MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF Al_2O_3 / P_2O_5 AND Al_2O_3 / B_2O_3 COMPOSITES FABRICATED BY SELECTIVE LASER SINTERING

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ABSTRACT

The feasibility of processing ceramic powders by Selective Laser Sintering has been reported in an earlier paper[1]. Material systems we have investigated include alumina based systems with ammonium phosphate or boron oxide as low temperature binders which are the systems discussed in this paper. With both systems, a secondary heat treatment is necessary to realize the high temperature properties of the materials. This paper will focus mainly on the mechanical properties of the composite bodies. In particular, the influence of particle size, powder mix composition, laser parameters and secondary heat treatment on density, strength and dimensional stability of the final product will be discussed.

INTRODUCTION

Deckard and Beaman[2] developed a new manufacturing technique called Selective Laser Sintering (SLS) to fabricate complex shapes without part-specific tooling or human intervention. In this process, a computer controlled laser beam is rastered on the surface of a powder bed. When the focussed beam impinges on the surface, powder heats up and localized bonding between particles take place. By laying down a number of such layers on top of each other and selectively sintering each layer, the shape is built in a matter of hours. SLS processing is ideally suited for low volume production environment like prototyping. Current prototyping techniques call for the fabrication of patterns, molds and dies. Fabricating these tools is both expensive and time consuming. SLS processing has the capacity to cut the lead time between design and part fabrication from weeks to a matter of hours.

The build rate depends on the complexity and size of the part, power output of the laser, the coupling between the laser and the material and the rheological properties of the material. Amorphous materials like ABS, PVC and wax do not exhibit a definite solid-liquid phase transformation temperature and the viscosity decreases slowly around the softening point of the material. On the other hand, crystalline materials like ammonium phosphate and boron oxide show a definite melting point at which the viscosity drops sharply.

The minimum energy to be supplied by the laser is the sum of the energy required to heat the powder bed to the melting point of the material and latent heat of fusion of the material. This minimum energy depends on the composition of the blend, the thermal properties of the powder such as the melting point and the thermal conductivity of the material and the porosity of the bed. In addition, the laser has to deliver enough energy to offset radiation losses from the powder bed and the energy to bond the topmost layer to the layer just below it. On the other hand, too much energy in the powder bed can lead to excessive differential contraction and high residual stresses. These residual stresses can cause shape distortion.

The application of this technique to process alumina / ammonium phosphate powder blend was reported in an earlier paper[1]. In this paper we report the effect of composition and particle size on the mechanical properties of the alumina - ammonium phosphate system. Initial studies on the alumina - boron oxide system is also reported.

MATERIAL SYSTEM

In the Al_2O_3 / $NH_4H_2PO_4$ system, alumina has a melting point of 2045°C while $NH_4H_2PO_4$ has a melting point of 190°C. When an alumina / ammonium phosphate blend is processed with a laser, the lower temperature material melts to form a glassy material and bonds the alumina particles. A secondary heat treatment is necessary to develop the full strength of the material. During heat treatment at 850°C, the following net reaction takes place.

$$Al_2O_3 + 2NH_4H_2PO_4 \text{ (glassy)} \rightarrow 2AlPO_4 + 2NH_3(g) + 3H_2O(g) \quad \text{---- (1)}$$

The reaction results in an Al_2O_3 / $AlPO_4$ composite in which aluminum phosphate forms a thin layer around the alumina particles. The volume fraction of the $AlPO_4$ depends on the initial mix composition.

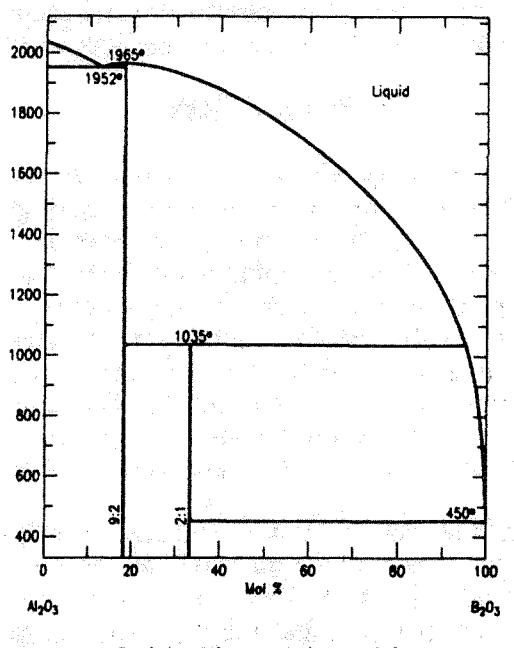

Fig. 1: Alumina - Boron Oxide Binary Phase Diagram.

In the Al_2O_3 / B_2O_3 powder blend, B_2O_3 with a melting point of 460°C acts as the low temperature phase. When heat treated Al_2O_3 reacts with B_2O_3 to form either $9Al_2O_3.2B_2O_3$ or $2Al_2O_3.B_2O_3$ depending on the Al_2O_3/B_2O_3 ratio in the initial mixture. The Al_2O_3 - B_2O_3 binary phase diagram[3] (Fig.1) indicates that the $9Al_2O_3.2B_2O_3$ phase is stable to 1950°C while the $2Al_2O_3.B_2O_3$ phase is stable to 1035°C. Rypinski et al [4] indicate that the $9Al_2O_3.2B_2O_3$ phase is stable only to 1200°C. At temperatures greater than 1200°C they report decomposition of $9Al_2O_3.2B_2O_3$ resulting in a loss of strength of the composite. This decomposition reaction depends on the B_2O_3 partial pressure over the solid.

MATERIAL PROCESSING CONDITIONS

To enhance the coupling between the laser and the powder bed, an low purity form of alumina was used. The composition of alumina as reported by the vendor* is Al_2O_3 95.13wt%, TiO_2 3wt%, SiO_2 0.75wt%, Fe_2O_3 0.46wt%, MgO 0.25wt%.

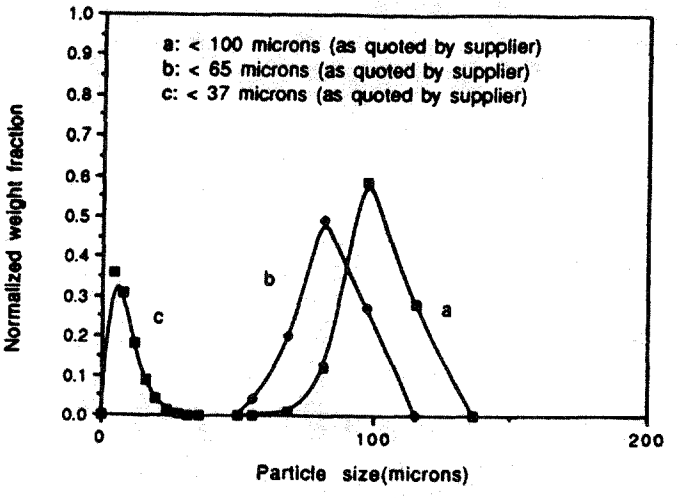

Fig2: Alumina Powder Size Distribution

The alumina particles were irregular in shape and their size distribution is shown in Fig.2. The ammonium phosphate particle size was kept constant at less than 37 microns throughout the experiment reported in this paper .

The powder mixes were processed using a Q-switched Nd:YAG (wavelength 1.06microns) laser operating at 40 kHz in the TEM00 mode with 20W incident power. No biasing temperature was used.

The laser processed material is subjected to secondary heat treatment according to the schedule shown in Fig. 3.

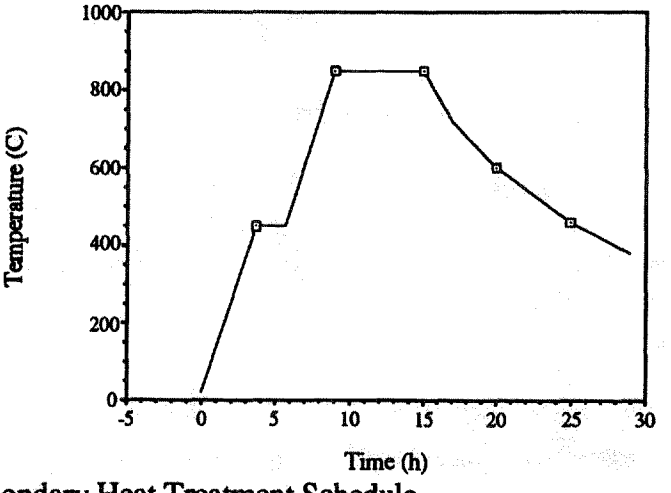

Fig 3: Secondary Heat Treatment Schedule

* Washington Mills Electro Minerals Corp. New York.

Firing shrinkage was measured on samples 76.2mm long, 25.4mm wide and 6.35mm thick. Shrinkage was calculated by measuring the change in dimensions of the sample after firing. The same specimens were used to determine the Modulus of Rupture by subjecting them to 4-point bending loads in an Instron Universal Testing Instrument. The build direction is parallel to the thickness of the specimen and the scan fast axis is parallel to the length of the specimen. Prefiring and postfiring densities were measured on samples with nominal dimensions of 12.7mm x 25.4mm x 25.4mm. Density was calculated by dividing the mass of the samples by their true volume determined from linear dimensions.

RESULTS AND DISCUSSION

Density of the laser sintered material depends on the efficiency of powder packing in the bed. Currently two different types of random packing are recognized in the literature. Loose random packing is obtained when the powder is simply poured into a container without any vibration. An upper limit of 0.60 has been determined[5] as the relative packing density of a unimodal spherical powder in loose packing. Tapping the loose packing arrangement would change the packing configuration to a close random packing arrangement and result in a small increase in packing (~ 0.63)[6]. For a bimodal distribution, packing efficiency is increased because the smaller particles occupy the voids between the larger particles. Packing efficiency in this case depends on both the ratio of the particle sizes and the fraction of fines in the mix.

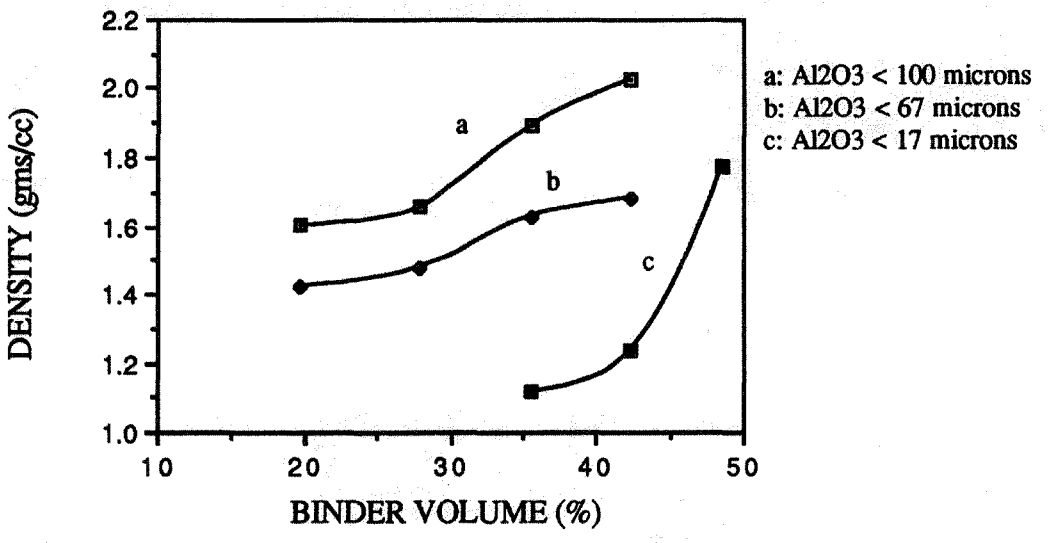

Fig. 3a. Variation of prefired density of Al_2O_3 - $NH_4H_2PO_4$ with alumina powder size and initial blend composition[7].

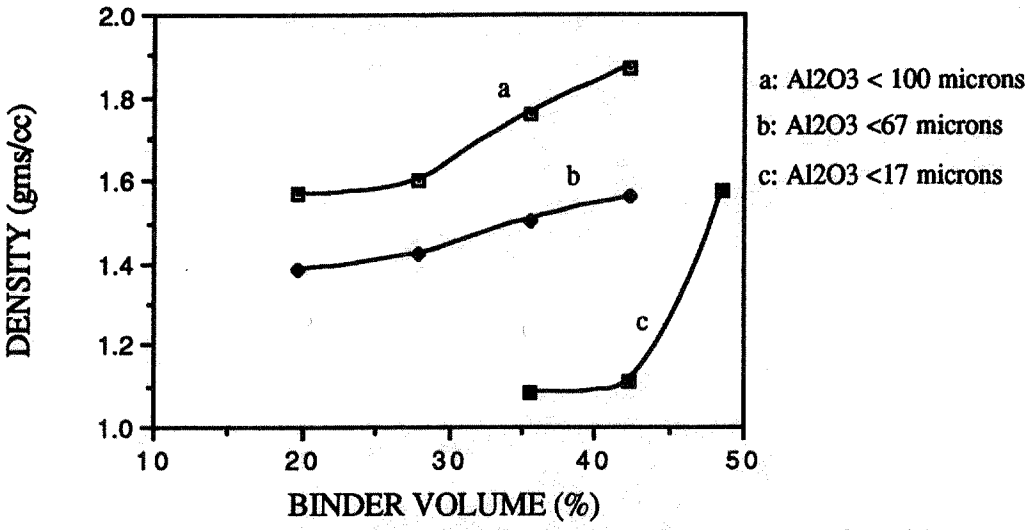

Fig3b. Variation of the density after firing of Al_2O_3 - $NH_4H_2PO_4$ with alumina powder size and initial blend composition[7].

The effect of alumina particle size and powder blend composition is seen in Figs.3a and 3b. In both figures curves a and b represent samples containing coarse alumina (<100 microns and <65 microns respectively) and fine ammonium phosphate (<37 microns). Curve c is for samples containing alumina (<17 microns) and ammonium phosphate (<37 microns) particles of similar sizes. It is seen that as the alumina particle size is increased from <17 microns to <100 microns for the same composition, density increases. This is largely due to the finer ammonium phosphate particles occupying the voids between the alumina particles in curves a and b. In curve c, the particles are of similar sizes and packing efficiency is low.

Besides powder packing efficiency, density is also affected by the extent to which the liquid phase can flow into the voids between the solid phase and decrease the porosity. This effect is manifested in the increase in density as the low temperature phase content increases for all three powders.

The decrease in density after firing is due to the loss of mass due to evolution of NH_3 and H_2O during the firing process and the lack of any significant firing shrinkage as discussed in the next section.

DIMENSIONAL STABILITY

The variation of shrinkage in the long direction after firing with the percentage of low temperature phase and the alumina particle size is shown in Fig.4. Shrinkage is $<\pm$ 1% and does not change significantly in all three directions within the size and composition ranges tested. The low shrinkage is apparently due to a balance between two competing phenomena. On one hand during firing, NH_3 and H_2O are given off which tends to increase the volume of the compact. This is counteracted by the normal shrinkage due to pore closure.

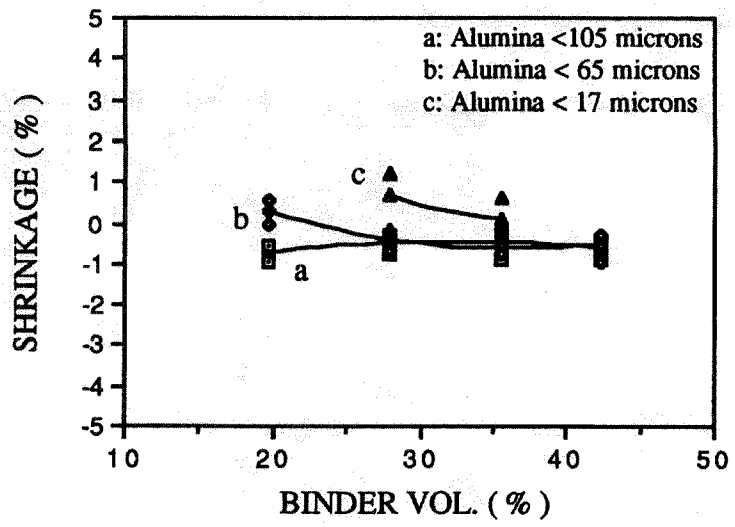

Fig 4: Shrinkage of Al_2O_3 - $NH_4H_2PO_4$ composite when fired at 850°C[7]

MECHANICAL PROPERTIES

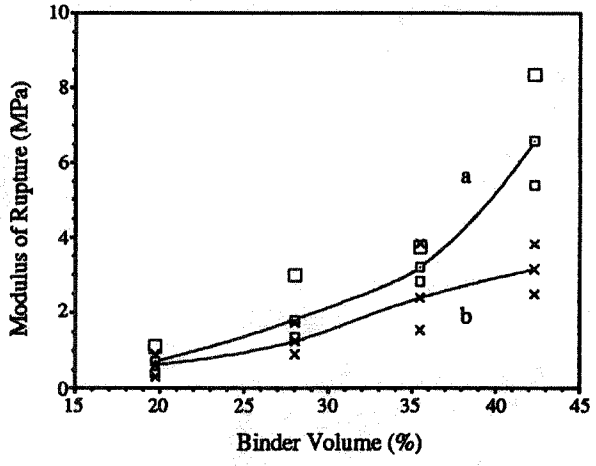

Fig 5a: Variation of modulus of rupture of Al_2O_3 - $NH_4H_2PO_4$ fired at 850°C[7]

As seen in Fig.5 the variation of Modulus of Rupture (MOR) of the fired samples with composition and particle size follows the same behavior as the density. MOR increases as the alumina particle size is increased and when the binder volume percentage is increased. Gonzalez and Halloran[8] have reported a MOR of 34MPa when a 90% phosphate bonded alumina plastic with density of 2.1 gms/cc is fired at 900°C. The difference in strength reported in this paper and that reported in Ref.8 is primarily attributed to a difference in density. Firing above 850°C leads to a decrease in bend strength due to decomposition as shown in Fig. 5b.

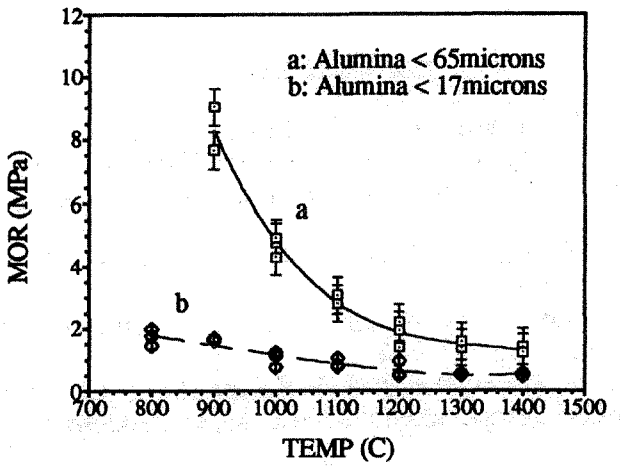

Fig 5b: Effect of firing temperature on the MOR of Al2O3 - NH4H2PO4 composite

ALUMINA - BORON OXIDE SYSTEM

Single layer and three layer experiments with alumina (95% pure, < 65μm) blended with 25wt% boron oxide (< 37μm) were performed using the same conditions as for the alumina- ammonium phosphate system except that the laser scan speed was decreased to 1.1 cm/s and the distance between scans was decreased to 0.25mm. The reduction in scan speeds and in the distance between scans provide sufficient energy to melt B_2O_3 which has higher melting point than $NH_4H_2PO_4$. The scan speed and distance between scans were determined to be the optimum based on a series of single layer experiments.

X-Ray powder diffraction analysis of the samples after laser processing indicates the presence of crystalline alumina and boron oxide. After the samples are heat treated at 850°C for 4 hours, Al_2O_3 and $2Al_2O_3.B_2O_3$ are present. Additional research to determine the microstructure and mechanical properties is now underway.

SUMMARY

The successful fabrication of complex shapes by SLS processing of ceramic blends depends on understanding the influence of material and laser parameters on the microstructure and mechanical properties of the end product. A model system, Al_2O_3 / $NH_4H_2PO_4$ has been chosen for study. Density depends both on the powder packing efficiency in the bed and the extent to which the voids in the bed are filled by the liquid phase during SLS processing. The modulus of rupture depends on the density of the samples after firing. Based on our understanding of the various factors influencing the properties of the laser sintered material, we are at present developing other systems like Al_2O_3-B_2O_3, Al_2O_3-glass ceramic and Si_3N_4 - B_2O_3.

ACKNOWLEDGEMENT

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