

Effect of Particle size on SLS and post-processing of Alumina with Polymer binders

P. Kamatchi Subramanian, J.W. Barlow and H.L. Marcus
Center for Materials Science and Engineering
The University of Texas at Austin.

Abstract

Alumina powders with mean particle size of 15 μm , 2 μm and 0.5 μm were processed by SLS using polymer binders. The 2 μm and 0.5 μm powders were given a thermal agglomeration treatment before SLS. The green shapes after SLS were infiltrated with a colloid of aluminum oxide. After infiltration the samples were given suitable heat-treatment to remove the polymer binder by thermal decomposition followed by a sintering treatment at 1600C. Green densities were in the range of 45% of theoretical density for the agglomerates of 2 μm and 0.5 μm powders while it was about 36% of theoretical density for the 15 μm powders. Sintered densities were about 55% of theoretical density for the samples from agglomerates of 2 μm and 0.5 μm powders while it was 42% of theoretical density for the samples from 15 μm powders. The strength of samples were measured in the green state and after sintering to determine the effect of particle size.

Introduction

Selective Laser Sintering (SLS) of ceramics using polymer binders has been investigated at the University of Texas [1-5]. Single phase alumina has been obtained by processing the ceramic powder as follows [6]: i) SLS with polymer binder, ii) infiltration of the green shape with alumina colloid, iii) removal of the binder by thermal decomposition and iv) sintering at high temperatures of the ceramic samples after binder removal. In this paper we will examine the effects of particle size on the SLS and post-processing of alumina using polymer binders.

Experimental work

Alumina powders of 15 μm mean particle size were spray-coated with a copolymer containing 80 mole% methyl methacrylate and 20 mole% butyl methacrylate. The 2 μm alumina powders could not be processed by spray-drying with polymer binders. They were given a thermal agglomeration treatment at 1400°C for 3 hrs [5]. After the agglomeration treatment the cake that formed was broken down and agglomerates less than 125 μm were mixed with the polymer powder (20 vol% polymer) obtained by spray-drying of polymer emulsion. For the 0.5 μm alumina powder the thermal agglomeration treatment was conducted at 1300°C because the cakes obtained at 1400°C could not be broken down easily due to the accelerated sintering of the small particle size. These agglomerates were also mixed with the polymer powder (20 vol% polymer) obtained by spray-drying.

The spray-coated powder and the powder mixtures were processed by SLS and bend strength specimens (3"x1"x0.25") were made. The specimens in the green state (as SLS) were tested for density and green strength. Some of the specimens were infiltrated with alumina colloid

by immersing the samples in the colloid. After infiltration with colloid the samples were dried at 120°C and then given a debinding treatment [6]. This was followed by a sintering treatment at 1600°C for 6 hrs.

Results and Discussion

In the case of green samples the particle size affects the green strength depending upon the surface area to be bonded by the polymer. A comparison of the strengths of green samples from agglomerates of 0.5 μm alumina mixed with 20 vol% copolymer powder, agglomerates of 2 μm alumina mixed with 20 vol% copolymer powder and 15 μm alumina coated with 25 vol% copolymer is shown in Figure 1.

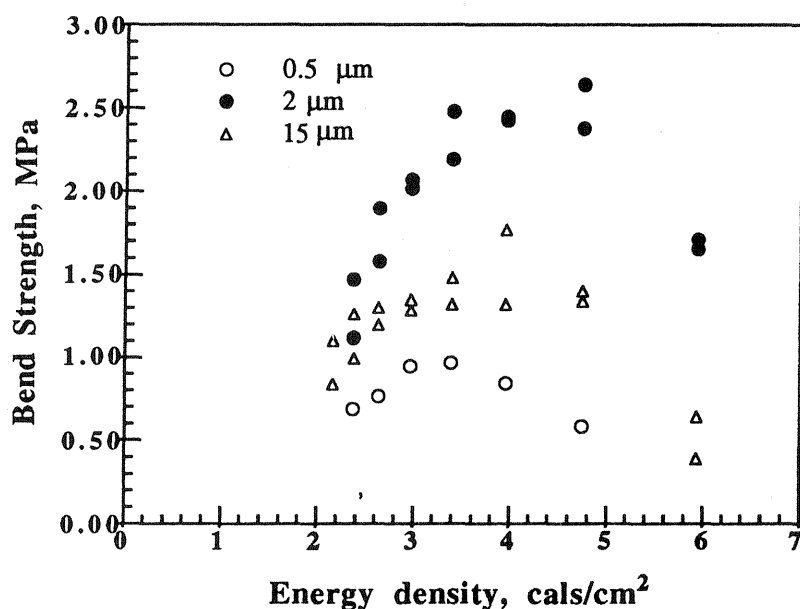


Figure 1. Effect of particle size on green strength of samples

For the 0.5 μm alumina the agglomeration into spherical agglomerates at the lower temperature probably resulted in weakened agglomerates and therefore lower bend strength. The 15 μm alumina has a higher volume fraction of polymer. However it will have more area to be wet by the polymer than the 100 μm agglomerates made from the 2 μm alumina. Hence the strength obtained is lower even with higher volume fraction of the polymer. The decrease in bend strengths at higher energy densities is associated with polymer degradation and is reported elsewhere [6,7]. The densities of the samples are shown in Figure 2. Fully dense alumina is 3.97 g/cm³.

From these it can be seen that the density for the samples from agglomerates of 2 μm powder marginally increases with energy density, and the density of samples from this mixture is slightly higher than that obtained from agglomerates of 0.5 μm . The difference in green strengths cannot be related to the difference in density between the two materials. The difference in strength

is probably due to the difference in surface area to be wet by the polymer. The density of the 15 μm powder samples is lower than that of the other two because that powder does not pack as well as the other two and the polymer content is higher.

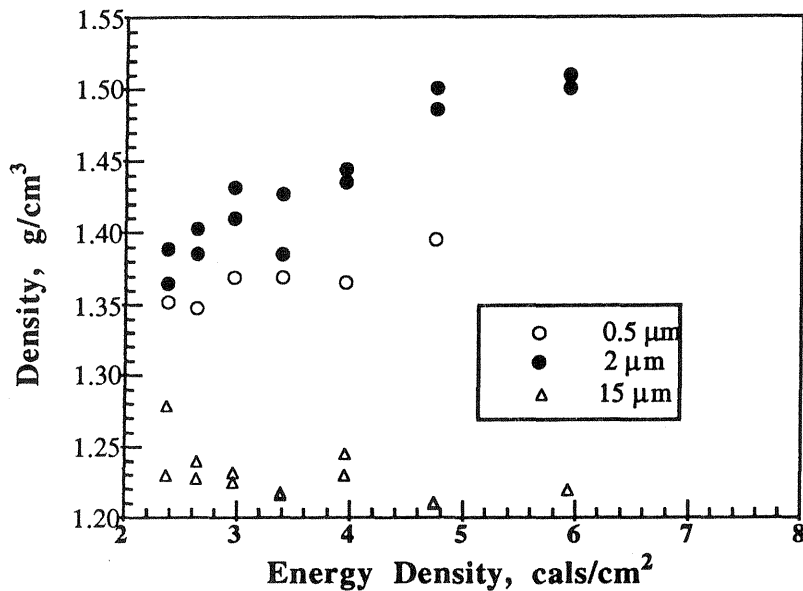


Figure 2. Effect of particle size on the green density of samples

Upon debinding and sintering, following the cycle described earlier, the samples from agglomerates of 0.5 μm and 2 μm densify to about 55% of theoretical density while the samples from 15 μm densify to only about 40% of theoretical density, Figure 3. This is due to the higher sintering kinetics of the smaller particles at the sintering temperature. The independence with energy density is due to the high temperature sintering controlling the strength instead of the polymer distribution.

Regarding the strength of samples after sintering, Figure 4, a couple of general observations can be made. The samples from agglomerates of 0.5 μm powder are stronger than samples from other two because of the higher sintering kinetics for the smaller particles. The strengths all decrease with increasing incident energy used during laser processing of the green samples. With increasing incident energy density more of the polymer is decomposed. The rate of heating in SLS processing is of the order of 600°K/10ms [8]. This high heating rate will cause sudden expansion of gases formed by decomposing the polymer, in the powder bed leaving behind larger defects. The heating rate in thermal decomposition of the binder after infiltration is only of the order of 5°K/min. Hence the diffusion of the gases can occur without causing defects. Since

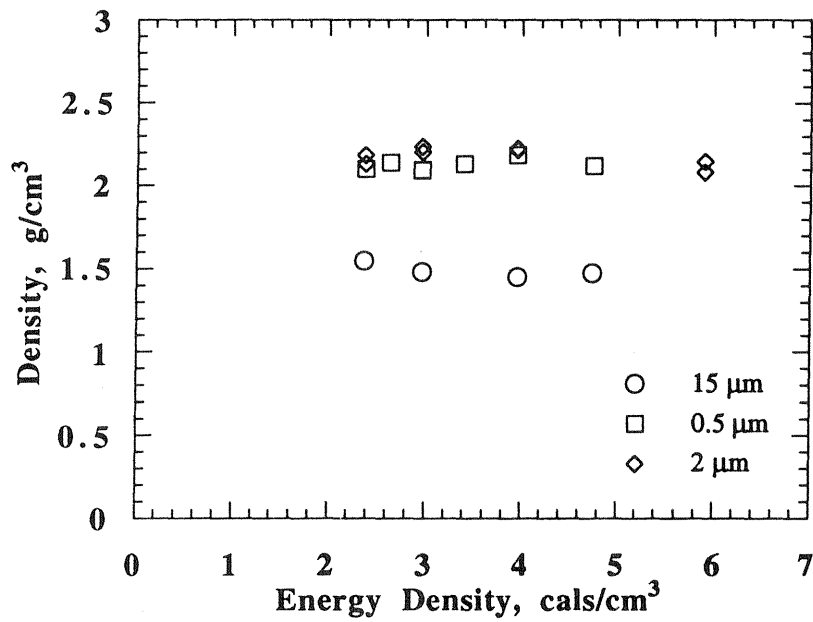


Figure 3. Effect of particle size on density of sintered samples

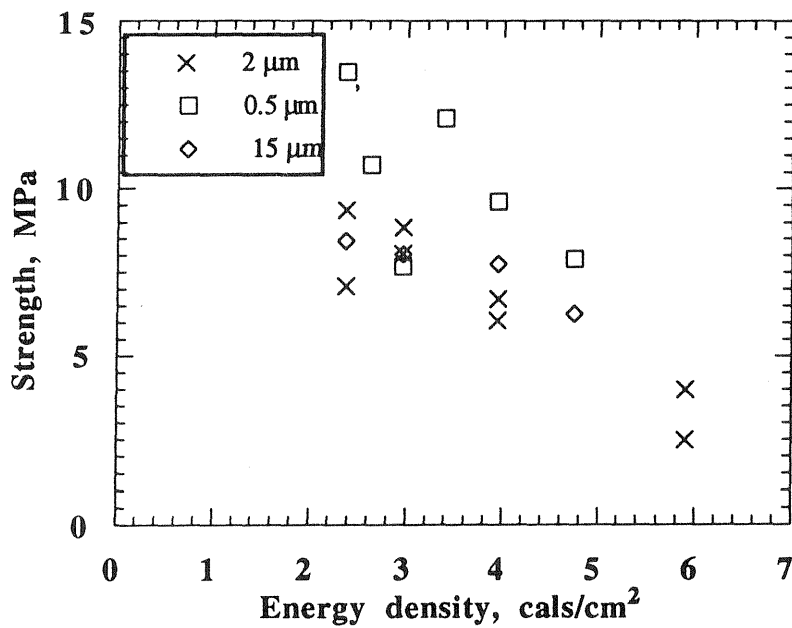


Figure 4. Effect of particle size on strength of sintered specimens.

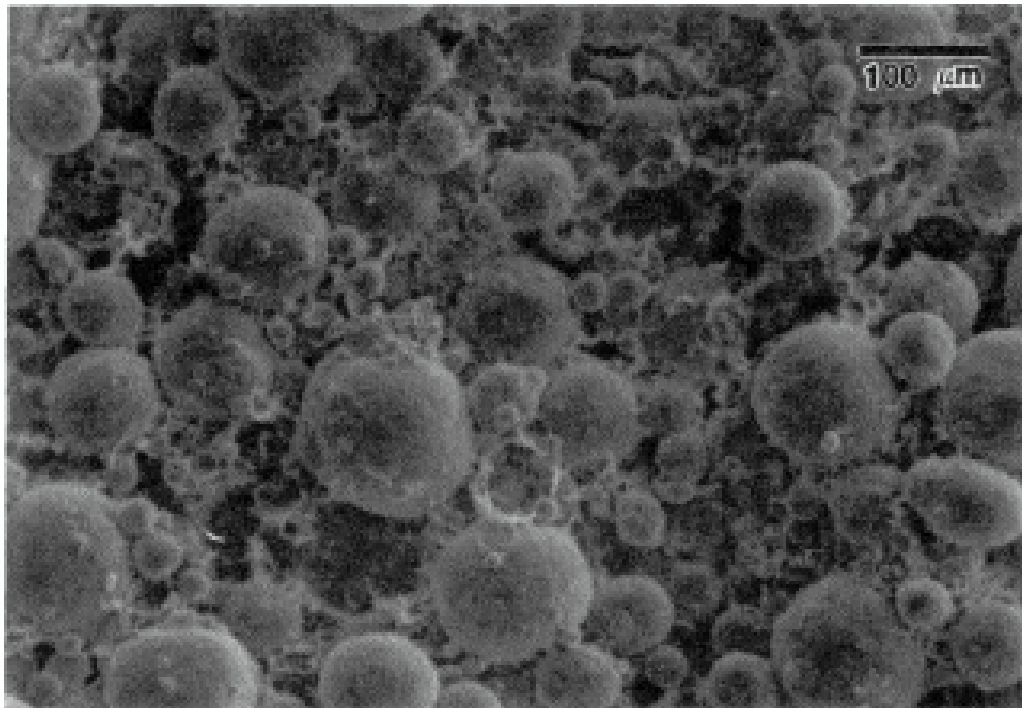


Figure 5. Cross-section through sintered sample from 2 μm alumina [6].

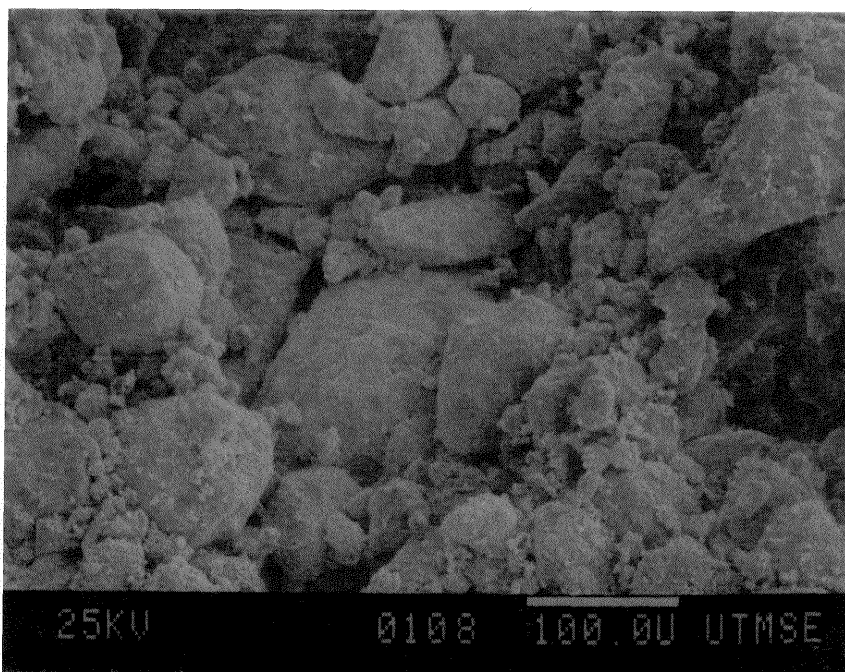


Figure 6. Cross-section through sintered sample from 0.5 μm alumina

the strength is inversely proportional to defect size, the strength decreases with increasing energy density. Due to the difficulty of evaluating fracture surfaces of porous materials, this hypothesis could not be confirmed.

Microstructure of sintered specimens

The section through sintered samples are shown in Figures 5 and 6. It may be seen that there are lacy regions corresponding to alumina from sintered colloid. In the case of the 2 μm samples the agglomerates remain spherical even after the 1600 $^{\circ}\text{C}$ heat treatment. However in the 0.5 μm sample the agglomerates no longer appear spherical because of extensive solid state sintering and wide neck formation during sintering. This contributes to the higher strength observed.

Summary

The effect of particle size on SLS and post-processing of alumina has been examined using three particle sizes of alumina 15 μm , 2 μm and 0.5 μm . The finer powders needed to be agglomerated before processing by SLS. After SLS processing the samples undergo infiltration, debinding and sintering at 1600 $^{\circ}\text{C}$. The sintered densities obtained were about 55% of theoretical density for the 0.5 μm and 2 μm powders while it was about 40% for the 15 μm powders. Sintered samples from the agglomerates of 0.5 μm were stronger than the other two because of the higher sintering kinetics of the finer particles. The sintered samples exhibited effects due to the decomposition of the polymer during the SLS process.

Acknowledgment

Support for the research reported here was received from ONR Grant # N00014-92-J-1514.

References

1. Vail, N.K., and Barlow, J.W., "Microencapsulation of Finely divided Ceramic powders", Proceedings of the Solid Freeform Fabrication symposium, August 6-8, 1990, editors: J.J. Beaman, H.L. Marcus, J.W. Barlow and D.L. Bourell, The University of Texas at Austin, p.8
2. Vail, N.K., and Barlow, J.W., "Effect of Polymer coatings as intermediate binders on Sintering of Ceramic parts", Proceedings of the Solid Freeform Fabrication symposium, August 12-14, 1991, editors: H.L. Marcus, J.J. Beaman, J.W. Barlow, D.L. Bourell and R.H. Crawford, The University of Texas at Austin, p.195
3. Vail, N.K., Barlow, J.W., Beaman, J.J., Marcus, H.L., and Bourell, D.L., "Development of a Poly(Methyl Methacrylate-co-n-Butyl Methacrylate) Copolymer Binder system," Journal of Applied Polymer Science, 1994, **52**, p. 789

4. Subramanian, P.K., Zong G., Vail N.K., Barlow, J.W., and Marcus, H.L., "Selective Laser Sintering of Alumina", Proceedings of the Solid Freeform Fabrication symposium, August 9-11, 1993, editors: H.L. Marcus, J.J. Beaman, J.W. Barlow, D.L. Bourell and R.H. Crawford, The University of Texas at Austin, p. 350
5. Subramanian, P.K., Vail, N.K., Barlow, J.W., and Marcus, H.L., "Anisotropy in Properties of Alumina processed by SLS", Proceedings of the Solid Freeform Fabrication symposium, August 8-10, 1994, editors: H.L. Marcus, J.J. Beaman, J.W. Barlow, D.L. Bourell and R.H. Crawford, The University of Texas at Austin, p. 330
6. Subramanian, P.K., Vail, N.K., Barlow, J.W., and Marcus, H.L., "Selective Laser Sintering of Alumina with Polymer Binders", Rapid Prototyping Journal, Vol. 1, No. 2, 1995, p.24
7. Vail N.K., "Preparation and Characterization of Microencapsulated, Finely Divided Ceramic Materials for Selective Laser Sintering", Ph.D. Dissertation, The University of Texas at Austin, 1994.
8. Nelson J.C., "Selective Laser Sintering: A definition of the process and an Empirical Sintering model", Ph.D. Dissertation, The University of Texas at Austin, 1993