

SELECTIVE LASER SINTERING OF CERAMIC MATERIALS.

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ABSTRACT

This paper will focus on efforts to develop the alumina - ammonium phosphate material system for Solid Freeform Fabrication. When the powder mix is irradiated with a laser beam, ammonium phosphate (m.p. $\sim 190^{\circ} \text{C}$) melts and forms a glassy phase between the alumina grains. The "green part " obtained by laser processing is then subjected to secondary heat treatment to optimize the properties of the final composite. The effect of various material, laser and machine parameters on the density, strength, surface finish and microstructure of the final part are described. One of the applications for selective laser sintering is its use in directly manufacturing ceramic molds for the investment casting process. We will describe some of the the results we have obtained so far in fabricating composite ceramic molds directly and using them to cast metals.

INTRODUCTION

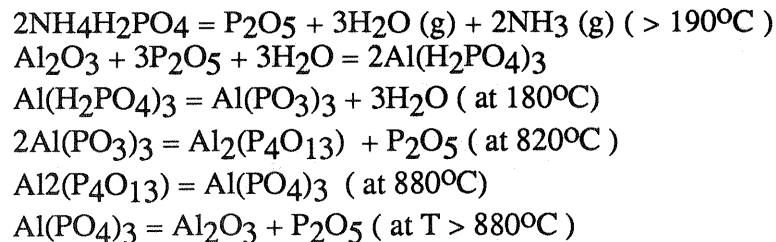
Solid Freeform Fabrication (SFF) is a computer integrated manufacturing process that enables us to fabricate three dimensional objects directly from a CAD database without any part specific tooling. There are several SFF techniques being investigated by researchers in this area. In this paper, we will discuss the " Selective Laser Sintering " process as applied to the alumina - ammonium phosphate system.

The process starts by laying down a very thin layer (~ 5 mils) of the powdered material. This surface is then scanned by a computer controlled high energy laser beam. The intensity of the laser beam is modulated by the computer according to the predetermined cross sectional pattern of the object. The beam is turned on where the powder is to be processed into a solid section and turned off where we do not want any processed powder. The laser beam causes localized heating of the powder being irradiated. As a result of this heating, the powder particles bond together. Once this layer has been completely scanned, a second layer is laid on top of the first layer and the process is repeated. The intensity of the laser should be high enough to cause the second layer to bond to the first. By laying down a number of such layers, a three dimensional object can be fabricated. This process is explained in detail in references 1-3.

MATERIAL SYSTEM

A wide variety of polymeric, metallic and ceramic materials can be used to fabricate monolithic or composite parts by Selective Laser Sintering. In this paper we report on the selective laser sintering of a ceramic binary composition consisting of a

high temperature phase - alumina with a melting point of 2045°C and a secondary component - ammonium phosphate with a low melting point of 190°C. When this binary composition is irradiated with the laser, ammonium phosphate melts and forms a glassy phase around the alumina particles. This imparts sufficient "green strength" to the part so that it can be removed from the processing chamber and the nonirradiated powder removed. To develop the final strength of product, it is fired in a furnace when ammonium phosphate decomposes evolving ammonia and water vapor as gases. The phosphorus pentoxide left behind reacts with the alumina to form aluminum phosphate. The reactions between alumina and ammonium phosphate at different temperatures are given below [4]:



MATERIAL PROCESSING

In the initial stages of the research, both high purity alumina (99.99 %) and low purity alumina (95 %) were mixed with ammonium phosphate and processed with the laser. The impure form of alumina absorbs radiation at 1.06 μm better than pure alumina. Hence all the work presented in this paper was done with low purity alumina.

Ammonium phosphate crystals were ground in a ball mill using alumina satellites. The -120 mesh (< 125 μm) fraction was sieved out and mixed with alumina powder in the ratio 1:4 by weight. The size and shape of the alumina and ammonium phosphate particles are shown in Figs. 1 and 2. The mix was then processed with a pulsed Nd:YAG laser under the following conditions.

$\lambda = 1.06 \mu\text{m}$
 Frequency = 40 kHz
 Incident power = 20 - 25 W
 Scan speeds = 2 cm/s - 6 cm/s
 Beam diameter = 0.5 mm
 Substrate temperature = 21°C to 60°C

Once the green part has been fabricated in the laser sintering chamber, it is taken out, the nonirradiated powder removed and fired in a microprocessor controlled furnace. The firing sequence used in this study is shown in Fig. 3.

RESULTS AND DISCUSSION

Following the processing steps outlined, we have been successful in fabricating complicated 3-dimensional shapes (Figs. 4a, 4b). The part in Fig. 4a fulfills one of the objectives of the SLS process. The part has the shape visualized by the designer but has neither the dimensional accuracies nor the surface finish to be used as a functional part.



Fig 1. Micrograph of the as received Al₂O₃ powder (< 150μm) showing the irregular shape of the particles.

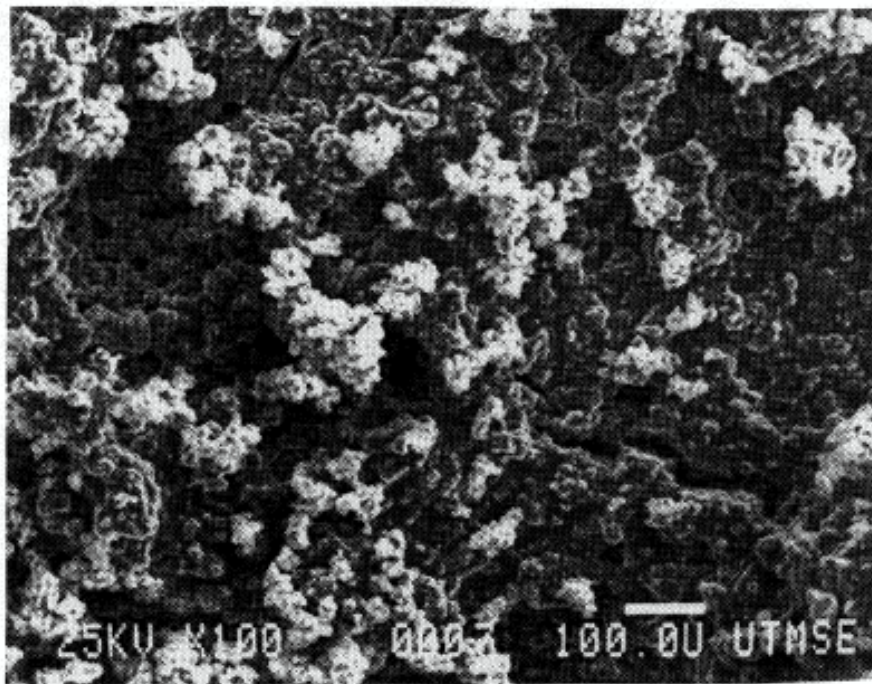


Fig2. Ammonium Phosphate particles ground to less than 44μm.

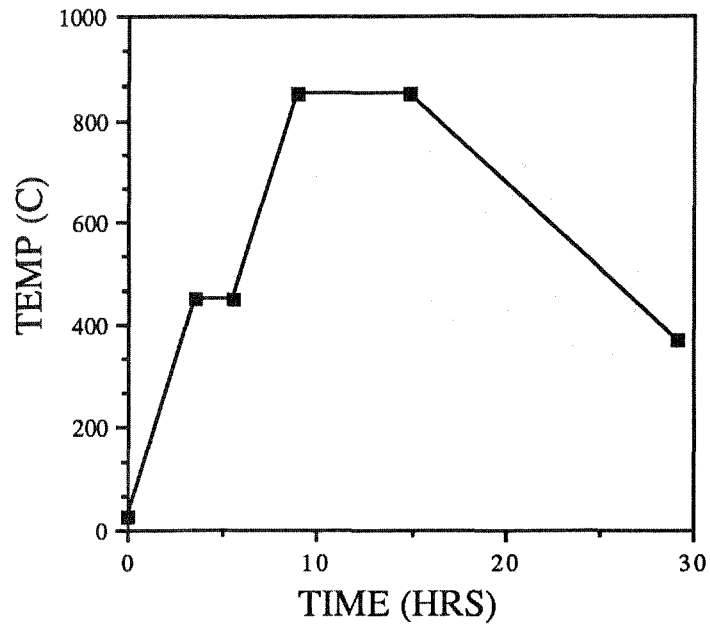


Fig3. Temperature -Time plot for secondary heat treatment of SLS processed Al₂O₃/NH₄H₂PO₄ mix.

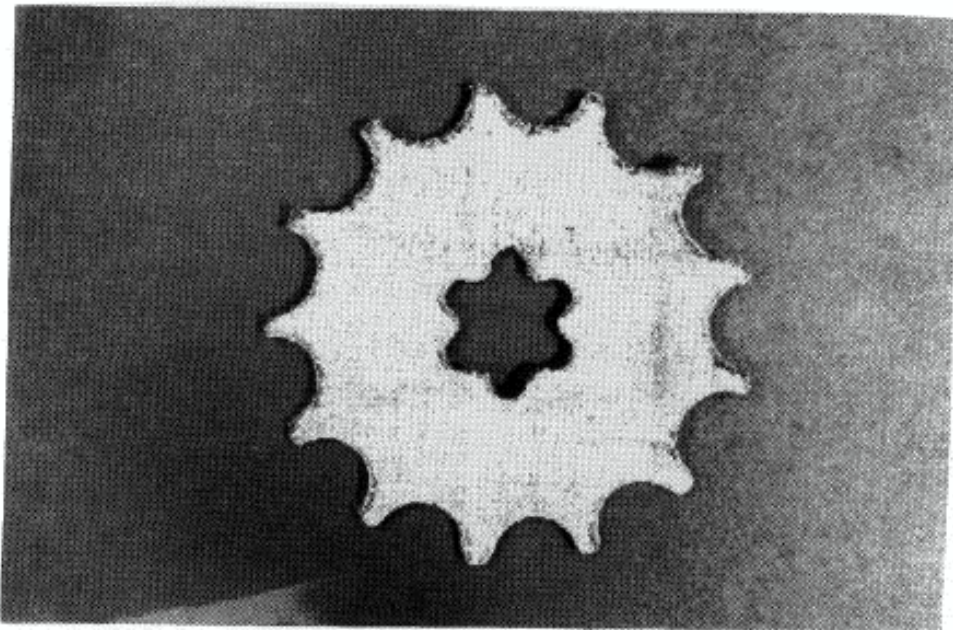


Fig4a. Ceramic gear produced by SLS of Al₂O₃/NH₄H₂PO₄ binary mix.

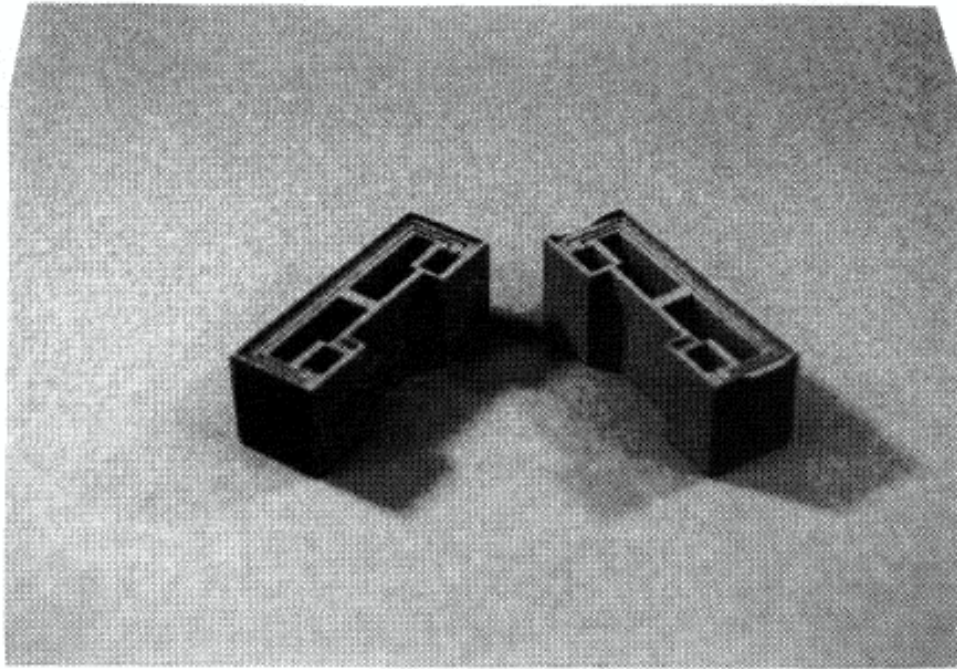


Fig4b. Complex three dimensional shapes exhibiting excellent part definition fabricated by SLS.

Fig.4b shows two similar parts that have both definition and dimensional tolerances. Still the part has a very rough surface. The surface finish in this case is dictated by the size of the alumina powder which was -220 mesh ($< 60 \mu\text{m}$). To improve the finish of the final product, finer powders are now being tested.

MICROSTRUCTURAL ANALYSIS: Fig.5a shows the microstructure of a specimen that has been processed with the laser but has not been heat treated. Figs.5b and 5c depict the distribution of Al and P respectively in the area shown in Fig.5a. The presence of large regions of high phosphorous concentration indicates that at this stage the binder has not coated the alumina grains. However after heat treatment, the binder reacts with the alumina grains to form a film of $\text{Al}(\text{PO}_4)_3$ around the alumina grains (Figs.6a,6b and 6c).

X-Ray powder diffraction was done to identify the structure of the binder before and after heat treatment. Prior to heat treatment, at very low laser energy, the binder retained its crystalline form. As the laser energy is increased, the binder melts and resolidifies into a glassy phase. After heat treatment, we found that the binder had reacted with alumina to form aluminum phosphate.

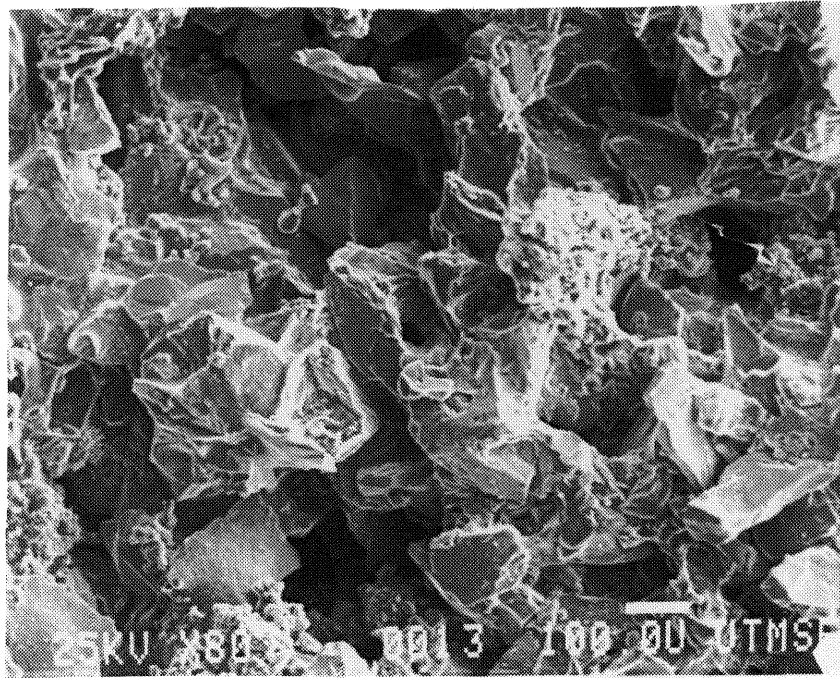


Fig5a. Microstructure of laser processed $\text{Al}_2\text{O}_3/\text{NH}_4\text{H}_2\text{PO}_4$ binary composition before heat treatment.

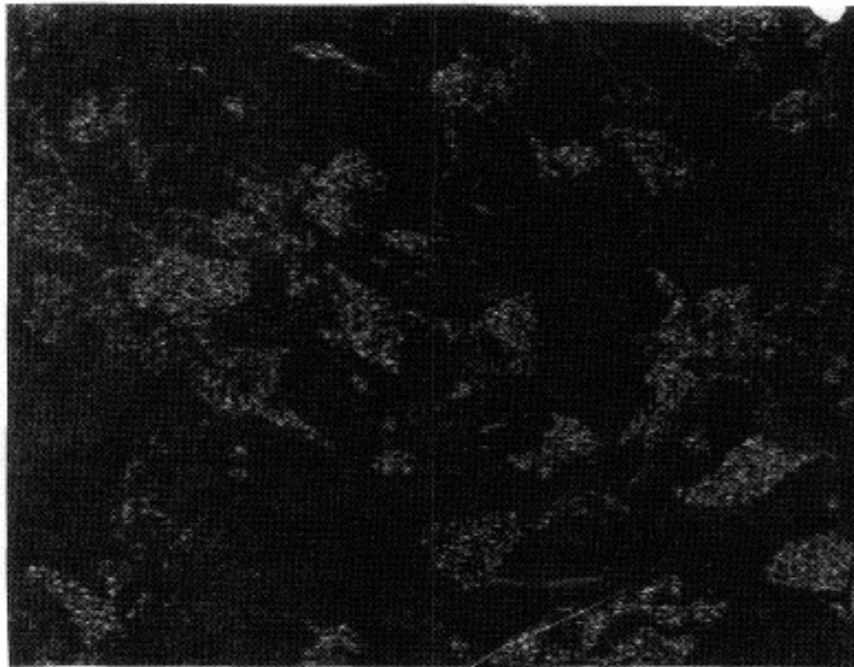


Fig5b. Elemental (Al) distribution map showing the location of Al_2O_3 phase in Fig5a.

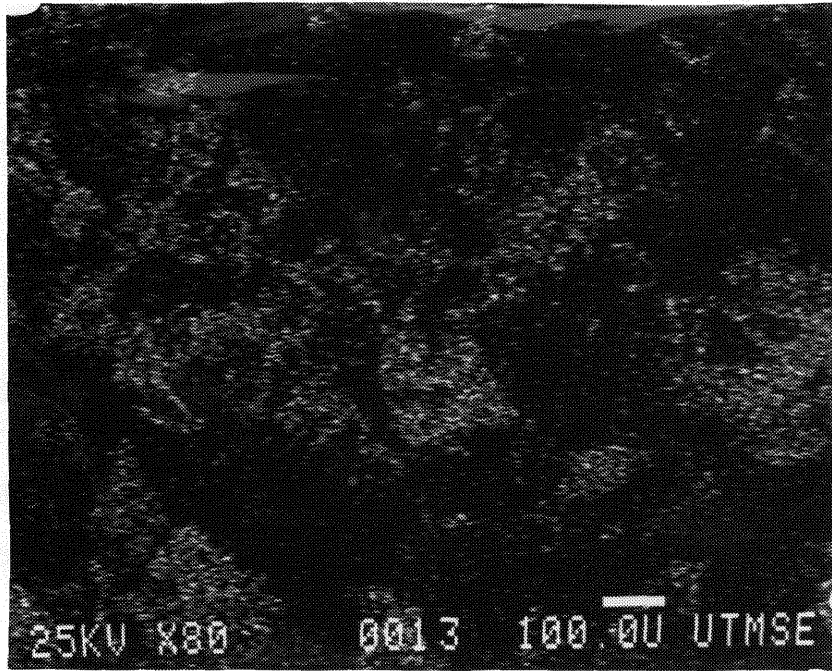


Fig5c. Elemental (P) distribution map showing the location of the binder phase in Fig 5a.

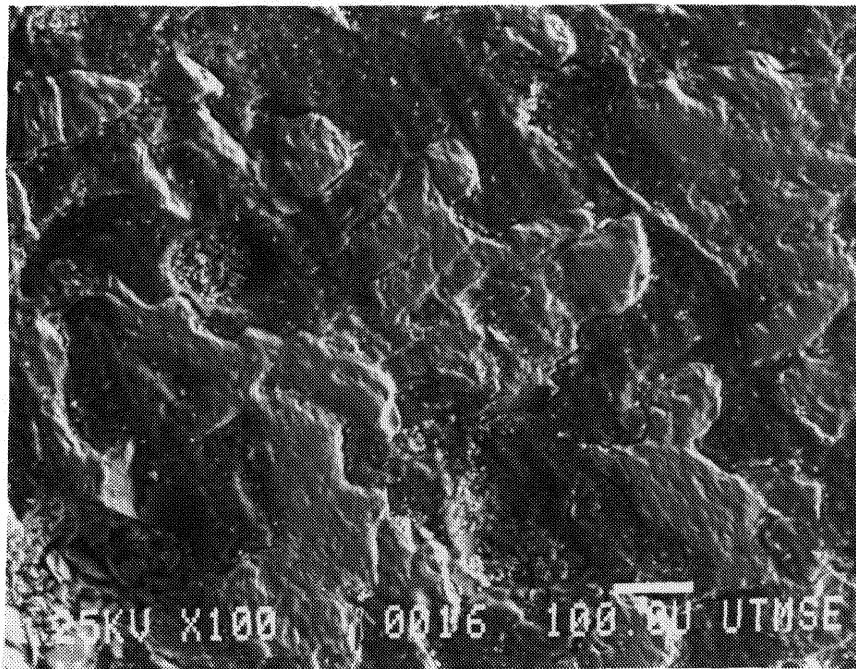


Fig6a. Microstructure of laser processed $\text{Al}_2\text{O}_3/\text{NH}_4\text{H}_2\text{PO}_4$ binary composition after heat treatment.



Fig6b. Micrograph showing the distribution of Al₂O₃ phase in the area shown in Fig 6a



Fig 6c. Micrograph showing the distribution of the AlPO₄ phase as a coating around the alumina particles after heat treatment.

DENSITY MEASUREMENTS: To estimate the density of the compact after firing, we fabricated 1" cylinders with a height of 0.75 " and processed with the following parameters:

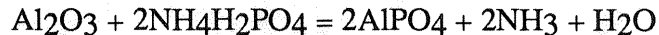
Scan speeds: 2-6 cm/s

Substrate Temperatures : 21°C and 60°C

Particle sizes: -150 mesh (<100µm),
-220 mesh (<67µm) and
-400 mesh (<27µm).

The bulk volume (v_b) of the sample before and after firing was determined by immersion in mercury. The mass of the sample (m) was measured before and after firing. Density was calculated as the ratio of the mass to the bulk volume of the compact.

The theoretical density after firing was calculated to be 3.53 gms/cc assuming that the reaction



goes to completion and no chemical species other than NH_3 and H_2O are evolved. This assumption is reasonable since the loss of weight in all specimens after firing was 7-9%. Stoichiometric calculations assuming the reaction predicted a 8% weight loss.

Initial results indicate that the density of the compact varies from 1.16 gms/cc to 1.84 gms/cc. The low density is primarily due to loose packing of the powder when the layers are being laid down in the work chamber. At present, we are developing a mathematical model to optimize the green packing of irregular particles in a powder bed.

FIRING SHRINKAGE: Firing shrinkage is a direct manifestation of the removal of some of the pores during firing. The volume shrinkage is equal to the pore volume removed[5]. Shrinkage can have a deleterious effect on the quality of the final part and must be accounted for in Solid Freeform Fabrication for dimensional accuracy. Besides the dimensional change, it can lead to warpage and in extreme circumstances, even cracking at stress concentration points.

To measure shrinkage in the alumina-phosphate system, 1" cubes were fabricated by SLS with the following processing parameters:

$\lambda = 1.06 \mu\text{m}$

Frequency = 40 kHz

Incident power = 22 W

Scan speed = 4 cm/s

Powder composition: 80 wt% Alumina (<27 µm) + 20 wt% ammonium phosphate (< 120 µm)

Dimensions of the specimens were measured before and after firing and linear shrinkage calculated. When these samples were fired at 850°C for 2 hours, no shrinkage was noticed. When the firing temperature was increased to 1100°C,

shrinkage varied between 0.2% and 2%. At 1500°C, the shrinkage ranged from 5-10%. The high shrinkage at 1500°C was due to the large porosity in the green part.

"LOST - LOST WAX" PROCESS

Investment casting is a well known foundry practice for metal casting. It involves the fabrication of a wax model by either sculpting or molding. From this model, a ceramic mold is made and molten metal is poured into it. Using Selective Laser Sintering the wax models have been made. We can also directly make the ceramic mold without fabricating the wax model. The cone shown in Fig 7. was made by such a process which we define as the "Lost-Lost-Wax" process. Efforts are now underway to cast more complex shapes by the Lost-Lost- Wax process.

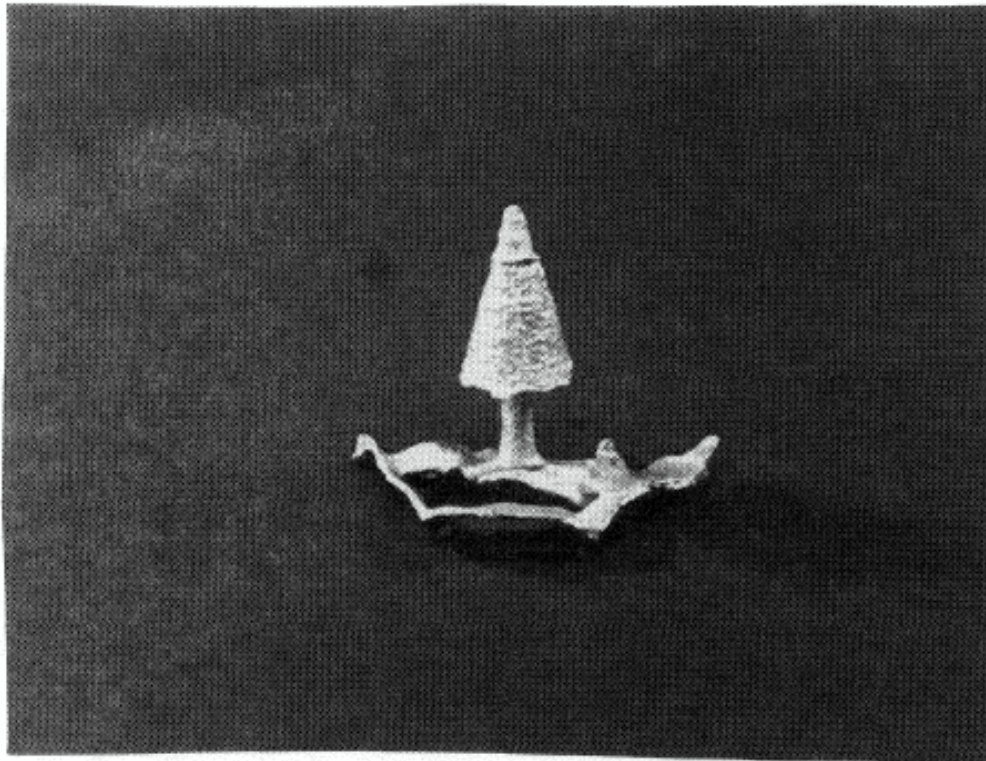


Fig7. Lead casting produced by pouring the metal in a ceramic mold. The ceramic mold was fabricated by SLS.

SUMMARY

We have demonstrated that an alumina - ammonium phosphate binary mixture can be used as the starting material in the SLS process to fabricate complex 3-D objects with reasonable dimensional accuracies and part definition. We have also demonstrated

the feasibility of fabricating ceramic molds to cast metals in the Lost-Lost-Wax process. The next phase of the research would focus on optimizing the laser and material parameters to enhance the density and surface finish of the final product. This would enable us to fabricate structurally sound parts which is the ultimate goal of this research endeavor.

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