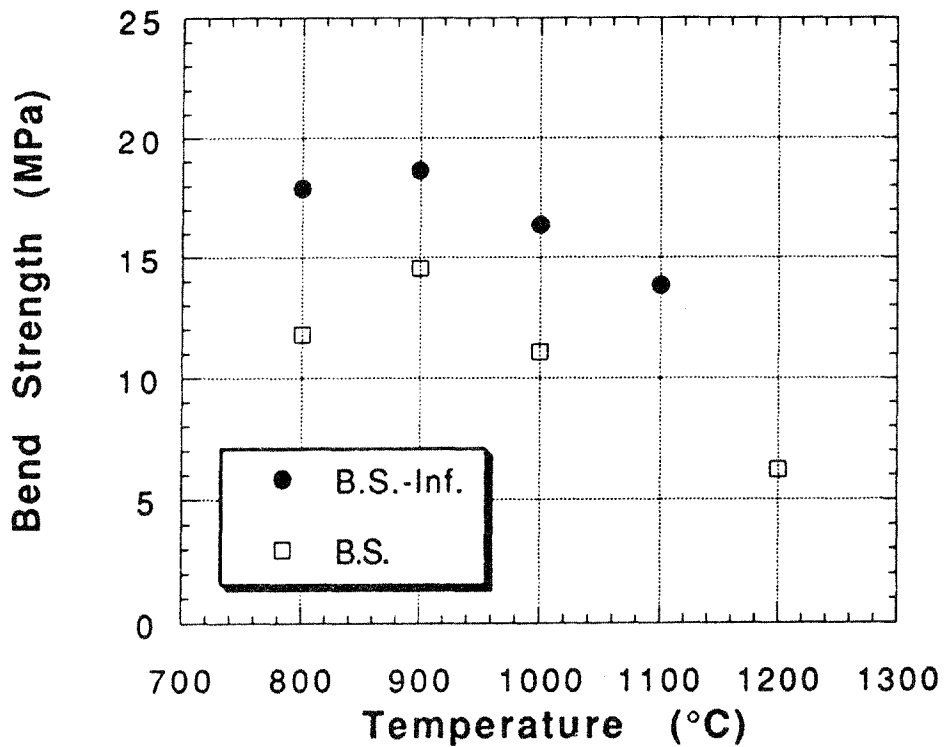


Figure 5. Effect of colloidal silica infiltration on bend strength of alumina/glass (7:3 by weight ratio) with firing temperatures.

Figure 5 illustrates the effect of firing temperature on the bend strength of alumina-glass composites infiltrated with the colloidal silica. The bend strength of infiltrated test bar shows at least 3-5 MPa higher than those of simple heat treated samples. However, the gain of bend strength after infiltration is less than expected. This is associated with the infiltrant behavior during the firing step. XRD patterns of infiltrated samples for firing temperature 800°C-1100°C shows a broad amorphous peak in addition to the crystalline phases. This suggests that the infiltrant may remain unreacted with the matrix materials. It is concluded that the amorphous silica, which simply fills up the voids, does not contribute to the significant increase of bend strength.

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References

1. D. L. Bourell, H. L. Marcus, J. W. Barlow, and J. J. Beaman, "Selective laser sintering of metals and ceramics," *The International Journal of Powder Metallurgy*, 28(4), 369, 1992.
2. D. Kochan, "Solid Freeform Manufacturing," *Manufacturing Research and Technology* 19, Elsevier, New York, 1993.
3. Insup Lee, A. Manthiram, and H. L. Marcus, "Selective Laser Sintering of Alumina-Boron Oxide Composites," *Proceedings of the Solid Freeform.Fabrication Symposium*, Austin, Texas, August 8-10, 339, 1994.
4. P. Kamatchi Subramannian, Guisheng Zong, and H. L. Marcus, "Selective Laser Sintering of Ceramic Composites," *Proceedings of the Solid Freeform.Fabrication Symposium*, Austin, Texas, August 3-5, 63, 1992.
5. U. Lakshminarayn, and H. L. Marcus, "An experimental study of relationship between microstructure and mechanical properties of a ceramic composites fabricated by selective laser sintering," *Proceedings of the Solid Freeform.Fabrication Symposium*, Austin, Texas, August 3-5, 44, 1992.