

A Potentially Useful Inorganic Binder for SLS of Alumina Powder

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알루미나 분말의 선택적 레이저 소결의 가능성을 보여주는 유용한 무기접착제

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초 록 저용융점을 가진 새로운 무기접착제인 단사정 HBO_2 가 알루미나 분말의 선택적 레이저 소결을 하기 위한 접착제로서 개발되었다. 120°C 로 유지된 진공오븐 안에서 Boron Oxide 분말을 탈수시키면 단사정 HBO_2 가 만들어진다. 이것을 이용하여 만들어진 green body는 현재까지 알루미나 분말의 선택적 레이저 소결을 위하여 개발된 다른 무기 접착제들인 알루미늄 (Al)과 Ammonium Phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$)을 이용하여 제조된 것에 비교하여 훨씬 높은 굽힘 강도를 가지고 있고 또 정밀도가 우수하였다. Green body를 열처리하여서 얻은 세라믹 시편도 똑같은 결과를 보여주었다. 이 이유는 단사정 HBO_2 가 낮은 점도를 보여주고 알루미나 분말에 대하여 좋은 젖음성을 가지고 있기 때문에 가능한 것으로 사료되어진다. 접착제로서 Boron Oxide의 양, 레이저 에너지 밀도 등이 SLS에 의하여 제조되어진 복합재료의 굽힘강도에 미치는 영향이 조사되었다.

Abstract A new low melting inorganic binder, monoclinic HBO_2 , has been developed for Selective Laser Sintering (SLS) of alumina by dehydration process of boron oxide powder in a vacuum oven at 120°C . It led to better green SLS parts and higher bend strength for green and fired parts compared to other inorganic binders such as aluminum and ammonium phosphate. This appeared to be due to its low viscosity and better wettability of the alumina particle surface. The role of boron oxide content, as a binder, and laser energy density on the bend strength of the composites, fabricated by the SLS process, were investigated.

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⁾ 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 a powder bed, binding loose powder, to make a thin layer of bound powder. The sintered layer is lowered from the sintering plane 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.²⁾ The overall schematic of the SLS process is shown in

Fig. 1.³⁾ The primary advantage of the SLS process is the flexibility of selection of material systems compared to other SFF techniques.⁴⁾

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.^{5~7)} The selection of an optimum material systems for this approach depends on material properties such as melting point of the binder material and interparticle wetting between the components in the composite powder blend.⁸⁾

In a suitably chosen system, the low melting phase melts 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 take 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 powder approach is an immediate access to the conventional low

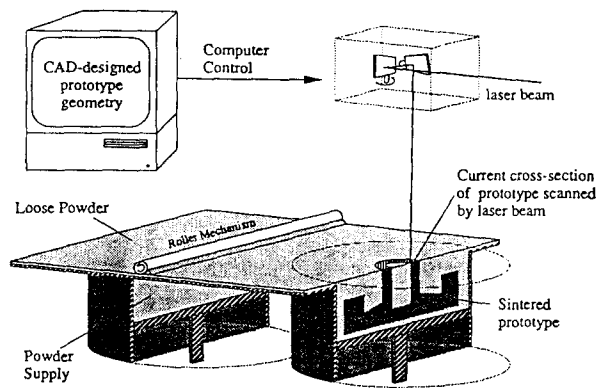
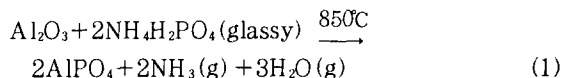


Fig. 1. Schematic representation of a SLS system.

temperature SLS equipment for processing of high melting ceramic and metal powders without requiring the SLS high temperature station. The second one is the possibility to avoid balling problem, which is frequently observed in the SLS process of single phase metal powders such as lead, zinc or tin.⁹ When the laser beam selectively scans the powder bed, the molten particles coalesce into a sphere rather than wet the solid particles. The diameter of the sphere is about the same as that of the laser beam spot size. This phenomenon is referred to as "balling".¹⁰ The third 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.

There are two kinds of intermediate binders for SLS of ceramic powders. One is an inorganic binder approach and the other is an organic binder, such as Poly Methylmethacrylate (PMMA), approach. Ammonium dihydrogen phosphate was first employed as an inorganic binder for the SLS of alumina.⁶ Ammonium dihydrogen phosphate has a low melting point (190 °C) and forms a glassy phase around alumina particles under the laser beam. During the subsequent firing step of green SLS part, the ammonium phosphate binder reacted with the alumina, resulting in aluminum orthophosphate (AlPO₄) as shown in Equation 1,



Thus, the composite after heat treatment was composed of Al₂O₃ and AlPO₄. This composite showed the bend strength of 2–8 MPa. The edge definition of the green and fired parts was not good. The significant decrease in density and strength of the fired composite as a result of the evolution of water and ammonia vapor precluded the possibility of application of that material at

higher temperatures above 880 °C.

Aluminum has recently been used as a binder for the SLS of alumina.⁷ Aluminum melts completely or partially under the laser beam and binds alumina particles. The subsequent heating step of the green part in air oxidized the aluminum into alumina completely. Even though post-thermal processing of the composite made single phase ceramic, the feature definition and the strength of the composite was poor. The weak strength of the green and fired parts is initially associated with the poor wetting between liquid aluminum and solid alumina, resulting in insufficient shape definition of the part. In addition, the residual stress developed by the differences in the coefficients of thermal expansion between aluminum and alumina caused a debonding between layers of the green SLS composite.

Therefore, development of better qualified inorganic binders for SLS of ceramic powder was an interesting research field. Boron oxide can be selected as a possible candidate for a new inorganic binder, since it has a low melting point and it is supposed that it melts easily during the laser beam irradiation. Furthermore, it is widely used in the glass industry. It is well 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.¹¹ 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.¹²

Especially, the selection of boron oxide as an inorganic binder is attractive for the SLS of an alumina–boron oxide composite system because boron oxide has a low melting point (450 °C) and the liquid generated due to the local melting of B₂O₃ 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. A better wetting of solid alumina powder by molten boron oxide can further enhance densification process.⁵

There are two stable crystalline compounds in the Al₂O₃–B₂O₃ system as seen in the phase diagram (Fig. 2).¹³ One is 9Al₂O₃ · 2B₂O₃, the other is 2Al₂O₃ · B₂O₃. Both the compounds have orthorhombic crystal structure. Even though the melting point of 9Al₂O₃ · 2B₂O₃ is 1950 °C according to the phase diagram, it is somewhat unstable above 1500 °C due to the vaporization of B₂O₃. The melting point of 2Al₂O₃ · B₂O₃ is 1035 °C. It is likely that the SLS of the Al₂O₃–B₂O₃ powder blend can offer

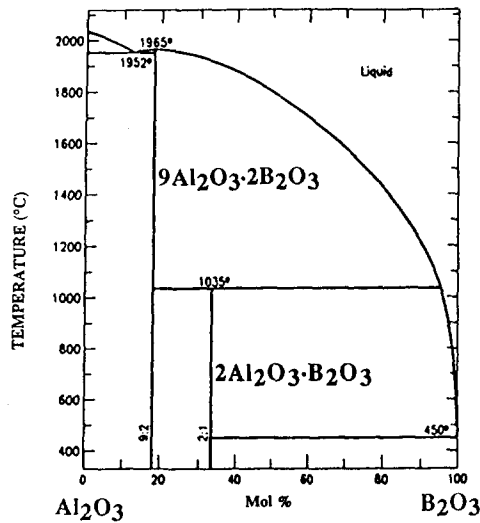


Fig. 2. Al_2O_3 - B_2O_3 phase diagram.

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 demerit of boron oxide as an inorganic binder for the SLS of alumina. Direct use of boron oxide as a low temperature phase for the SLS of alumina with a powder bed heating around 80°C causes a weak cake through the whole powder bed during the SLS process. The cake paralyzes the powder delivery and leveling system. The main reason for this phenomenon is attributed to the formation of boric acid (H_3BO_3) due to its much lower melting point (170°C) in comparison to boron oxide (450°C). X-ray diffraction pattern shows that the as-received boron oxide is amorphous and it transforms, upon exposure to air, to crystalline boric acid. As a result, the starting powder blend for laser sintering is in fact a mixture of alumina, amorphous boron oxide and boric acid.

It might be anticipated that a powder bed caking may be avoided during SLS processing if the powder bed heating is eliminated. However, curling of the previously sintered layers took place in the absence of the powder bed heating, which made the powder leveling difficult due to the displacement of those layers. It is known that the residual stresses induced by a negative temperature gradient between layers or within each layer result in curling.

2. Experimental Procedure

In order to overcome the powder bed caking and curling of sintered layers, the boric acid in the initial powder blend must be eliminated. Furthermore, the amorphous boron oxide needs to be transformed to another

phase to prevent further transformation into boric acid during the 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 temperature. Table 1 shows the physical properties of various forms of metaboric acid HBO_2 .¹¹⁾ Therefore, conversion of the initial B_2O_3 or H_3BO_3 to HBO_2 might be an attractive solution to this problem. 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. Among three kinds of metaboric acid HBO_2 , monoclinic HBO_2 was determined to be suitable for an inorganic binder for the SLS of alumina powder.

Table 1. Physical properties of crystalline metaboric acid HBO_2 .

	CN* of B	Density (g/cm^3)	Melting Point ($^\circ\text{C}$)
Orthorhombic	3	1.784	176
Monoclinic	3 and 4	2.045	201
Cubic	4	2.487	236

* CN refers to coordination number

It was also found that baking-out of a large quantity of boron oxide powder in order to transform it to monoclinic HBO_2 powder yielded a strong powder cake, which was hard to grind. In order to overcome the powder cake problem, mixtures of alumina and boron oxide powder were baked out instead of pure boron oxide powder. Thus, alumina and boron oxide powders were mixed in the ratio 3:1 (25 wt.% B_2O_3), 4:1 (20 wt.% B_2O_3), and 5.65:1 (15 wt.% B_2O_3) by weight. Each powder mixture was baked out in the vacuum oven. Furthermore, powder mixture after baking-out process delayed the phase transformation of monoclinic HBO_2 to boric acid due to less chance of exposure to air in comparison to the unmixed case; since monoclinic HBO_2 is metastable, it will eventually change to boric acid.

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 dimensions $0.076\text{ m} \times 0.025\text{ m} \times 0.00625\text{ m}$ ($3'' \times 1'' \times 0.25''$) were fabricated in an inert nitrogen environment using the operational parameters listed in Table 2. The performance of monoclinic HBO_2 as an inorganic binder for the SLS of alumina was evaluated

Table 2. SLS operational parameters of alumina- boron oxide powder blends.

Laser Power (W)	Bed Temperature (°C)	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

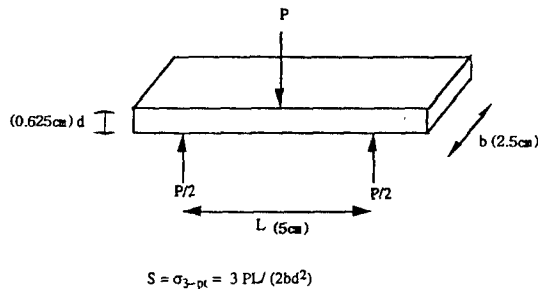
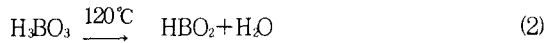


Fig. 3. Schematic of three point bend test.

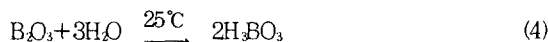
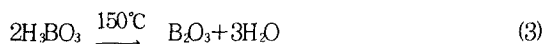
by the bend strength of the parts in the green state as well as after firing at 900 °C for 6 hours with respect to the key SLS operational parameter such as laser energy density. Energy density is defined as laser power / (scan spacing \times scan speed).³⁾ Fig. 3 shows the schematic of the three point bend test.

3. Results and Discussion

The conversion to HBO_2 requires a partial dehydration of boric acid above 100 °C as shown in Equation 2,



The selection of the baking out temperature was based on the experimental results. The ground and sieved (less than 75 μm) boron oxide powder, which contain some boric acid (H_3BO_3) due to exposure to air, yielded a weak agglomeration which contains orthorhombic HBO_2 phase after a baking out at 120 °C for 13 hours. However, the amorphous boron oxide still remained as indicated by an amorphous background in the X-ray diffraction pattern. Above a baking temperature of 150 °C, the powder produced strong agglomeration. X-ray diffraction pattern of this agglomeration showed reflections corresponding to H_3BO_3 and an amorphous background implying to the amorphous boron oxide after this bake-out procedure. This is because H_3BO_3 decomposes around 150 °C directly to B_2O_3 and H_2O as shown in Equation 3 and B_2O_3 absorbs moisture during grinding process to give H_3BO_3 as given in Equation 4,



Above 180 °C, the powder was completely fused and stuck to the bottom of the pyrex beaker. Thus, it was very hard to separate the fused powder from the beaker.

Therefore, the baking out temperature was selected as 120 °C. The powder baked out at 120 °C for 13 hours was ground to a fine powder using a mortar and a pestle by breaking the weak agglomeration. A careful dehydration of this powder at 120 °C in a rough vacuum oven for about another 30 hours and slow quenching after bake-out yielded monoclinic metaboric acid HBO_2 whose melting point is 201 °C. 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 monoclinic HBO_2 via the orthorhombic HBO_2 during the second bake-out process (Fig. 4). It was found that monoclinic HBO_2 avoided the powder bed caking phenomenon with a powder bed heating at 80 °C and reduced the curling problem significantly during SLS process. It is known that the residual stresses induced by a negative temperature gradient between layers or within each layer results in curling.

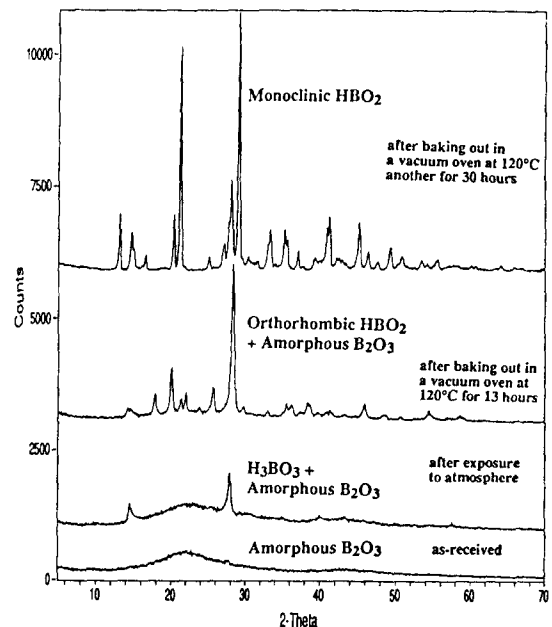


Fig. 4. X-ray diffraction patterns showing phase transformations of the initial boron oxide.

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 plays 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 orthorhombic HBO_2 .

Fig. 5 shows the effect of binder content on bend strength of the composites (both green and after firing at 900°C for 6 hours). 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 ($2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$) whiskers (Fig. 6) at the surface of the alumina particles. The strength of the parts fired at 900°C for 6

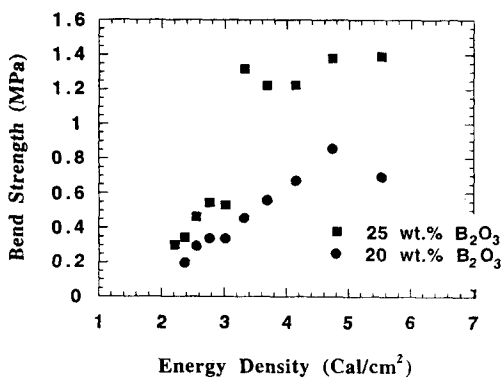


Fig. 5. (a) Bend strength of green test coupons fabricated with $15\ \mu\text{m}$ alumina-boron oxide powder blends.

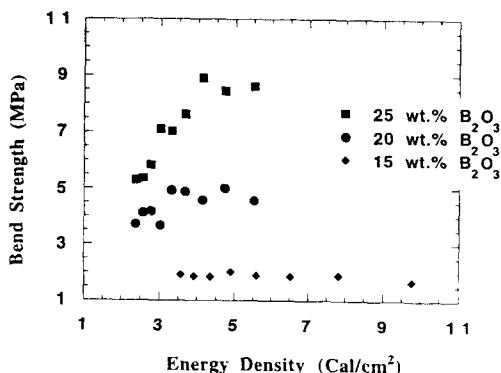


Fig. 5. (b) Bend strength of coupons fabricated with $15\ \mu\text{m}$ alumina-boron oxide powder blends after firing at 900°C for 6 hours.

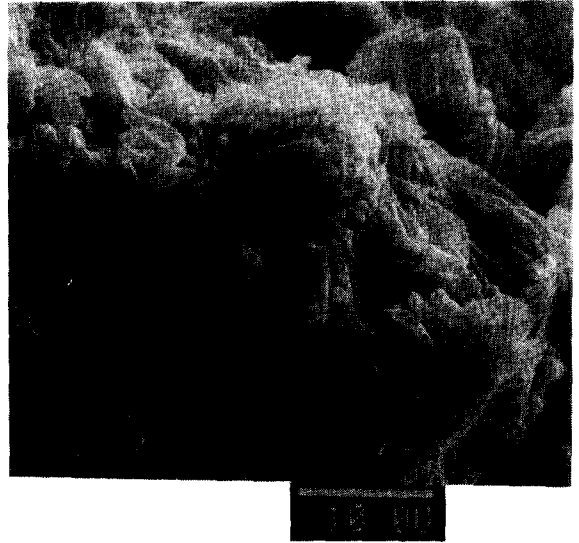


Fig. 6. (a) SEM Micrograph of fracture surface of samples fabricated with alumina-25 wt.% boron oxide after firing at 900°C for 6 hours.

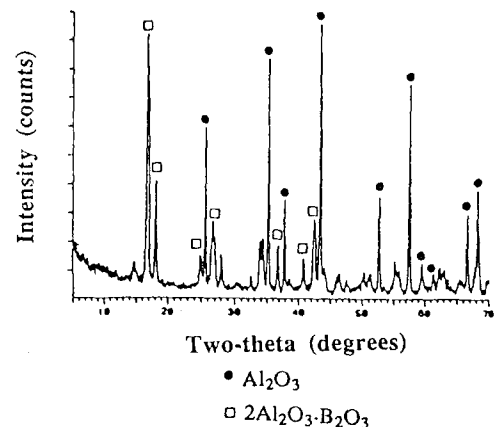


Fig. 6. (b) X-ray diffraction pattern of samples fabricated with alumina-25 wt.% boron oxide after firing at 900°C for 6 hours.

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. However, the bend strengths of these SLS samples were quite lower compared to a conventionally sintered Al_2O_3 (200–350 MPa).

The effect of laser energy density on bend strength is also shown in Fig. 5. 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. 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 laser

energy density, more ceramic particles are encapsulated by the molten binder compared to at lower energy density as revealed by SEM. Also, the green and fired part density increases as the energy density increases, 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. For this system, it was required that the process be done at higher powder bed temperature (100°C) 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.

4. Conclusions

It has been shown that a new low melting inorganic binder, monoclinic HBO₂, for the SLS of alumina powder can be developed successfully by dehydration process of boron oxide powder in a vacuum oven at 120°C. It was also demonstrated that a composite body Al₂O₃-2Al₂O₃ · B₂O₃ could be successfully fabricated by selective laser sintering and reactive sintering of the Al₂O₃-B₂O₃ material system. The bend strength of the composite body increased as the binder content increased. At higher laser energy density, the composites showed higher bend strength due to higher density.

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