# Selective Laser Sintering of Alumina-Boron Oxide Composites

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## Abstract

The selection of an optimum composite system for selective laser sintering (SLS) is based on materials properties such as the melting point and the wettability between the components in the composite powder. The alumina-boron oxide composite system is attractive for SLS because the presence of the low melting component $B_2O_3$ (melting point 450° C) can enhance sintering. A better wetting of solid alumina powder by molten boron oxide can also aid densification process. The alumina-boron oxide composite system has been investigated by SLS and selective laser reactive sintering (SLRS). The role of boron oxide content as a binder, laser power density, and secondary heat treatment on the microstructure and mechanical properties is discussed.

## Introduction

Solid freeform fabrication (SFF) techniques have recently been developed to overcome some of the barriers of conventional manufacturing techniques, such as difficulties in tooling complex-shaped ceramic parts and long production time in fabricating prototypes [1]. 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 [2].

The two-phase powder approach to SLS, which involves binding high temperature ceramics such as alumina and silicon carbide with a low melting inorganic binder, is a promising technology to fabricate ceramic composite parts [3,4,5]. The selection of an optimum materials system for this approach depends on materials properties such as the melting point of the binder material and interparticle wetting between the components in the composite powder [6].

It is known that the role of boron oxide in borosilicate glasses is to reduce the thermal expansion coefficient and to improve workability by decreasing the viscosity [7]. The low viscosity of boron oxide is attributed to its linked ring structure, since there is a high probability that the bonds between rings are more susceptible to failure than the bonds within the rings [8].

The selection of the system $Al_2O_3$-$B_2O_3$ for SLS provides an advantage in densification. Boron oxide has a low melting point (450° C) and the liquid generated due to the local melting of $B_2O_3$ powder during laser beam irradiation can aid the sintering process. In addition, the molten boron oxide completely envelops the neighboring solid alumina particles due to its low viscosity and better wetting.

## Materials and Experimental Procedure

High purity, electronic grade 15μm, aluminum oxide powder provided by Lanxide Corporation and a 60 mesh 99% boron oxide powder from Johnson Mathey are the starting materials.

Fig. 1 shows the overall steps associated with SLS process and material characterization. The initial boron oxide powder of 250μm was ground by a Szegvari attritor system and sieved to less than 75μm. Alumina and boron oxide powder blends in various ratios by weight were baked out in a vacuum oven at 120° C for 30 hours. Pre-thermal treatment caused the powder blends to form weak powder cakes, which were subsequently broken and sieved. Baked-out powder blends were immediately sintered in a SLS system of the University of Texas at Austin. Test specimens with

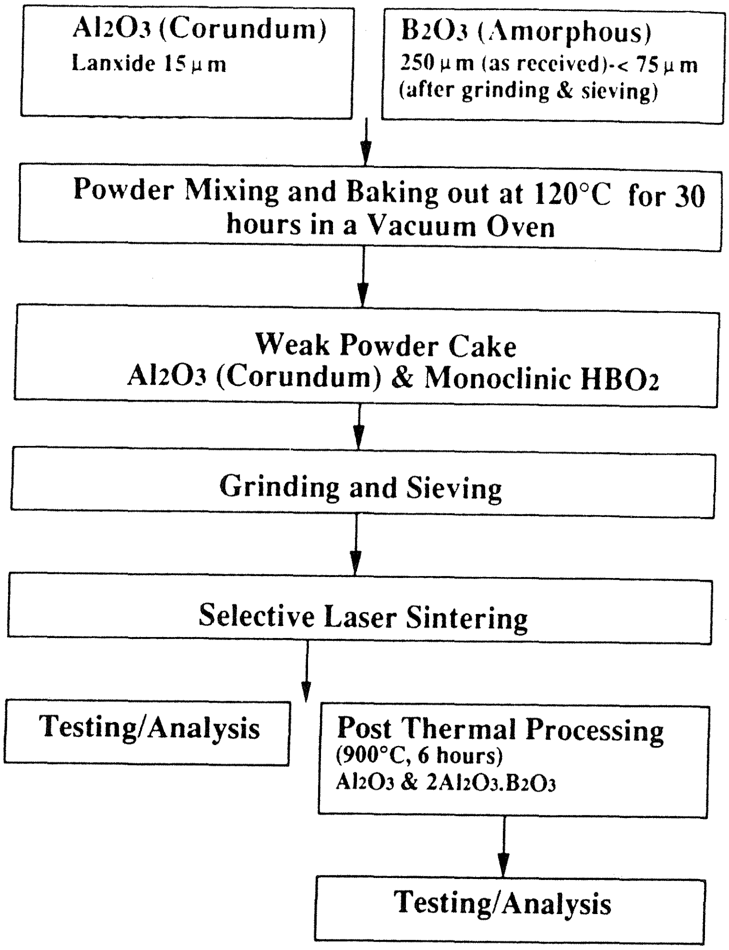


Figure 1. Flow chart for selective laser sintering of alumina-boron oxide composites

dimension of 1"x3"x0.25" were fabricated in an inert nitrogen environment using the operational parameters listed in Table I.

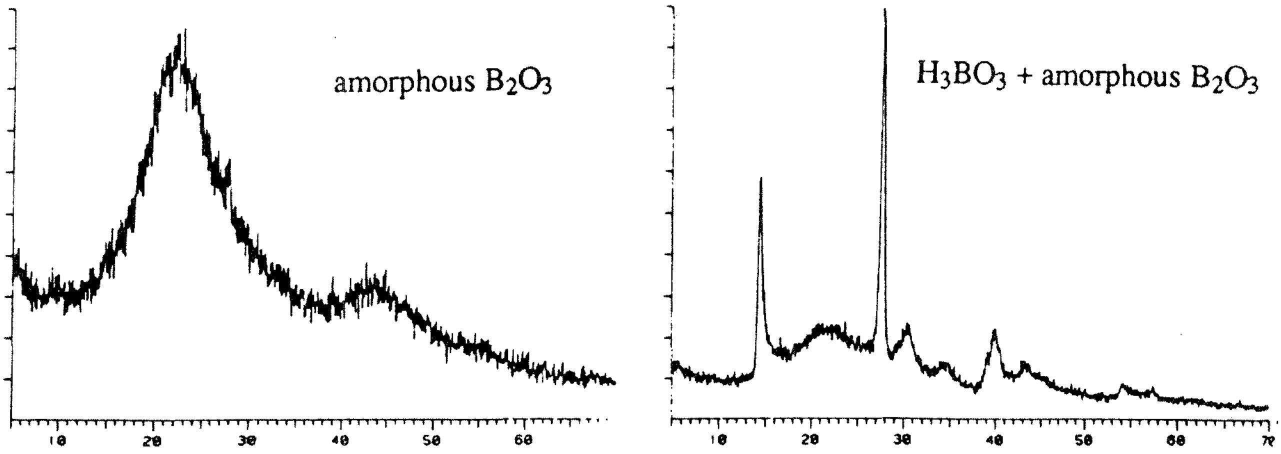
Table I. SLS operational parameters

| Laser Power (W) | Bed Temperature (°C) | Scan Spacing (mils) | Layer Thickness (mils) | Scan Speed (inch/sec) |
|---|---|---|---|---|
| 14-16.5 | 80-100 | 5 | 8 | 12.5-47 |

The strength of green and samples fired at various temperatures for 6 hours was determined by 3-point bend test using a 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.

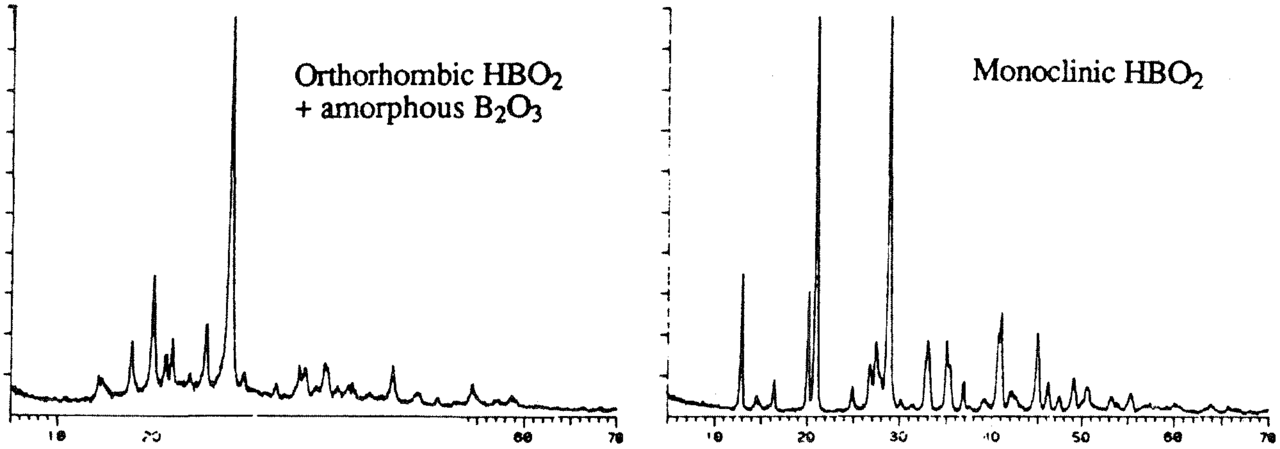
## Results and Discussion

Fig. 2 shows the phase transformation of the initial boron oxide upon reaction with atmospheric water. The as received boron oxide is amorphous. It reacts with moisture in air and transforms into boric acid ($H_3BO_3$) very quickly. As a result, without baking out before laser sintering, the starting powder blend for laser sintering is a mixture of alumina, amorphous boron oxide and boric acid. Because boric acid has much lower melting point (170°C) than boron oxide (450°C), it causes a weak bed cake through the whole powder bed during SLS process with bed heating



(a) as received

(b) after exposure to the atmosphere



(c) after baking out in a vacuum oven at 120°C for 13 hours

(d) after baking out in a vacuum oven at 120°C for 30 hours

Figure 2. X-ray diffraction analysis showing phase transformation of the initial boron oxide

around 80°C. The cake paralyzes the powder delivery and leveling system. Without employing bed heating system, it was possible to avoid the bed caking. However, curling of the previously sintered layers takes place, making powder leveling difficult due to the displacement of those layers.

In order to overcome bed caking and curling of sintered layers, the boric acid in the initial powder blend must be removed. Dehydration of boric acid gives different forms of metaboric acid $HBO_2$ or boron oxide $B_2O_3$ depending on the temperature. Table II shows the physical properties of various forms of metaboric acid $HBO_2$ [7].

Table II Physical properties of crystalline metaboric acid $HBO_2$

| | CN* of B | Density ($g/cm^3$) | Melting Point (°C) |
|---|---|---|---|
| Orthorhombic | 3 | 1.784 | 176 |
| Monoclinic | 3 and 4 | 2.045 | 201 |
| Cubic | 4 | 2.487 | 236 |

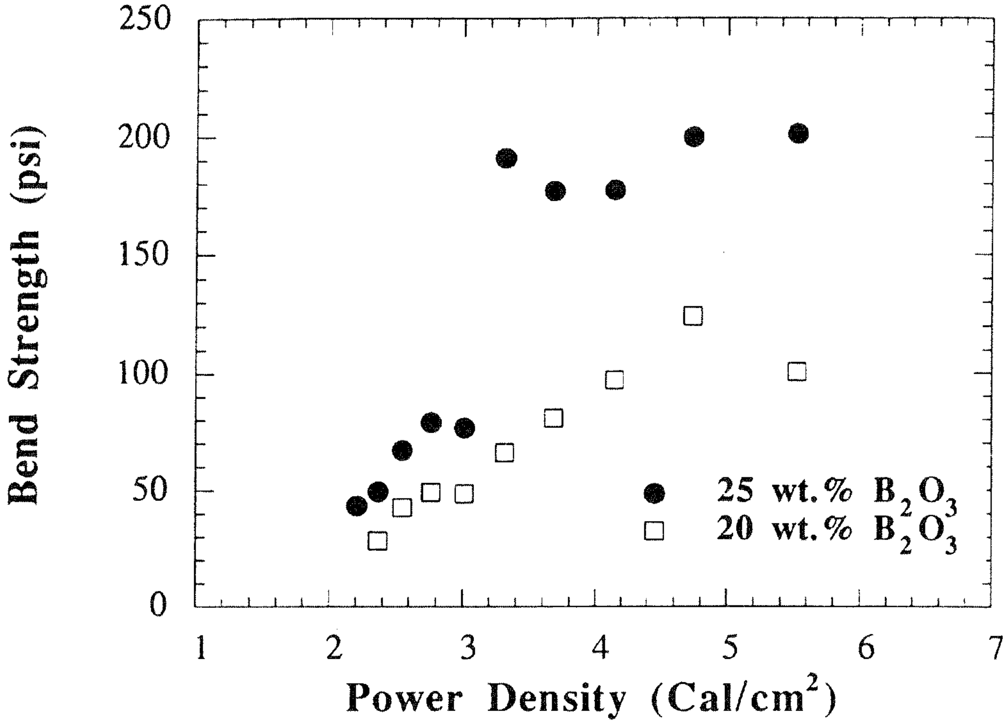
* CN refers to coordination number

Careful dehydration of boric acid at 120°C in a rough vacuum oven for 30 hours and slow quenching after bake-out yields monoclinic metaboric acid $HBO_2$ whose melting point is 201°C. Orthorhombic $HBO_2$ can be generated after 13 hours of heat treatment under the same conditions. It is found that monoclinic $HBO_2$ avoids the bed caking phenomenon with powder bed heating at 80°C and reduces the curling problem significantly during SLS process.

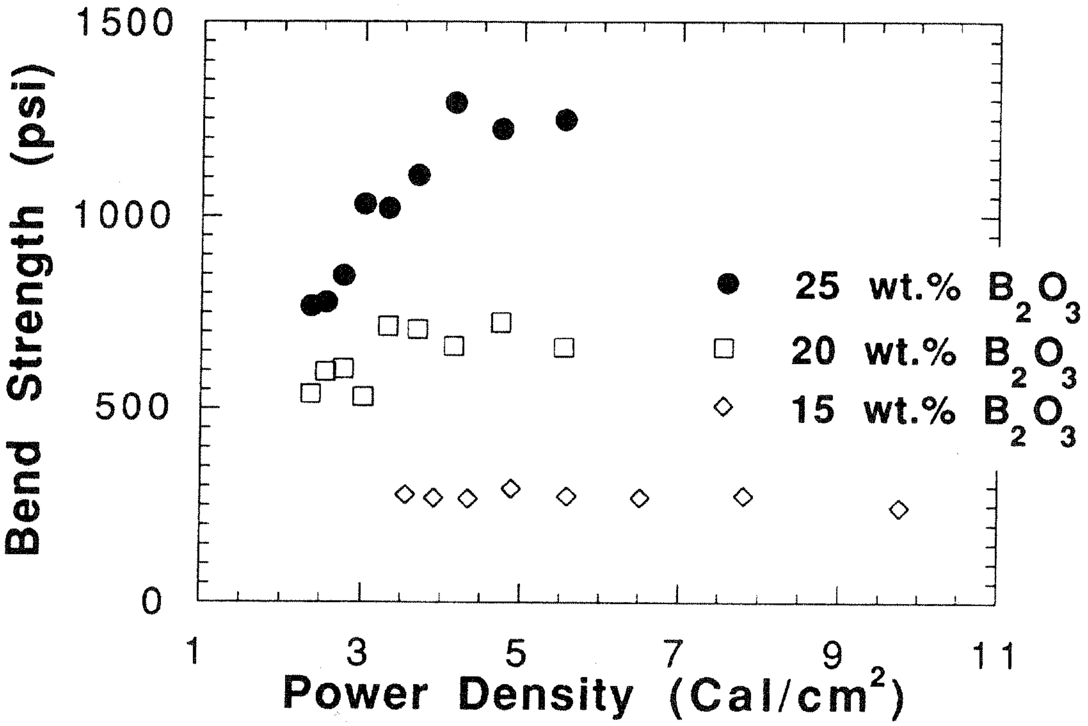
Fig. 3 shows the effect of the binder content on bend strength of both green and fired (at 900°C for 6 hours) composites. The bend strength of the composites increases as the binder content increases since all the ceramic interparticle bonds that provide the strength of the composites originate from the melting of the binder and the coating of ceramic (alumina) particles during laser beam irradiation.

The effect of laser power density on bend strength is also shown in Fig. 3. Power density is defined as laser power / (scan spacing x scan speed) [9]. At lower power density, the green composites show poor strength due to insufficient melting and flowing of the binder compared to at higher power density where molten binder coats the ceramic particles completely as revealed by SEM. Similarly, the bend strength of fired parts fabricated with 25 and 20 wt.% boron oxide powder blends is proportional to the power density. Because at higher power density, the laser beam locally melts the binder sufficiently, the binder flows and encapsulates more ceramic particles than at lower power density as revealed by SEM. As a result, the green and fired density increases as the power density increases. Therefore, at higher power density, the fired composites show higher strength due to a higher density (Fig.4). However, bend strength of fired test bars made with 15 wt.% boron oxide is independent of power density. For this system, it was required that the process be done at higher bed temperature (100°C) and at higher power density in order to melt the small amount of the binder completely and bind ceramic particles together. Consequently, there might be a threshold power density to melt the whole binder thoroughly and fabricate green parts which can keep the shape. Above this value, the strength of the fired parts will almost be independent of power density since there is no more additional binder which will coat the ceramic particles.

Fig. 5 illustrates the effect of firing temperature on the mechanical properties of parts fabricated with 25 wt.% boron oxide powder blends. At intermediate firing temperatures at around 800-1100°C, the test bars show higher bend strength due to the formation of aluminum borate ($2Al_2O_3 \cdot B_2O_3$) at the surface of the alumina particles by the reaction of alumina and boron oxide at around 800° C. According to X-ray diffraction analysis (Fig. 6), the amount of $2Al_2O_3 \cdot B_2O_3$ increases relative to that of alumina as the firing temperature increases up to 1100°C. At 1200°C, $9Al_2O_3 \cdot 2B_2O_3$ phase is formed by the reaction: $2\ (2Al_2O_3 \cdot B_2O_3) + 5Al_2O_3 \rightarrow 9Al_2O_3 \cdot 2B_2O_3$ [10]. Below 700°C, it was found that there was no substantial reaction. The bend strength of samples fired at 1300, and 1500°C decreases due to the decomposition of the compound

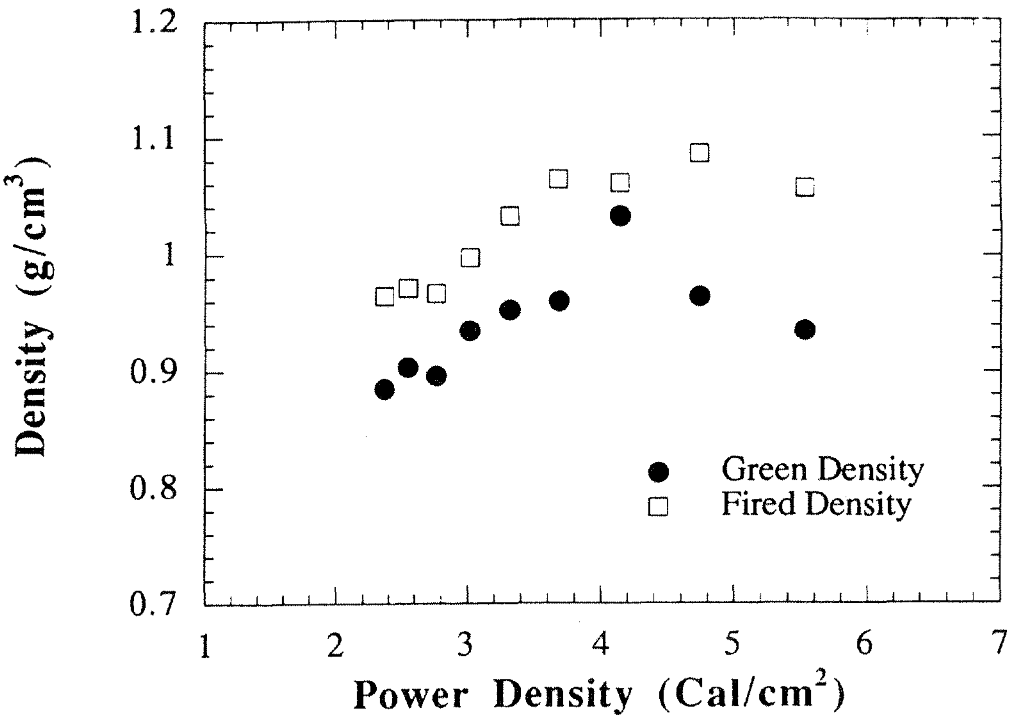


(a) green parts

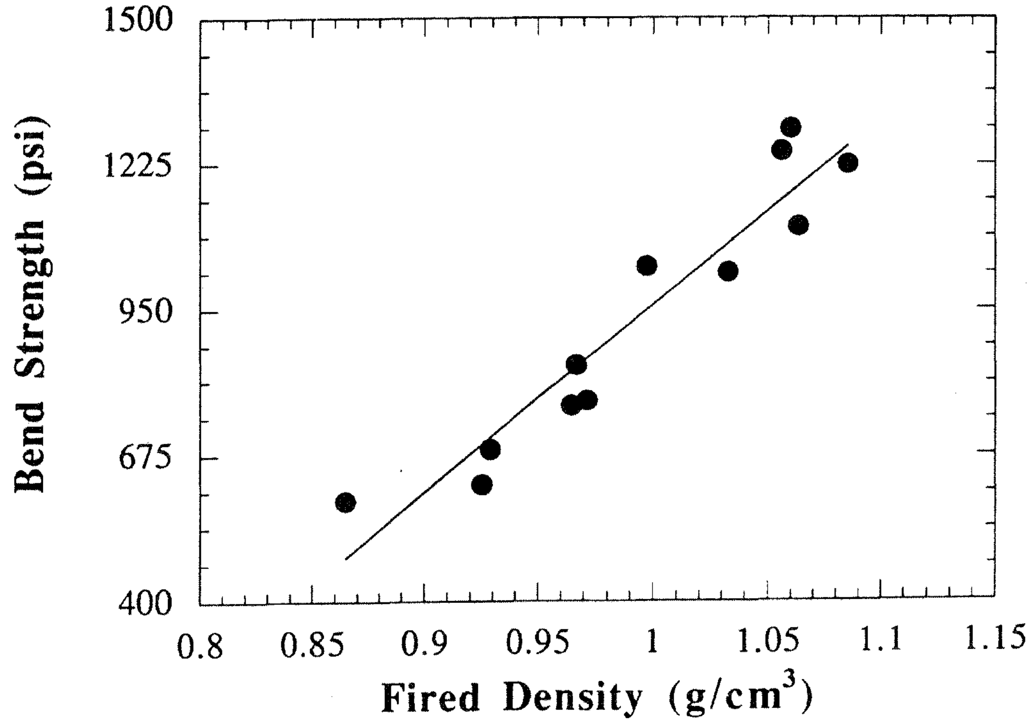


(b) after fired at 900°C for 6 hours

Figure 3. Bend strength of test coupons fabricated with Lanxide 15 μm alumina-boron oxide powder blends

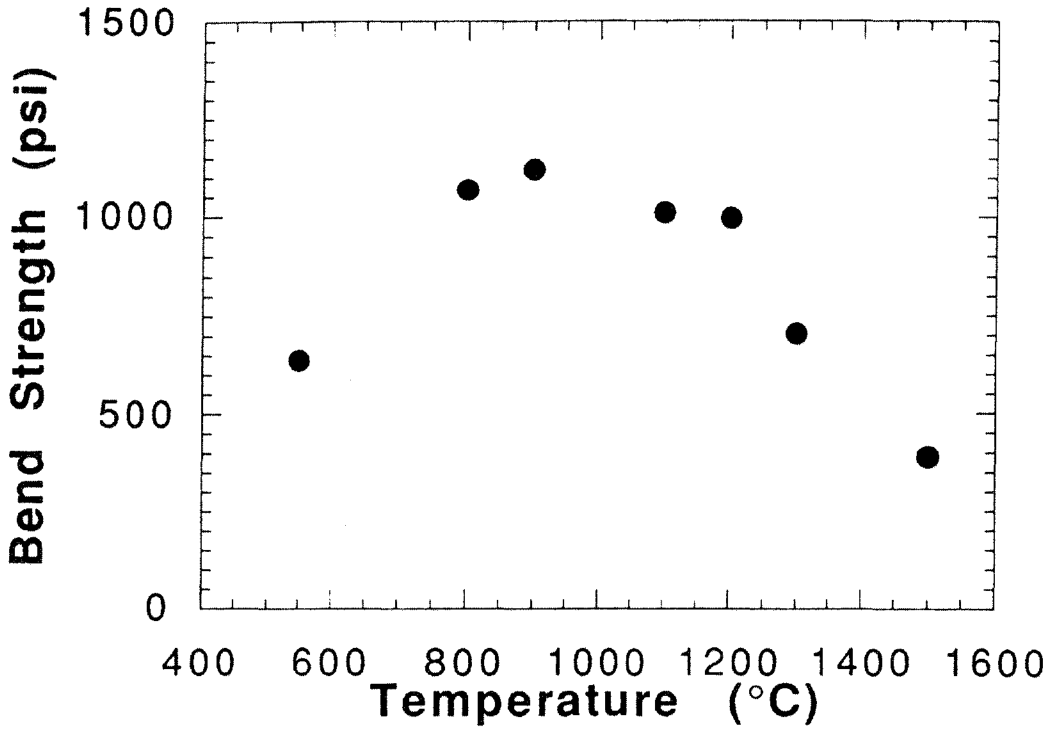


(a) Effect of laser power density on the density

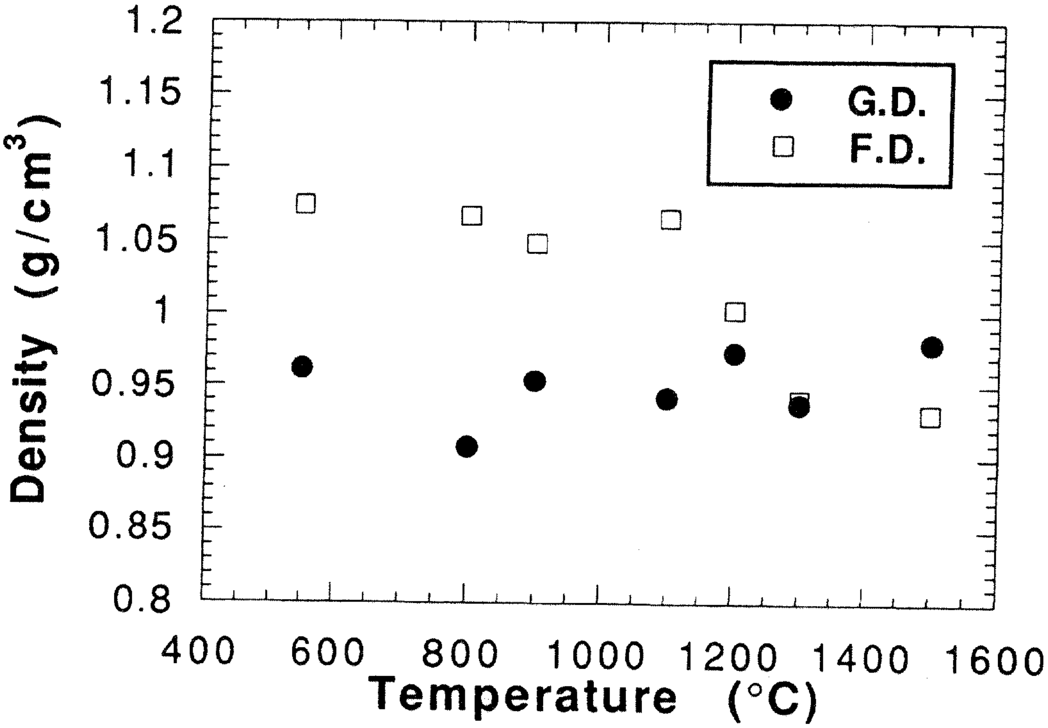


(b) Effect of fired density on the bend strength

Figure 4. Mechanical properties of green samples and samples, fired at 900°C for 6 hours, made from alumina-25 wt.% boron oxide powder blend

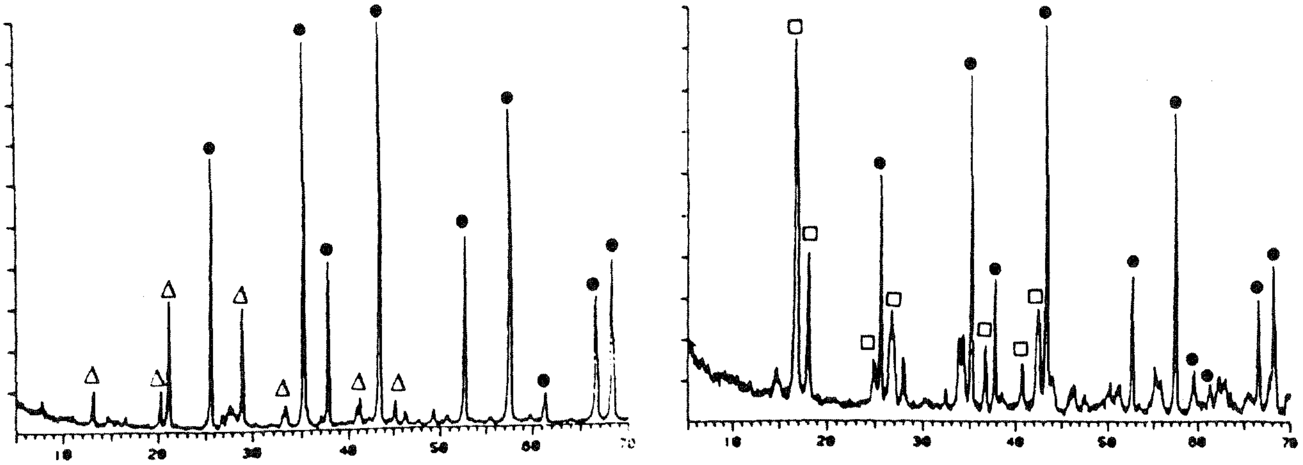


(a) Bend strength



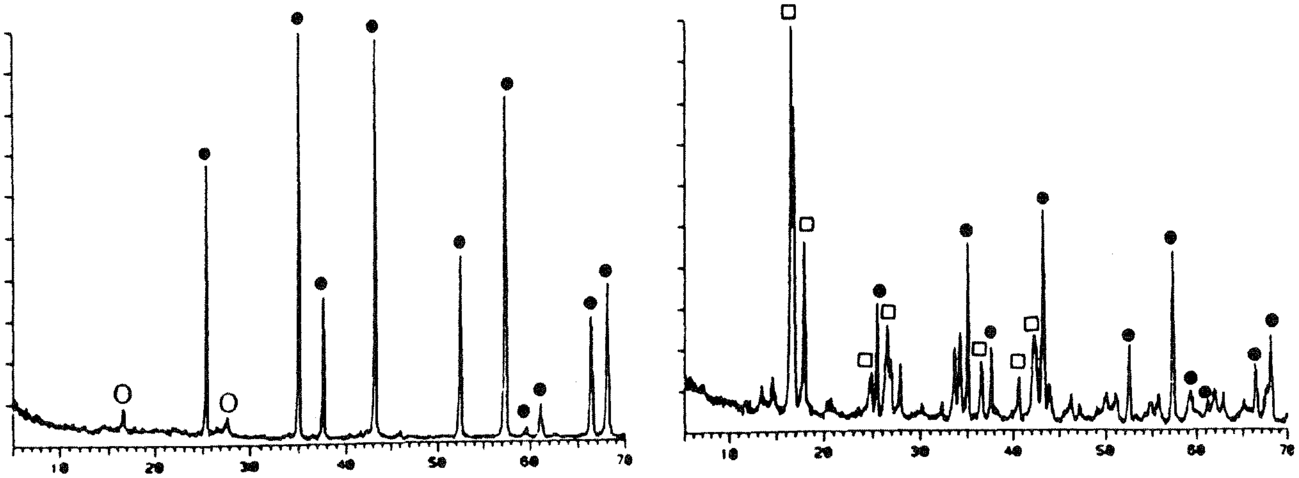
(b) Density

Figure 5. Effect of firing temperature on the mechanical properties of samples made from alumina-25 wt.% boron oxide powder blend



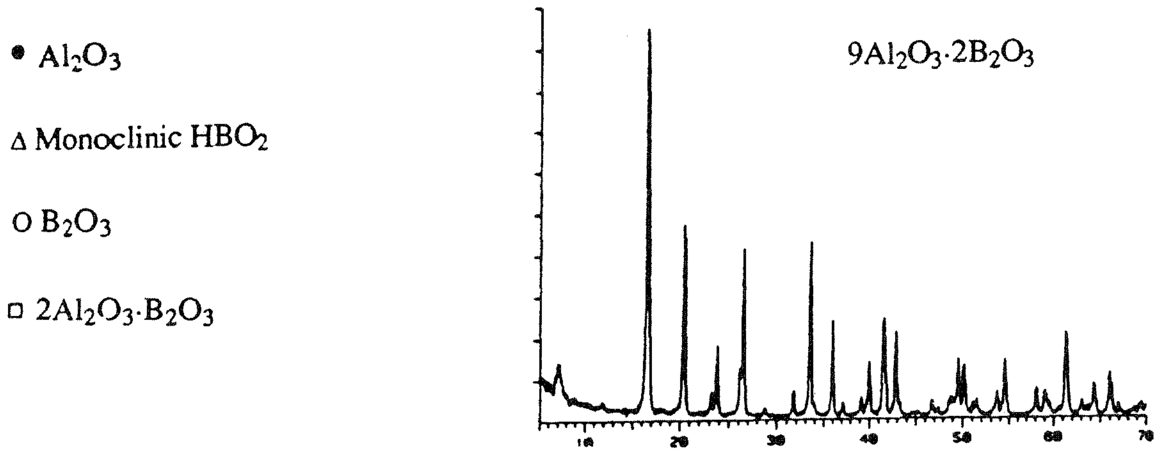
(a) before SLS

(c) fired at 800°C



(b) fired at 700°C

(d) fired at 1100°C



(e) fired at 1200°C

Figure 6. X-ray diffraction analysis of alumina-25 wt.% composites fired at various temperatures for 6 hours

$9Al_2O_3{\cdot}2B_2O_3$ [11]. Below 1300°C, secondary heat treatments increase the density, whereas above 1300°C, fired density is lower than the green density due to the increase in porosity associated with the decomposition of the $9Al_2O_3{\cdot}2B_2O_3$ phase (Fig. 5(b)).

## Summary

It was demonstrated that both a composite body $Al_2O_3$-$2Al_2O_3{\cdot}B_2O_3$ and a monolithic material $9Al_2O_3{\cdot}2B_2O_3$ could be successfully fabricated by selective laser sintering and reactive sintering of the material system $Al_2O_3$-$B_2O_3$. The bend strength of the composite body increases as the binder content increases. At higher laser power density, the composites show higher bend strength due to higher density. At intermediate firing temperatures around 800-1100°C, test bars show higher bend strength due to the formation of aluminum borate ($2Al_2O_3{\cdot}B_2O_3$) at the surface of the alumina particles by the reaction of alumina and boron oxide at around 800°C.

## Acknowledgments

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