

An Experimental Study of the Relationship between Microstructure and Mechanical Properties of a Ceramic Composite Fabricated by Selective Laser Sintering

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ABSTRACT

Alumina-ammonium phosphate powder blends were processed with Selective Laser Sintering. Ammonium phosphate with a melting point of 190°C, acts as a binder when processed with a laser and holds the alumina (m.p. 2300°C) particles together to form a "green" body. When the green body is heat treated at 850°C for 6 hours, ammonium phosphate decomposes evolving ammonia and water vapor. Residual P₂O₅ reacts with alumina to form aluminum phosphate. This results in a composite of unreacted alumina with a coating of aluminum phosphate around the alumina particles. The variation of compressive strength of these low density ceramic composites was investigated in terms of the particle size distribution the amount of binder in the initial blend. It was observed that the strength depends on the relative density and initial blend composition and the critical flaw size. A constitutive equation was formulated to characterize the influence of the relative density, binder composition and the critical flaw size on the strength of the composite.

INTRODUCTION

The concept of Solid Freeform Fabrication (SFF) to generate parts directly from the CAD data without part-specific tooling has been described earlier [1]. Selective Laser Sintering (SLS), one of the Solid Freeform Fabrication (SFF) techniques being investigated at the University of Texas was first described by Deckard and Beaman [2]. The SLS process employs a focused laser beam scanned on the surface of the powder bed to induce selective particle - particle bonding in a thin layer of powder. The part is generated by sintering appropriate cross-sections on layers of powder stacked on top of each other. The unsintered powder in each layer remains in the powder bed during processing to support overhangs and other structures in subsequent layers.

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The absence of part-specific tooling in SLS makes the process economical in small-scale production runs where the fabrication of tools for conventional processes constitute a substantial fraction of the cost of the parts. Initial applications for SLS include design verification models made with engineering plastics such as polycarbonate or nylon and wax patterns for investment casting. In these applications, surface finish and dimensional accuracy are of primary importance and strength is of secondary importance. However, the application of SLS to generate ceramic and metal parts for functional applications requires a detailed understanding of the factors affecting the strength of the part. In this paper, the effect of initial particle size, the composition of the precursor powder and the intrinsic defects on the fracture behavior of the composite is considered.

POWDER PROCESSING BY SLS

The processing of alumina - ammonium phosphate powder blends by SLS was described in detail in references [3] and [4]. During laser processing, ammonium phosphate with a melting point of 190°C melts and holds the alumina particles (m.p. 2300°C) in the desired shape. A Nd:YAG laser (wavelength = 1.06µm, Q-switched at 40KHz) focused to a beam diameter of 0.5mm was used as the energy source to melt ammonium phosphate. Laser energy was maintained at 20W and the scan speed was 4cm/s. The distance between scans was 0.5mm. The layer thickness was 125µm. The bed biasing temperature was room temperature.

The "green" part from the SLS processing equipment was fired at 850°C for 6 hours. During the secondary heat treatment the temperature was ramped up at 2°C/min with an intermediate soak at 450°C to drive off reaction products. After firing, the parts were cooled in the furnace [3]. During heat treatment, ammonium phosphate decomposed evolving ammonia and water vapor as by-products. Residual phosphorus pentoxide reacted with the alumina to form aluminum phosphate. Thus a composite of alumina and aluminum phosphate capable of withstanding intermediate temperatures was obtained in a net-shape by SLS using a blend of alumina and ammonium phosphate as the precursor powders.

Compressive strength of the samples was measured on specimens having nominal measurements of 0.5"x1"x1". The specimens were oriented during SLS processing such that the build plane was parallel to the 1"x1" cross-section. The samples were ground flat and subjected to compressive stresses in an Instron Universal Testing Instrument with a cross-head speed of 1 mm/s. The loads were applied perpendicular to the build plane.

INITIAL POWDER ANALYSIS

X-ray powder diffraction analysis of the as-received precursor powders indicated that the alumina was in its α -form and the ammonium phosphate was in its tetragonal form. Preliminary investigation indicated that a 95.0% pure alumina absorbed laser radiation at 1.06 μ m better than the purer form (99.9%). Hence, the research work reported in this paper was confined to the less pure form of alumina. The major impurities in 95 % pure alumina are¹:

TiO₂-2.91%, SiO₂-0.71%, Fe₂O₃-0.35%, MgO-0.14%.

Three different alumina particle sizes were tested during our experiments. The mean and standard deviation of the particle size distribution of the coarse, medium and fine alumina are shown in Table. 1. The ammonium phosphate particle size was maintained below 44 μ m throughout our experiments.

Manufacturer's Designation	Average Size (μ m)	Standard Deviation (μ m)
Duralum 150	80.0	11.8
Duralum 220	69.0	9.2
Duralum 400	8.7	5.0

Table 1. Mean particle size and standard deviation of alumina particles used in experiments.

RESULTS AND DISCUSSION

The compressive strength of a porous ceramic composite depends on three microstructural factors: 1. porosity (or relative density), 2. binder content and 3. crack size. Each of these factors is considered briefly here.

In general, it has been observed that the strength of a porous material decreases as its porosity increases [5,6,7]. As porosity increases the load bearing area decreases resulting in a reduction of the strength of the material. Balshin [5] and Knudsen [6] have proposed equations 1 and 2 respectively to relate the strength of the composite to its porosity.

$$\sigma = \sigma_0(1-P)^m \quad \text{---- (1)}$$

$$\sigma = \sigma_0 e^{-bP} \quad \text{---- (2)}$$

where σ = Strength of porous solid

σ_0 = Strength of a fully dense solid ($P = 0.0$)

P = Porosity of solid

¹Analysis supplied by Washington Electro-Minerals Niagara, NY.

b and m are constants.

Both equations are based on the reduction of strength due to a reduction in load bearing area. Rice [7] on the other hand proposed an equation of the form

$$\sigma = (\pi/2)(\eta/\tan\eta)^{1/2}(E\gamma(R+L))^{1/2} \quad \text{---- (3)}$$

where $\eta = \pi R/(R+\lambda)$

σ = Strength of porous material

R = Pore radius

E = Young's modulus of material

γ = Surface fracture energy

L = Fraction of the grain size

λ = Pore spacing = $4R(1-P)/3P$ for evenly distributed spherical pores

to relate the effect of porosity on the strength of the material in terms of the stress concentration induced at the tip of the pores. From equations 1-3 it can be generalized that a decrease in the load bearing area and stress concentration at pore tip reduce the strength of the material.

Eqn. 4 relates the effect of the binder content to the strength of the composite [8]. The $G^{-0.5}$ term in Eqn. 4 is derived from the Griffith crack criterion for the fracture of brittle materials. Here it is assumed that the crack size controlling the strength of the material is equal to the grain size. The $(V_b/V_p)^{0.75}$ term accounts for the energy spent by the intergranular crack to propagate through the binder. As is evident in Eqn. 4, as the amount of binder increases, the strength of the composite increases.

$$\sigma = k(V_b/V_p)^{0.75}(\gamma E/G)^{0.5} \quad \text{---- (4)}$$

where σ = Strength of porous material

k = Constant

V_b = Volume content of binder in composite

V_p = Volume content of primary phase in composite

γ = Surface fracture energy

E = Young's modulus

G = Grain size.

The effect of a surface flaw (length a) or an internal flaw (length 2a) on the strength of a brittle material is given by the Griffith's crack criterion (Eqn. 5).

$$\sigma = Y(E\gamma/a)^{0.5} \quad \text{---- (5)}$$

where σ = strength of porous solid

Y = Geometrical factor

E = Young's modulus

γ = Surface fracture energy

a=crack size

As shown in Eqn. 5, strength varies in an inverse square relationship with the crack length. As a first approximation, it is reasonable to assume that the crack size equals grain size [8]. Based on this assumption, Knudsen [6] formulated Eqn. 7 combining the effects of the pore size and the porosity on strength in one equation.

$$\sigma = kG^{-a}e^{-bP} \quad \text{---- (6)}$$

where σ =strength of porous solid

G=Grain size

P=Porosity of solid

k, a and b are constants.

Based on the discussion thus far, it is inferred that the strength of the alumina - aluminum phosphate composite depends on its relative density, the binder content and the flaw size. The increase in density with alumina particle size and the amount of binder in the initial powder blend was discussed in an earlier report [1]. Fig. 1 shows the variation of the compressive strength of the alumina - aluminum phosphate composite fabricated by SLS with the binder content and the alumina particle size. It is seen that at a composition (i.e. 35%), the strength of the material increases with the alumina particle size. This is attributable to two reasons. As the alumina particle size decreases, the relative density of the material decreases [9]. In addition, as will be discussed later, very large cracks were observed in compacts with fine alumina (9 μ m). The presence of large cracks lowers the strength of the material.

In Fig. 2, the strength of composite is plotted against its relative density showing its linear dependence. Considering composites at a particular relative density, specimens fabricated with the finest alumina had the highest strength. It was pointed out in an earlier report [4] that the composites using fine alumina required a higher binder content than when using coarse alumina to get the same relative density. The presence of a large binder content results in a stronger material. From the preceding paragraphs, it is clear that the strength of the alumina-aluminum phosphate composites depends on its relative density, binder content and the crack size.

To predict the relationship between the strength of an alumina / aluminum phosphate composite and its porosity, composition and crack size, an equation was formulated (Eqn.7).

$$\sigma = B(1-P)a^{-0.5}(V_b)^p \quad \text{---- (7)}$$

σ =Strength of the porous alumina - aluminum phosphate composite.

B and p are constants

a=Crack size

P and V_b have been defined earlier.

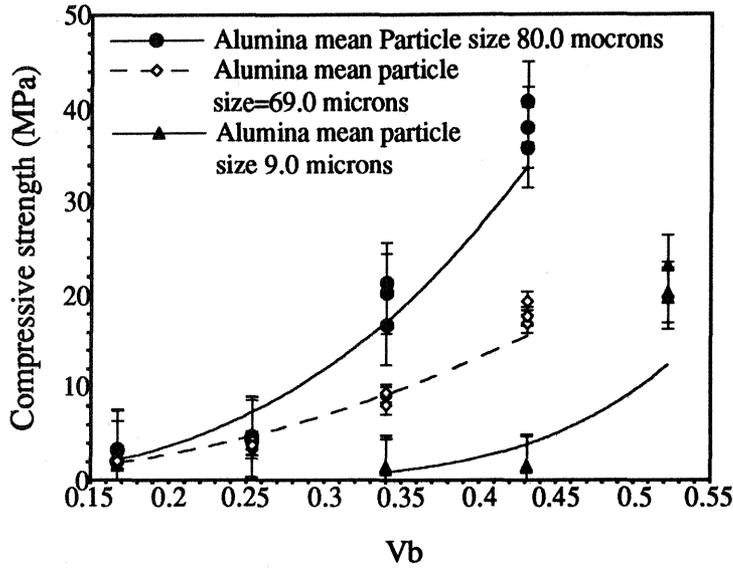


Fig. 1. Compressive strength of alumina - aluminum phosphate composites fabricated by SLS using different alumina particle sizes and varying amounts of aluminum phosphate in the composite.

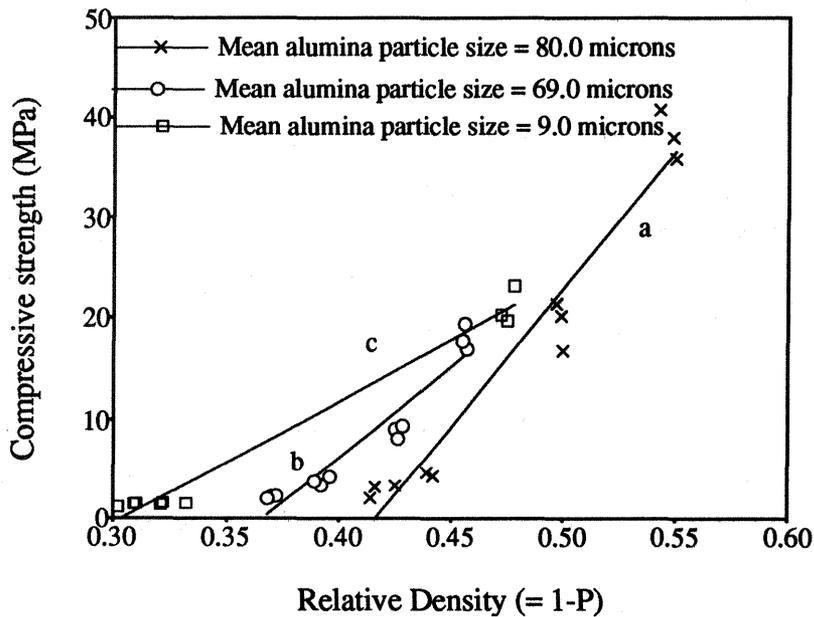


Fig. 2. Variation of the compressive strength of the alumina - aluminum phosphate composites with their relative densities and alumina particle sizes.

In equation 7, the term (1-P) accounts for the dilution in the strength of the composite due to porosity. The exponent of the (1-P) term was assumed to be 1 based on the experimental observation in Fig. 2. V_b accounts for the area of the aluminum phosphate through which the crack has to propagate. The $a^{-0.5}$ term is introduced to characterize the influence of the surface crack size on the material strength. The exponent of the crack length is -0.5 for mixed mode fracture that occurs during compressive loading [10]. B and p are constants. Assuming that the material is completely dense (P=0) and $V_b=1$, Eqn. 7 reduces to

$$\sigma = B \cdot a^{-0.5} \quad \text{---- (8)}$$

From Eqn. 8, it can be inferred that B should correspond to the fracture toughness of a pure aluminum phosphate specimen with no pores under compressive loading. No data for the fracture toughness of aluminum phosphate is available in the literature. However, the mode I (K_{IC}) fracture toughness of alumina is between 3 - 5 $\text{MPa}\sqrt{\text{m}}$ [10].

As a first approximation, assume that for the coarsest alumina (80 μm) grain size equals the crack size. By plotting $\ln(V_b)$ vs $\ln(\sigma \cdot \sqrt{a}/(1-P))$, B and p were determined to be 5.0 $\text{MPa}\sqrt{\text{m}}$ and 2.6 respectively. These values were then substituted in Eqn. 7 to calculate the strength of the composites containing 69.0 μm and 9.0 μm alumina powder assuming that the crack size in each composite equals the alumina grain size (Figs. 3 and 4).

Comparing the actual and calculated strengths of the alumina-aluminum phosphate composites in Figs 3 and 4, it can be inferred that equation 7 predicts the trends in the strength behavior of the composites accurately. However, the calculated values of the strength of the composite assume that the flaw size equals the average alumina grain size. But as seen in Table 1, there is a size distribution for the alumina particles. Hence the intrinsic crack size is greater than the average alumina particle size. This results in an overestimation of the composite strength if we assume that the grain size equals flaw size in the material (Figs. 3 and 4). Processing flaws as large as 400 μm have been observed on surface of composites made with fine alumina powder (9 μm). If a flaw size of 400 μm is used in Fig. 4, then the agreement between calculated and measured values improves. Further microstructural analysis is essential to understand the effect of material and processing parameters on the flaw size in the material.

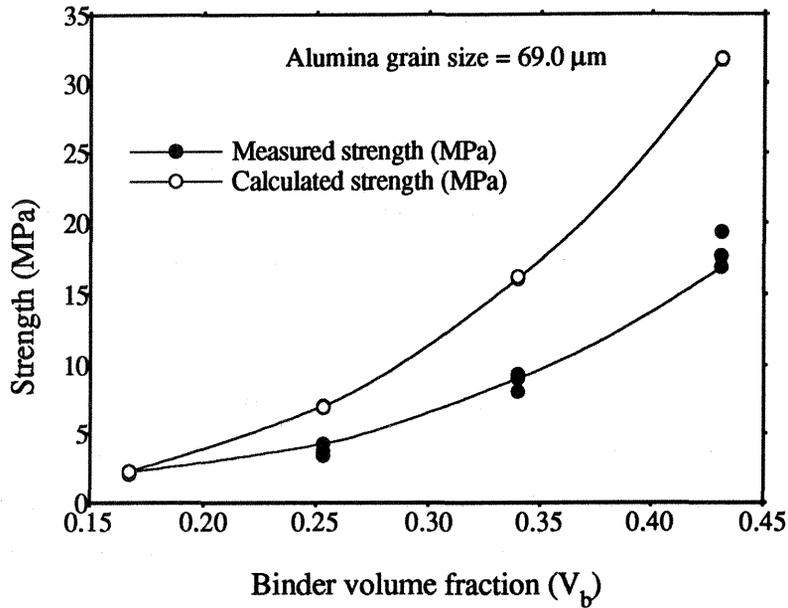


Fig. 3. Measured and calculated compressive strength of alumina - aluminum phosphate composites fabricated by SLS. Eqn. 7 was used in calculating the strength. It was assumed that the crack size = alumina particle size = $69\mu\text{m}$, $B = 5.0\text{MPa}\sqrt{\text{m}}$ and $p = 2.6$.

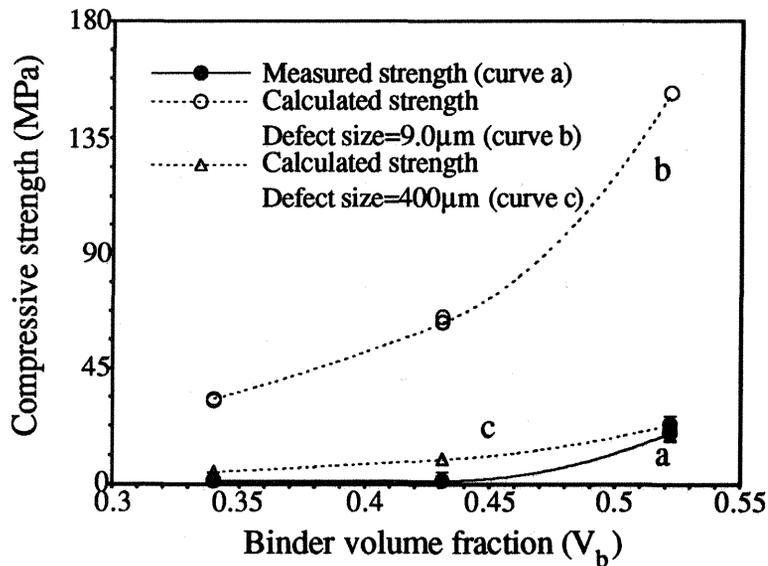


Fig. 4. Calculated and measured compressive strength of alumina - aluminum phosphate ceramic composites fabricated by SLS. The calculated values were determined

using $B=5.0\text{MPa}\sqrt{\text{m}}$ and $p=2.6$ in Eqn. 7. Curve b assumes a crack size of $9.0\ \mu\text{m}$ (alumina particle size in initial blend) and curve c assumes a crack size of $400\ \mu\text{m}$.

CONCLUSIONS

The compressive strength of the alumina - aluminum phosphate composites fabricated by SLS was studied as a function of the porosity, binder content and the surface flaw size. The strength of the composite increases as the binder content increases and as the porosity and defect size decrease. Hence factors such as alumina particle size and binder content which influence the microstructure have a strong effect on the strength of the composites. A constitutive equation was formulated to relate the effects of the microstructural factors on the strength of the composite. While the equation predicted the general trends in the variation of the strength with microstructural factors, more detailed investigation into the crack size controlling the strength of the material is required in order to use the constitutive equation as a predictive tool.

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