Journal of the European Ceramic Society 23 (2003) 921–925
www.elsevier.com/locate/jeurceramsoc

Solid freeform fabrication of alumina ceramic parts through a lost mould method

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Received 2 December 2001; received in revised form 9 June 2002; accepted 22 June 2002

Abstract

A new rapid prototyping method is developed by combining SLS (selective laser sintering) and gelcasting technique for the fabrication of complex-shaped Al_2O_3 ceramic parts. Based on the specially selected composite plastic powders, SLS is utilized to fabricate sacrificial moulds for the ceramic parts. Aqueous gelcasting technique is utilized to form high mechanical strength Al_2O_3 green body by the *in situ* polymerization of high solids loading Al_2O_3 slurry containing monomer and cross-linker. Because of the high green strength of the Al_2O_3 parts, the desired geometry of the ceramic structure is successfully retained after sintering of the ceramics. Ceramic slurry composition and binder removal cycle development work for alumina ceramics are also described in detail in this paper.

Keywords: Al_2O_3; Forming; Gelcasting; Lost mould forming; Selective laser sintering; Sintering

1. Introduction

The high hardness, stiffness and fragility render alumina ceramics difficult for mechanical processing. The conventional fabrication technique is a costly, time-consuming, and inflexible process when a few ceramic prototypes or when small quantities of parts are needed. Solid freeform fabrication (SFF) is an advanced manufacturing technology which generates accurate geometrical objects directly from a three-dimensional computer image without part-specific tooling or human intervention.[1] This means that designers have the freedom to produce physical models of their drawings more frequently, allowing them to check the assembly and function of the design as well as discussing downstream manufacturing issues with an easy-to-interpret, unambiguous prototype. Consequently, errors are minimized and product development costs and lead times substantially reduced.

To date, several SFF techniques for the fabrication of complex-shaped ceramics, such as three-dimensional printing (3DP), laminated object manufacturing of ceramic green tapes and robocasting, etc., have been developed.[2–4] However, many of these approaches rely directly on the ceramic feedstocks that contain 40–70 wt.% organic species which results in debinding issues. Moreover, a low build rate seems inevitable because the characteristic of the ceramics material. Selective laser sintering (SLS) is a form of SFF. In this process, a thin layer of powder is spread across the build platform via a roller mechanism. The first slice or cross section of the object is selectively drawn on the layer of powder using a CO_2 laser. The laser energy heats the powder to a temperature just below the melting point of the material and bonds the powder into a solid mass. The laser power is modulated so that powder only in the areas described by the object's geometry is fused. The build platform is lowered and the roller deposits another layer of powder across the build platform. The steps are repeated until the object is complete. The primary advantage of SLS process is the flexibility in selecting material systems compared to other SFF techniques.[1] Gelcasting is a novel near-net-shape forming method for fabricating complex-shaped ceramic bodies. In this process monomer, crosslinker, initiator, catalyst and ceramic powder are thoroughly mixed in water to form a homogeneous suspension with

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PII: S0955-2219(02)00229-7

high solids loading and low viscosity, then by means of *in situ* polymerization a macromolecular network is created to bind the ceramic particles together. The polymerized product accounts for less than 4 wt.% of the dried solids.[5] A detailed flowchart of the gelcasting process is shown in Fig. 1.

In order to put forward a more efficient SFF approach, in this article a new lost mould method is successfully designed by combining SLS and gelcasting technique. Fig. 2 shows a graphic depiction of the process. First, a composite polymer powder is developed for SLS to fabricate sacrificial moulds having a negative of the desired structure for gelcasting. Then a homogeneous alumina slurry with high solids loading and low viscosity is poured into the moulds. During the sintering of the ceramic parts the polymer mould is removed entirely. Because the solidified green bodies have high strength even at elevated temperature, the desired geometry of the ceramic parts is successfully retained after sintering. Complex alumina parts are successfully produced by this way.

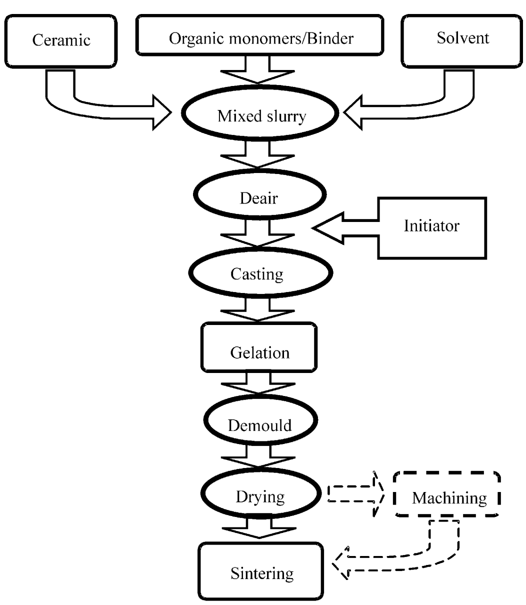

Fig. 1. Detailed flowchart of the gelcasting process.

2. Experimental

The alumina powder is a commercial product An-0.5 provided by Henan Xinyuan Aluminum Inc. of China with an average particle size of the 2.0 μm. Acrylamide (C_2H_3CONH, AM) and *N,N*-methyl-enebisacrylamide ($(C_2H_3CONH)_2CH_2$, MBAM) are used as the monomer and the crosslinker, respectively. *N,N,N′,N′*-tetramethylethylenediamine (TEMED) and $(NH_4)_2S_2O_8$ are used as catalyst and initiator for the polymerization, respectively. AM and MBAM are dissolved in deionized water to give the premix solution. Triammonium citrate (TAC) is selected as the dispersant to give well dispersed homogeneous ceramic suspension. Before casting the ceramic powder and dispersant are added into the premix solution and are thoroughly ball-milled for 24 h. After being de-aired for 15 min the polymerization is initiated by adding initiator and catalyst. Then the slurry is cast into the sacrificial plastic moulds, which is fabricated by an AFS SLS machine produced by Beijing Longyuan Co., China. The Zeta potential of the ceramic particles is determined by a Zeta Plus analyzer (Brookheaven Instrument, USA) and the viscosity of the alumina slurries is determined by an advanced MCR300 rheometer (Physica, German). The details of how the sintered mould structure and gelcast polymers are pyrolyzed are determined via thermogravimetric analysis (TGA) in air by using a Dupont Thermal Analyzer 2000. The microstructure of the laser sintered polymer mould is observed by a HITACHI S-450 scanning electron microscopy (SEM).

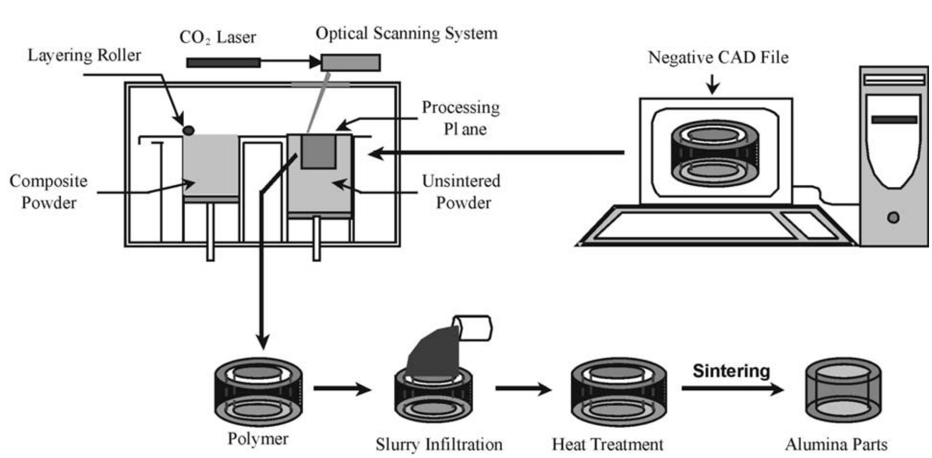

Fig. 2. Schematic of the steps in the lost mould approach for fabricating alumina ceramics.

3. Results and discussion

3.1. Colloidal chemistry and rheological property of the Al_2O_3 suspension

It is of prime importance to be able to obtain a stable and homogeneously dispersed ceramic suspension in order to obtain high quality ceramic parts by gelcasting. The rheological behavior or viscosity is related to the suspension property, which is determined by attractive and repulsive forces in the system. Attractive van der Waals forces can be counteracted by repulsive forces resulting from either overlapping of the electrical double layers (electrostatic stabilization) and/or layering of materials adsorbed on the surface (steric stabilization). The magnitude of the van der Waals forces is mainly determined by the nature of the particles and the solvent while the repulsive forces can be modified over a wide range by addition of dispersants.[6] The repulsive forces can be characterized by the Zeta potential and the potential of the particles as a function of pH value are shown in Fig. 3. 0.1 vol.% Al_2O_3 suspensions were regulated by HCl and NaOH to fixed pH value and ultrasonicated for 2 min prior to analysis. The higher this potential with the same polarity is, the more important the electrostatic repulsion between particles. Contrarily, when close to the isoelectric point (IEP), the particles tend to flocculate. From Fig. 3 we can see that the IEP of the powder is at about pH 4.8 and it has a Zeta potential value of −10 mV at pH 7. With the addition of TAC (1 wt.% of the alumina) the IEP is moved to about 2.7 mV and the Zeta potential at pH 7 is doubled, suggesting that TAC has a electrostatic stabilization mechanism for good dispersion. Adding the monomer does not shift the IEP but it slightly decreases the relative value of the Zeta potential. This indicates that the uncharged AM molecule either screens the charge that is developed by the powders in solution or preferentially absorbs onto the surface of the alumina particles. Viscosity of the alumina slurries as a function of the shear rate is illustrated in Fig. 4. We can see that TAC can greatly decrease the viscosity, agreeing well with the Zeta potential results. The shear thickening behavior of the slurries with TAC at higher shear rate is due to the increase of the ‘‘phase volume fraction’’ at high solids loading.[7] For a dispersant there exists an optimum concentration at which just enough dispersant is present to provide maximized coverage of the ceramic powder and any excess dispersant may be harmful in decreasing viscosity.[8] The optimum concentration of TAC is about 0.3% by weight of Al_2O_3 powder.

3.2. Selection of materials for SLS and sintering cycle development

A large range of materials can be used in SLS, such as nylon, ABS, sand, wax, metals and polycarbonate, etc. However, some problems must be considered when selecting a material. During heat treatment the sacrificial mould should burn out clearly without leaving any residue that may be detrimental to the properties of the ceramic parts. Therefore all organic constituents materials system should be adopted. Here a polystyrene based composite powder is developed to make the sacrificial mould. In fact, polystyrene is frequently used in lost foam casting due to its thermal degradation property.[9] Because a general polystyrene product may result in large geometry distortion upon heat treatment, the composite powder is specially processed by reactive blending of PS, rubber, antioxidant, impact modifier and other additives through twin crew extruder. It is also necessary to cool the part when it becomes too hot in order to prevent distortions in the final piece. Therefore wax is not a suitable material because it needs a long cooling cycle on the machine although it can also be removed easily. From the SEM photograph of the cross section of a sintered mould shown in Fig. 5 we can

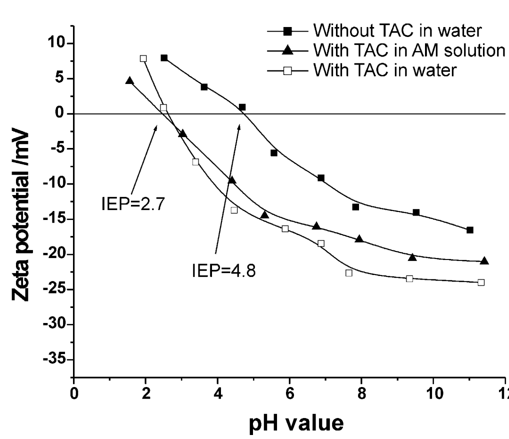

Fig. 3. Zeta potential versus pH value of different alumina suspensions.

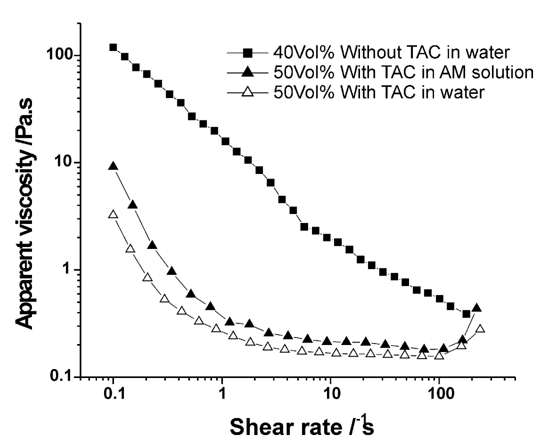

Fig. 4. Effect of dispersant and monomer on the viscosity of different ceramic slurrys.

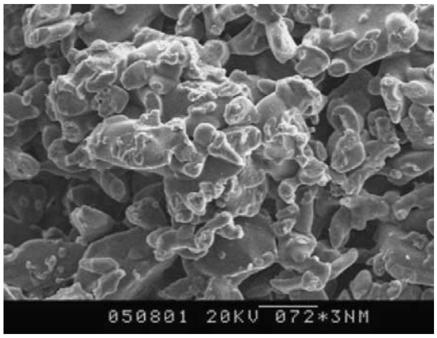

Fig. 5. SEM photograph of the microstructure of the sintered polymeric mould materials.

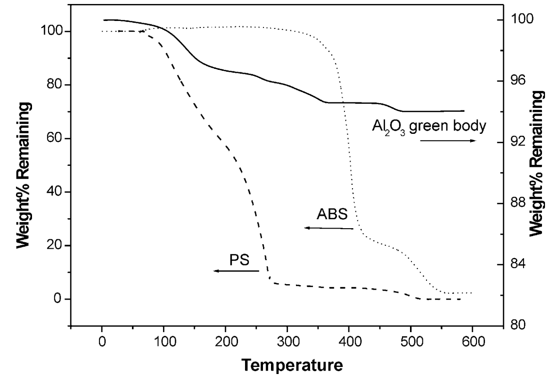

Fig. 6. TGA curves of the polymeric mould, ABS resin and a cast alumina sample.

see a porous network structure, which is helpful in preventing distortion.

The details of the thermogravimetric curves (4 °C min^{-1} in air) of the sintered moulds and that of a green Al_2O_3 cast ceramic sample (50 vol.% solids loading) are shown in Fig. 6. The mould material starts evaporating at about 85 °C and it losses 94% of its weight at 85∼300 °C. At a higher temperature a slow burnout occur that ends at about 510 °C with no residue left. The gelcasting sample starts evaporating at about 120 °C and before 500 °C only a 6% mass loss happens due to the trapped water and the burnout of the crosslinked polymerized AM network. Because of the low mass loss temperature and the porous structure of the polymeric mould, green ceramic structures have sufficient strength to hold the structure during evaporating. As a result the geometry of the ceramic part is well preserved. The mould material should evaporate first before the binder evaporates or else collapsing of the ceramics caused by the deformation or flow of the plastic mould may happen during heating. In fact collapsing occurs when other polymer materials such as ABS are used as the mould materials (see Fig. 6). The binder removal and detailed sintering procedure of dry ceramic powder infiltrated moulds were determined based on the TGA results. The heating cycle consists of three steps. During the first part of the cycle (room temperature to 600 °C), mould material and crosslinked polymer binder evaporate. Secondly, one hour of constant temperature at 600 °C is maintained to remove the remnants of the decomposed polymers. At higher temperature, densification of Al_2O_3 occurs. A final sintering temperature of 1550 °C and a hold time of 2 h are used for the alumina samples. The ultimate sintered ceramic parts are shown in Fig. 7. Generally the mass ratio of polymer mould to Al_2O_3 slurry is about 5:100 before sintering. The polymeric mould material can be sintered with a relatively low-powered laser in a short time. A 2×2×2 cm polymer mould needs just half an hour to be fabricated. Using adaptive slicing which generates different slice thicknesses between 0.08 and 0.3 mm based on the local slope of the part, the build rate can also be increased. Therefore the cost of the mould is acceptable and it is an economical SFF method in fabricating ceramic parts.

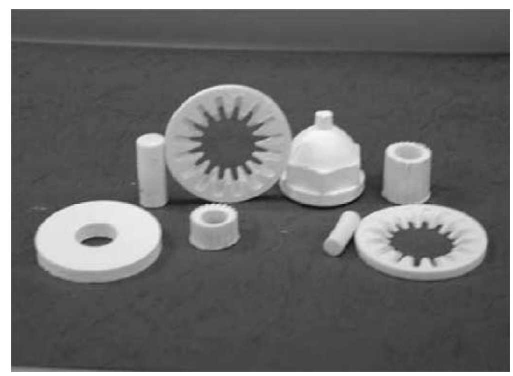

Fig. 7. Illustration of the ultimate alumina ceramic parts fabricated by the lost mould approach.

4. Conclusion

SLS (selective laser sintering) in combination with gelcasting technology have been utilized to fabricate three-dimensional Al_2O_3 parts. By using a polystyrene based composite material SLS is utilized to fabricate sacrificial moulds for the ceramic parts, which are infiltrated with ceramic slurry containing monomer, crosslinker, initiator and catalyst. Then the system is heated and subjected to binder removal and sintering cycles. Complex shaped Al_2O_3 parts are successfully fabricated by this approach.

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