알루미나 분말의 선택적 레이저 소결을 하기 위한 새로운 무기 접착제의 개발

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Development of a New Inorganic Binder for Selective Laser Sintering of a Alumina Powder

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초   록 저용융점을 가진 새로운 무기 접착제인 단사정 HBO_2가 알루미나 분말의 선택적 레이저 소결을 하기 위한 접착제로서 개발되었다. 이것을 이용하여 만들어진 green body는 현재까지 알루미나 분말의 선택적 레이저 소결을 위하여 개발된 다른 무기 접착제들인 알루미늄(Al)과 Ammonium Phosphate($NH_4H_2PO_4$)을 이용하여 제조된 것에 비교하여 훨씬 높은 굽힘 강도를 가지고 있고 또 정밀도가 우수하였다. Green Body를 열처리하여서 얻는 세라믹 시편도 똑같은 결과를 보여주었다. 이 이유는 단사정 HBO_2가 낮은 점도를 보여주고 알루미나 분말에 대하여 좋은 젖음성을 가지고 있기 때문에 가능한 것으로 사료되어진다. 알루니마 분말과 단사정 HBO_2 분말의 균일한 혼합체를 선택적 레이저 소결 처리에 의해서 얻어진 Green Body는 후속의 열처리를 받음으로써 저밀도 단상 세라믹 $Al_{18}B_4O_{33}$과 다상 세라믹 복합재료 Al_2O_3-$Al_4B_2O_9$으로 된다. $Al_{18}B_4O_{33}$과 $Al_4B_2O_9$의 결정립의 모양은 휘스커 구조와 유사하였다. 재료인자와 가공변수가 이 세라믹의 기계적 및 물리적 성질에 미치는 영향이 조사되었다.

Abstract A new low melting inorganic binder, monoclinic HBO_3, has been developd for Selective Laser Sintering (SLS) of alumina. It leads to better green SLS parts and higher bend strength for green and fired parts compared to other inorganic binders such as aluminum and ammonium phoshate. This appears to be due to its low viscosity and better wettability of the alumina particle surface. A low density single ceramic borate ($Al_{18}B_4O_{33}$), and multiphase ceramic composites, Al_2O_3-$Al_4B_2O_9$, have been successfully developed by laser processing of alumina-monoclinic HBO_3 powder blends followed by post-thermal procedding; both $Al_{18}B_4O_{33}$ and $Al_4B_2O_9$ have whisker-like grains. The physical and mechanical properties of these SLS-processed ceramic parts are correlated to the materials and processing parameters.

1. Introduction

Solid Freeform Fabrication (SFF) is an advanced manufacturing technology which generates geometrical objects directly from a three-dimensional image without part-specific tooling or human intervention[1~2]. These 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. 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 the powder bed and bind the loose powder, making a thin layer of powder. The sintered layer is lowered from the sintering plane
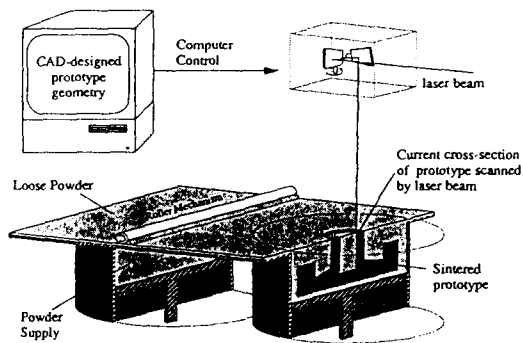
Fig. 1. Schematic representation of a SLS system.

and a new layer of the powder is spread again. 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[3~4]. The overall schematic of the SLS process is shown in Figure 1. The primary advantage of the SLS process is the flexbillty of selection of material systems compared to other SFF techniques.[5]

The two-phase powder approch to SLS, which involves binding high temperature ceramics such as alumina and sillicon carbide with a low melting inorganic binder, is a promising technology to fabricate ceramic composite parts[6~9]. The selection of an optimum materials system for this approch depends on materials properties such as the melting point of the binder materials and interparticle wetting between the components in the composite powder blend[10].

In a suitably chosen system, the low melting phase completely or partially under the laser beam and binds the high melting phase particles. Furthermore, it can react in some cases with the high melting phase or with the atmosphere. Further reaction can also takes place in a subsequent heating step. As a result, either another compound may incorporate into the matrix or a single phase compound may result.

The first advantage of this two-phase pow-

der approach is an immediate access to the conventional low temperature SLS equiment for processing of high melting ceramic and metal powders without requiring the high temperature station. The second one is the possibility to avoid balling problem, which is frequently observed in the SLS process of single metal powders such as lead, zinc or tin[11~12]. When the laser beam selectively scans the powder bed, the molten particles coalesce into a sphere than wet the solid particles. The diameter of the sphere is about the same as that of the laser beam. This phenomenon is referred to as "balling"[13]. The thrid one is the capability to introduce a second phase such as intermetallics and compounds into the matrix or to synthesize a new single phase if the material system is relevantly selected.

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[14]. The low viscosity of boron oxide is attributed to its linked-ring structure, since threr is a high probability that the bonds between rings are more susceptible to failure than the bonds within the rings[15].

The alumina-boron oxide composite system is attractive for SLS because boron oxide has a low melting point (450℃) 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[5]. A better wetting of solid alumina powder by molten boron oxide can further enhance densification process.

There are two stable crystalline compounds in the Al_2O_3-B_2O_3 system as seen in the phase diagram (Figure 2)[16]. One is $9Al_2O_3 \cdot 2B_2O_3$, the other is $2Al_2O_3 \cdot B_2O_3$. Both the compounds have orthorhombic crystal structure. Even though the meiting point of $9Al_2O_3 \cdot 2B_2O_3$ is 1950℃ according to the phase diagram, it is
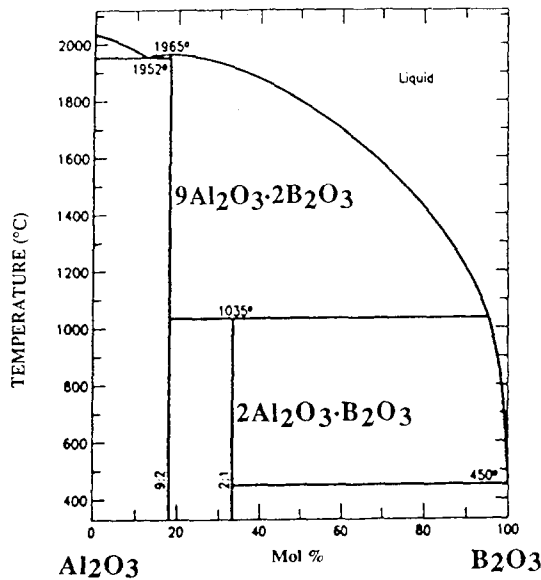
Fig. 2. Al₂O₃-B₂O₃ Phase diagram

Fig. 3. Flow chart for selective laser sintering of alumina-boron oxide composites.

somewhat unstable above 1500℃ due to the vaporization of B₂O₃. The melting point of 2Al₂O₃ · B₂O₃ is 1035℃. It ls likely that SLS of Al₂O₃-B₂O₃ powder blend can offer the possibility of incorporating compounds into the alumina matrix or of generating a single phase if the composition is suitably selected.

However, there is a disadvantage of boron oxide as an inorganic binder for SLS of alumina. Direct use of boron oxide as a low temperature phase for SLS of alumina with bed heating around 80℃ causes a weak cake through the whole powder bed during SLS process. The cake paralyzes the powder delively and leveling system. In order to overcome this barrier, phase transformation of boron oxide into various metaboric acid HBO₂ by dehydration process has been carried out. The selection of one of metaboric acid HBO₂ as a binder instaed of boron oxide for SLS of alumina might solve that problem.

This paper present (1) the experimental procedures related to the development of a new inorganic binder, monoclinic HBO₂, for SLS application, and (2) the synthesis of a single phase ceramic or multiphase ceramic composites by laser processing of alumina-monoclinic
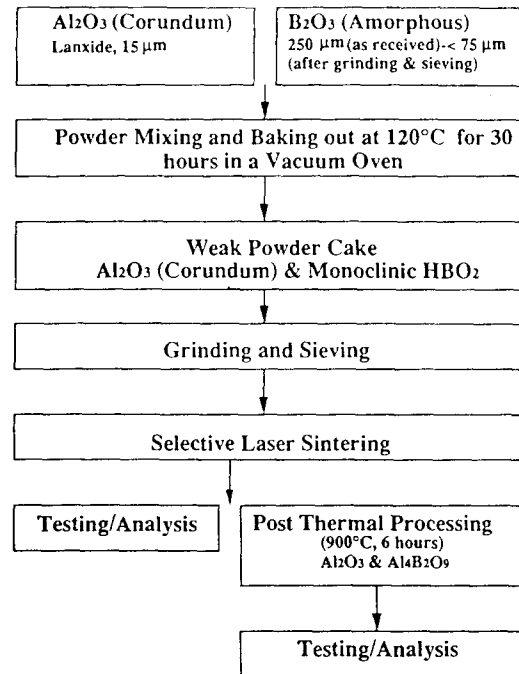
HBO₂ powder blends followed by post-thermal processing. The roles of materials, as well as laser and processing parameters on the mechanical and microstructural properties of the green and post-processed SLS pars are discussed.

2. Materials and Experimental Procedures

High purity alumina (melting point 2050℃) was chosen as a high melting component since it is one of the most widely used advanced and is relatively low in cost in comparison to other high temperature ceramic materials. Boron oxide (melting point 450℃) was selected as a staring low melting phase.

For this reserach, high purity, electronic grade 15 μm, alumina oxide powder provided by Norton Materials Corporation and a 60 mesh (250 μm) 99% boron oxide from Johnson Mathey are the staring materials. The initail borton oxide powder of 250μm was ground by a Szegvari attritor system and sieved to less than 75 μm.

Table I. SLS operational parameters of alumina-monoclinic HBO$_2$ powder blends.

Laser Power (W)	Bed Temperature (℃)	Scan Spacing (μm)	Layer Thickness (μm) 25 × 30 Layers	Scan Speed (m/sec)
14～16.5	80 - 100	125	200 - 250	0.32～1.19

Figure 3 shows the overall steps associated with SLS process and materials characterization. Alumina and boron oxide powder blends in various ratios by weight were baked out in a vacuum oven at 120℃ for 30 hours. Pre-thermal treatment caused the powder blends to form weak powder cakes, which were subsequently broken and sieved. This powder was analyzed by X-ray Diffraction (XRD) to check the formation of monoclinic HBO$_2$. If the transformation of monoclinic HBO$_2$ is not complete, then the baking-out process is repeated. Baked-out powder blends were immediately sintered in a SLS system of the University of Texas at Austin. Single layer tests were carried out on these powders with various laser power and scan speed to determine optimum laser operational conditions. Test specimens with dimension of 0.076m × 0.025m × 0.00625m (3" × 1" × 0.25") were fabricated in an inert nitrogen environment using the opertional parameters listed in Table I.

When the SLS parts were complete, excess unsintered powder was removed by brusing off with a paint pen. The green parts were then heated to 800℃ with a heating rate of 5℃/ min and then to the final heat-treatment temperature with a heating rate of 2℃/min in a MoSI$_2$ furnace. After keeping at the final heat treatment for 6 hours, the parts were cooled back to 800℃ with a cooling rate of 2℃/min and then to room temperature with a cooling rate of 5℃/min.

The strengths of SLS parts in the green state as well as after firing at various temperatures for 6 hours were determined by 3-point bend test using an Instron constant displacement rate machine. Densities were obstained by direct measurement of dimension and mass.
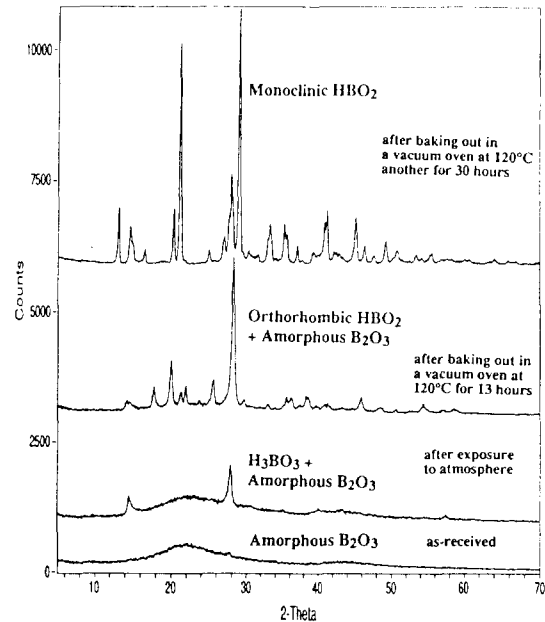

Fig. 4. X-ray diffraction patterns showing of alumina -boron oxide composites.

Indentification of phase and microstructural evolution at every step of processing was carried out by X-ray diffraction analysis and Scanning Election Microscope (SEM).

3. Results and Discussion

Fig. 4 shows transformation of the initial boron upon reaction with atmospheric water. The as received boron oxide is amorphous. It reacts with moisture in air and transforms into crystalline boric acid (H$_3$BO$_3$) 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℃) in comparison to boron oxide (450℃), it causes a weak bed cake through the whole powder bed during

SLS process with bed heating around 80℃. 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. Furthermore, the amorphous boron oxide needs to be transformed to another phase to prevent further transformation into boric acid during SLS process, because it is too hygroscopic. It is known that dehydration of boric acid gives different forms of crystalline metaboric acid HBO_2 or boron oxide B_2O_3 depending on the baking out temperature. Table II shows the physical properties of various forms of metaboric acid HBO_2 [14]. Therefore, conversion of the initial B_2O_3 or HBO_2 might be an attractive solution to this problem.

The conversion to HBO_2 requires a partial dehydration of boric acid above 100℃ as shown in Equation 1,

$$H_3BO_3 \xrightarrow{120℃} HBO_2 + H_2O \qquad (1)$$
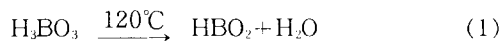
The dehydration process was carried out in a vacuum oven, manufactured by Cole-Parmer, that was connected to the housing vacuum line operating at a pressure of about 280 Torr.

The selection of the baking out temperature was based on the experimental results. The ground and sieved (less than 75μm) boron oxide powder, which contain some boric acid (H_3BO_3) due to exposure to air, yielded orthorhombic HBO_2 after a baking out ar 120℃ for 12 hours. However, the amorphous boron oxide still remained as indicated by an amorphous background in the X-ray pattern (Figure 4). A careful dehydration of this powder at 120℃ in a rough vacuum oven for about another 30

Table II. Physical properties of crystalline metaboric acid HBO_2.

|	CB * of B	Density (g/cm^3)	Melting Point (℃)
Orthorhombic	3	1.784	176
Monoclinic	3 and 4	2.045	201
Cubic	4	2.487	236

* CN refers to coordination number

hours and slow quenching after bake-out yielded monoclinic metaboric acid HBO_2 whose melting point is 201℃. Moreover, the amorphous B_2O_3 phase completely transformed to monoclinic HBo_2 after this process. It seems that the amorphous boron oxide absorbs moisture and transforms to boric acid during the grinding process, which then transforms into the monoclnic HBO_2 via the orthorthombic HBO_2 during the second bake-out process. It is found that monoclinic HBO_2 avoids the bed caking phenomenon with powder bed heating at 80℃ and reduces the curling problem significantly during SLS process.

Unfortunately cubic HBO_2 could not be obtained by the dehydration of boric acid (H_3BO_3). It is likely that the partial vapor pressure of boric acid inside the oven play an important role on the phase transformation. In addition, a higher baking out temperature is needed to obtain cubic HBO_2. Further study will be required in the future in order to understand the formation of cubic HBO_2 from boric acid through dehydration. Orthorhombic HBO_2 was determined to be too hygroscopic for SLS application; on the other hand, monoclinic HBO_2 was lightly hygroscopic since its transformation to boric acid was slow compared to orthormbic HBO_2.

The performance of monoclinic HBO_2 as an inorganic binder for SLS of alumina was evaluatet by the bend strength of the parts in the green state as well as after firing at 900℃ for 6 hours with respect to the key SLS operational parameter such as laser energy density.

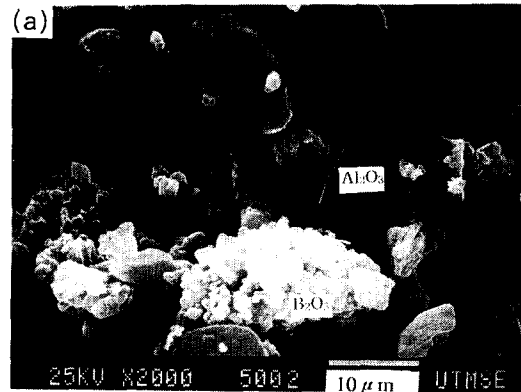The effect of binder content on bend strength of the composite (both green and after fir-
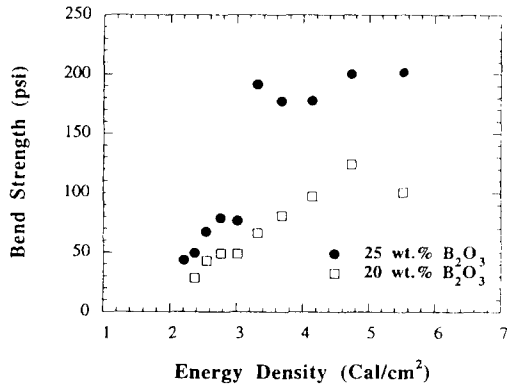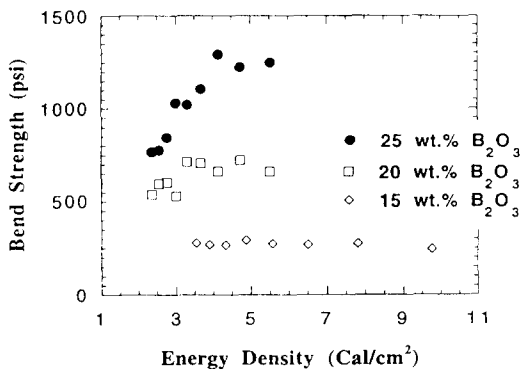
Fig. 5. (a) Bend strength of green test coupons fabricated with 15 μm alumina-boron oxide powder blends. (b) Bend strength of coupons fabricated with 15 μm alumina-boron oxide powder blends after firing at 900 ℃ for 6 hours.

Fig. 6. SEM Micrographs of the fracture surface of green parts fabricated with alumina-25 wt.% boron oxide powder blend: (a) low laser energy density and (b) high laser energy density.

ing at 900℃ for 6 hours) is illustrated in Figure 5. The bend strength of the composites increases as the binder content increases since all the ceramic interparticle bonds that provide the strength to the composites originate from the melting of the binder and the coating of ceramic (alumina) particles by the binder melt during laser beam irradiation. During post-thermal processing step, boron oxide reacts with alumina, resulting in aluminum borate $(2Al_2O_3 \cdot B_2O_3)$ whiskers at the surface of the alumina particles. The strength of the parts fired at 900℃ for 6 hours increases as the binder content increases. This is because the higher the binder content, the more would be the aluminum borate whiskers at the surface of alumina particles and hence higher would

be the strength.

The effect of laser energy density on bend strength is also shown in Figure 5. Energy density is defined as laser power/ (scan spacing X scan speed)[17]. At lower energy density, the green composites show poor strength due to insufficient melting and flowing of the binder compared to those at higher energy density where molten binder coats the ceramic particles completely as revealed by SEM (Figure 6). Similarly, the bend strength of fired parts fabricated with 25 and 20 wt.% boron oxide powder blends is proportional to the energy density due to an increasing local melting and flowing of the binder. As a result, at higher

(a) low laser energy density
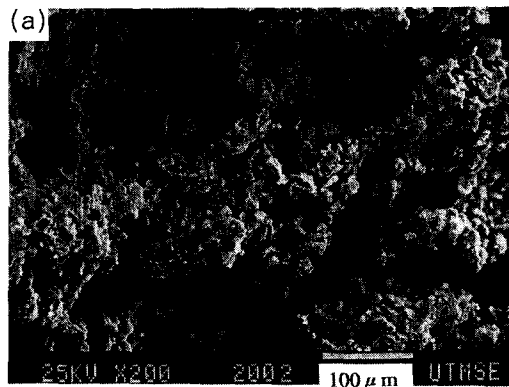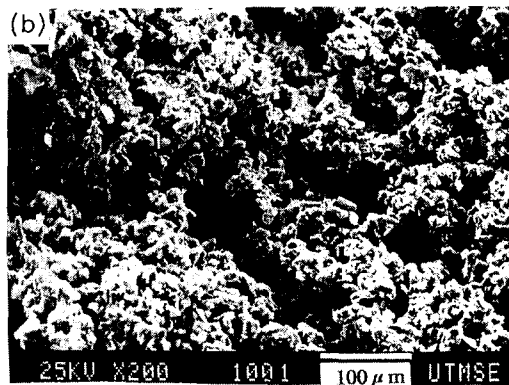

(b) high laser energy density

Fig. 7. SEM Micrographs of the fracture surface of parts fabricated with alumina-25 wt.% boron oxide powder blend after firing at 900℃ for 6 hours: (a)low laser energy density and (b) high laser energy density.

Energy Density (Cal/cm^2)

Fig. 8. Effect of laser energy density on the density of green samples and samples fired at 900℃ for 6 hours. The parts were made with alumina-25wt.% boron oxide powder blend.

laser energy density, more ceramic particles are encapsulated by the molten binder compared to at lower energy density as revealed by SEM (Figure 7). Also, the green and fired part density increases as the energy density increases (Figure 8), which is in accordance with increasing strength with increasing energy density. However, bend strength of fired test bars made with 15 wt.% boron oxide is independent of energy density (Figure 5). For this system, it was required that the process be done at higher bed temperature (100℃) and at higher energy density in order to melt the small amount of the binder completely and bind ceramic particles together. The higher energy density used might be above the threshold
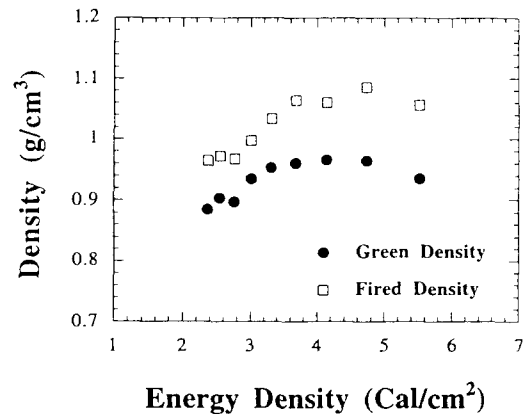
energy density required to melt the whole binder thoroughly and fabricate green parts which can keep the shape. Therefore, the strength of the fired parts is independent of energy density since there is no more additional binder which will coat the ceramic particles.

Figure 9 shows the effect of firing temperature on the mechanical and physical properties of parts fabricated with 25 wt.% boron powder blends. At intermediate firing temperature at around 800℃~1100℃, the test bars show higher bend strength due to the formation of aluminum borate (2Al$_2$O$_3$ · B$_2$O$_3$) at the surface of the alumina particles by the reaction of alumina and boron oxide at around 800℃. The morphology of 2Al$_2$O$_3$ · B$_2$O$_3$(Al$_4$B$_2$O$_9$) was identified by SEM to be a whisker structure (Figure 10). Below 700℃, it was found that there was no substantial reaction between alumina and boron oxide. Thus, the bend strength of the test bars fired at 550℃ is much lower than that of the samples fired at higher temperatures, even though the fired density of samples at firing temperatures up to 1100℃ is almost similar. Therefore, the formation of whisker-like aluminum borate (2Al$_2$O$_3$ · B$_2$O$_3$) grains at the surface of the alumina particles by the reaction beween alumina and boron oxide seems to play a key role on the increase of
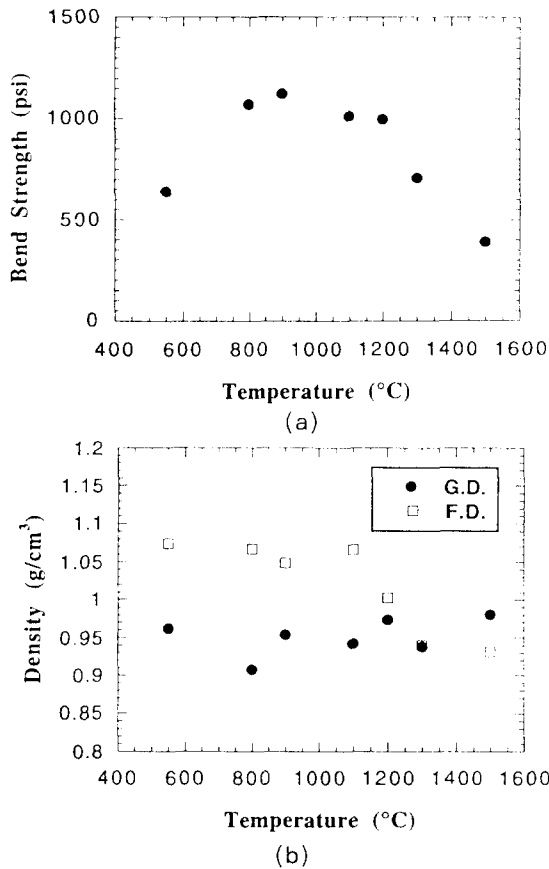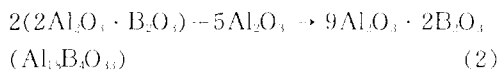
Fig. 9. (a)Effect of firing temperature on the bend strength of samples made with alumina-25 wt.% boron oxide powder blend. (b) Effect of fining temperature on the density of samples made with alumina-25 wt.% boron oxide powder blend.
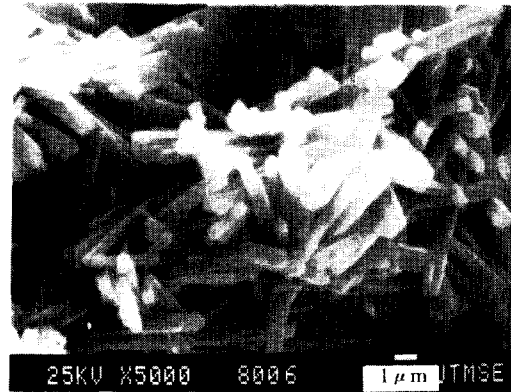

Fig. 10. SEM Micrograph of fracture surface of samples fabricated with alumina-25 wt.% boron oxide after firing at 800 C.

whereas above 1300°C, fired density is lower than the green density due to the increase of porosity associated with the vaporization of excess B_2O_3. Moreover, the morphology of the aluminum borate ($9Al_2O_3 \cdot 2B_2O_3$) whisker becomes clearer as the temperature increases as revealed by SEM. This is expected to be due to the vaporization with firing temperature of excess boron oxide that covers the spaces between $9Al_2O_3 \cdot 2B_2O_3$ whiskers.

4. Conclusions

It has been shown that monoclinic HBO_2 is a potentially useful inorganic binder for SLS of alumina to obtain structurally sound parts. It was also 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 sucessfully 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 energy density, the composites show higher bend strength due to higher density. For intermediate firing temperatures around 800°C~1100°C, test bars show higher bend strength due to the formation of whisker-like aluminum borate ($2Al_2O_3 \cdot B_2O_3$) grains at the surface of the alumina particles by the reaction of alumina and boron oxide. For a

bend strength. According to X-ray diffraction analysis, the amont of $2Al_2O_3 \cdot B_2O_3$ increases relative to that of alumina as the firing temperature increases up to 1100°C. For a firing temperature 1200°C, another aluminum borate ($9Al_2O_3 \cdot 2B_2O_3$) whisker forms by the reaction of alumina and aluminum borate ($2Al_2O_3 \cdot B_2O_3$)[5].

$$2(2Al_2O_3 \cdot B_2O_3) - 5Al_2O_3 \rightarrow 9Al_2O_3 \cdot 2B_2O_3$$
$$(Al_{18}B_4O_{33}) \tag{2}$$

The bend strength of samples fired at 1300°C, and 1500°C decreases due to loss of structural integrity resulting form the vaporization of excess B_2O_3 component after the formation of $9Al_2O_3 \cdot 2B_2O_3$[5]. Below 1300°C, secondary heat treatments increase the density,

firing temperature of 1200℃, single phase $9Al_2O_3 \cdot 2B_2O_3$ which has a whisker structure is formed by the reaction.
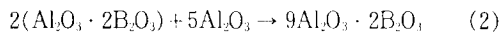
$$2(Al_2O_3 \cdot 2B_2O_3) + 5Al_2O_3 \rightarrow 9Al_2O_3 \cdot 2B_2O_3 \qquad (2)$$

The morphology of the aluminum borate ($9Al_2O_3 \cdot 2B_2O_3$) whisker becomes clerer as the firing temperature increases due to the vaporization with increase of firing temperature of excess boron oxide, which covers spaces between $9Al_2O_3 \cdot 2B_2O_3$ whiskers.

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