Rapid Tooling of Ceramic Parts and Molds using High-Pressure Slip Casting of Si_3N_4

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ABSTRACT

A novel rapid tooling technology for the fabrication of ceramic parts has been developed. A concentrated Si_3N_4 slurry is cast in a porous mold. Therefor, a high pressure slip casting device has been constructed which enables the use of relatively fragile polystyrene molds. Polystyrene molds have been produced using rapid prototyping techniques e.g. selective laser sintering. The required porosity is adjustable by variation of the process parameters. Mechanical and chemical methods to demold the ceramic green parts are demonstrated. The technology enables the fabrication of crackless Si_3N_4 parts, particularly molds with high and homogenous density and illustrates the possibility to transfer the results to other ceramics.

1 INTRODUCTION

The processing challenge in the forming of advanced ceramic parts is to achieve a defect-free microstructure in the final body. Forming a ceramic powder into an engineering part can be performed with a variety of methods, such as powder compaction, injection molding, extrusion, slip casting, pressure casting and more. In general the choice between these methods often depends on several important factors, such as product volume, size tolerance, cost, short cycle time to mention a few. Due to the high hardness of ceramic materials, it is almost always cost prohibitive to form a component by removing material from a solid ceramic block or shape.

In the last few years rapid prototyping technologies have been developed to a very high level and allow the direct production of components with complex shapes directly from CAD data. One drawback of most of these processes is the fact that only plastic and metal parts can be accomplished by these technologies /1/. To generate ceramic parts for industrial applications, especially for producing ceramic parts with complex geometries, there are still less possibilities.

Consolidating powders into uniform, near-net-shape powder compacts is an essential element of ceramic processing. Today there exist two major forming techniques for large-scale fabrication of ceramic components with complex shapes: injection molding and slip casting. In injection molding relatively large amounts of polymers are added, which have to be removed before sintering. In the slip casting process there is a liquid which has to be removed from the cast component. Pressure casting or pressure filtration in which a porous mold or a filter was used has been developed to accelerate the drying stage and to get more dense particle packing and hence a more favorable microstructure /2/.

The paper illustrates a rapid tooling technology and apparatus for the rapid production of Si_3N_4-parts and -molds using high-pressure slip casting in polystyrene molds. Procedures to obtain porous polystyrene molds applying selective laser sintering (SLS) and sintering in silicone molds are shown. In addition, demolding strategies were investigated to separate green part and polystyrene mold.

2 PRESSURE SLIP CASTING

Unlike slip casting, pressure casting derives its main driving force from an external pressure applied to the ceramic slurry which results in an increased rate of cake formation /8/.The kinetics of pressure casting obeys Darcy's differential equation /3/ for fluid flow through porous media, which, when integrated with appropriate boundary conditions, shows that the thickness of the consolidated layer L, formed when either pressure P, or time t, is kept constant, is parabolically related to the variation in the other of these experimental variables by the equation

$$L^2 = 2K\phi Pt/\eta(\phi_c-\phi)$$

where η is the viscosity of the slurry and ϕ and ϕ_c are the volume fractions of particles within the slurry and cake. The permeability K is inversely related to the resistance to fluid flow through the consolidated layer. This equation assumes unidirectional filtration, negligible mold resistance, constant rheological properties of the slurry, absence of particle setting, and constant permeability, i.e. the body is incompressible.

In practice, cakes are more or less compressible, depending on pressure level, interaction forces between particles and particle size distribution /4//5/. The rate of cake growth is therefore expected to follow a parabolic behavior /4/. That is, the cake should grow as a function of $(\text{time})^{1/2}$. This means that the cake builds up very quickly at the beginning of the casting, then slowly. When the thickness of the cake reaches some value, the rate of consolidation is about zero, because the thick cake will resist any further filtration. This is illustrated by the study of Schwelm /6/.

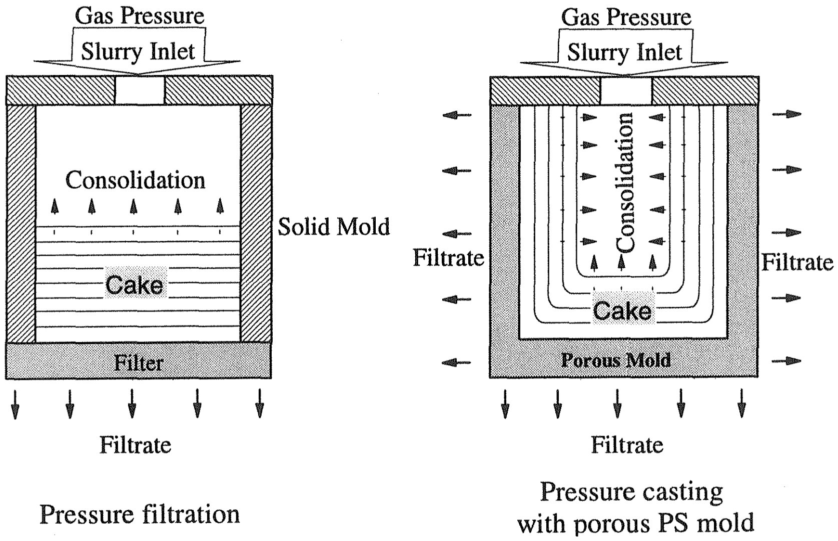

Figure 1: Schematic description of consolidation progress during pressure slip casting

Figure 1 is a schematic description of consolidation progress during casting. The progress of the consolidated fronts are indicated. According to the theory of consolidation, the cake builds up layer by layer until filtration ceases. By usual pressure filtration using a solid mold and plate filter, it is difficult to produce thick components, because at some thickness the consolidation rate is very slow. Besides this, there also exists a detectable gradient of green density in the direction of consolidation by unidirectional casting /6/. These density differences will cause anistropic shrinkage during sintering.

These problems could be resolved by pressure casting with a porous PS mold. Unlike usual pressure filtration, the consolidation by pressure casting with PS molds occurs not only in a direction opposite to that of the pressure, but also circumferentially, because the filtrate can go out around the mold, as indicated in right figure of figure 1. It should be noted that the consolidation rate in this way will increase with the additional surface area of the mold and therefore the possibility to cast a thick component will then be increased. Moreover with this new processing the density gradient will also be limited.

2.1 POWDER AND SLURRY PREPARATION

A submicron α-phase Si_3N_4 powder (M11, H.C. Starck, Germany) with a BET specific area of 11.5 m^2/g and a mean particle size (d_{50}) of 0.74μm, containing 5mass% of Y_2O_3 (AKP247, H.C. Starck, Germany) and 3mass% Al_2O_3 (AKP53, Sumitomo, Japan) as sintering additive, was mainly used for the slurry preparation. The particle size distribution of the powders was measured by He-Ne-Laser-Granulometer HR 850 (Cilas, France).

The slurries containing a 0.31 solid volume fraction of ceramic powder was homogenized by ball milling (a planetary ball mill, Si_3N_4 balls) for one hour in a Teflon container. The aqueous Si_3N_4–slurry was prepared by addition of 2-amino-2-methyl-propanol ($C_4H_{11}NO$, Fluka Chemie AG) as dispersant. For some slurries PVA was added as a binder and PEG as a plasticizer. After milling dissolved gas in the slurry was removed in a closed vessel under vacuum to prevent the formation of bubbles in the green body. The slurries were characterized by viscosity. The rheological measurements were performed with a rotational viscometer (SR500, Rheometric Scientific, USA) at a constant temperature of 25°C.

3 RAPID TOOLING PROCESS

Figure 2 schematically shows the developed pressure slip casting device designed to cast high concentrated ceramic slurries in porous polystyrene molds. The device consists of two major parts, a store tank and a pressure device. The porous polystyrene mold is glued on a silicone grease coated aluminium plate. The plate is used as a substratum to remove the mold after casting without damaging the inner ceramic cake. Silicone grease is necessary to allow a stress free shrinkage of the drying ceramic on its subtratum. The pressure slip casting device has to be turned to fill the pressure device container with fine sand. The whole device is put on a vibraxer to compress the sand, simultaneously the clamped support has to be installed and screwed in. After fixing the clamped support the device is turned and an amount of slurry (according to the volume of the mold) poured into the store tank. The store tank is air tight and a pressure pipeline is installed The pressure, regulated by a ER2000 pressure device from Dräger-Tescom, can be applied and the cake formation occurs. Pressurized N_2 gas was used to apply the pressure.

As the cake fills the whole mold pressure casting is finished, the pressure is reduced to atmospheric level and the device can be opened. Subsequently the pressure device has to be dismantled and the now solvent tinctured sand is poured out. To separate the mold from the pressure device the plate with the filled mold is pushed to the side. Experiments showed, that to ensure a crackfree shear the cake from the pressure device, the sprue gate of the substrate plate has to be edged. The porous polystyrene mold is glued on a silicone grease coated aluminium plate. The plate is used as a substratum to remove the mold after casting without damaging the inner ceramic cake. Silicone grease is necessary to admit a stress free shrinkage of the drying ceramic on its subtratum.

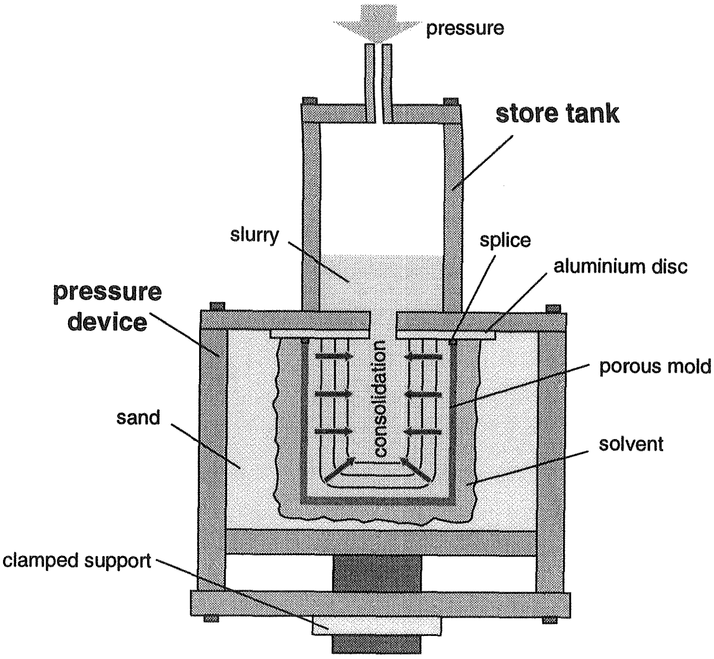

Figure 2: Pressure slip casting device

As the ceramic cakes still contain a high percentage of solvent (in this case we used water as a solvent) the cake has to be dried to get a green body. As during the drying, the ceramic shrinks, it is essential to demold the ceramic cake before drying, otherwise cracks are inevitable. As a matter of principle there exist two demolding methods: mechanical and chemical demolding. A thermal demolding is not applicable because by firing the polystyrene mold the outer regions of the cake are dried too fast and the moisture gradient in the cake causes innumerable cracks on the surface. The other demolding techniques are explained in section 4.3.

4 POROUS MOLDS

Polystyrene powder (from EOS), specially developed for the laser sintering process with an average particle size of 100 µm was used to generate the molds.

4.1 SELECTIVE LASER SINTERING

The laser sintering equipment was an EOSINT 350P having a cw CO_2 laser of 42W. In the experiments the beam power was kept at the maximum value to get a high process speed. Usually laser sintered prototypes should be as dense as possible. In contrast to that a porous polystyrene mold with an amount of pores was desired in this work. Therefor the building parameters have to be optimized to get porous molds with proper porosity and sufficient strength. At a constant hatch distance of 0,2 mm the beam energy density was adjusted by varying the beam scanning velocity from 1000 to 2500 mm/s. The layer thickness was 0,2 mm for all experiments. As support structures influence the homogenous density of the polystyrene molds the building process had to be realized without the commonly used support grid. Hence the first layer was sintered directly on the working platform by treble exposure at maximum power and a scanning velocity of 800 mm/s.

Considering the mechanical strength, samples built at 2500 mm/s cannot be used for pressure casting. Samples scanned at 2000 mm/s provide sufficient strength and proper porosity. For this reason they were chosen as mold material for further experiments. The open pores of these PS samples were measured by means of mercury porosimetry. It reveals an open porosity of about 11% with an average pore diameter of 27 µm. About 2/3 of pores are closed.

The beginning of cake formation is usually different from the rest of the process and depends on interactions between the particles of the slurry and the porous mold. The first consolidation behavior is very important and strongly affected by the characteristics of the ceramic powder and the slurry. Lyckfeldt /3/ summarized the factors which were found to have the main influence on the consolidation behavior of ceramic slurry. As the mean pore size of the sintered PS-molds is 20-50 times larger than the ceramic particle size used, a great amount of slurry gets infiltrated in the mold. To prevent this effect the mold had to be coated with gypsum. Therefor gypsum powder has been dissolved in isopropanol and painted on the molds by means of a paint-brush. The liquid gypsum infiltrates and occludes the pores establishing a porosity in the pores comparable with a gypsum mold. Experiments showed that the gypsum coating prevents the PS-mold from slurry infiltration and consequently accelerates the cake formation.

4.2 SINTERING IN SILICON MOLDS

In order to gain time and accuracy, another sintering procedure (see fig.3) has been applied. Starting from a stereolithography or other RP-model a silicone mold is cast.

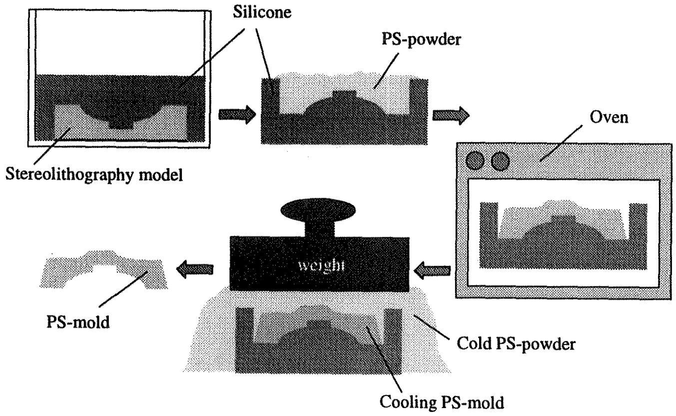

Figure 3: Sintering process in silicone molds

The silicone mold is filled with PS-powder, covered, and given in an oven which is gently heated up. The slow increase of temperature guarantees an equable heating of silicone mold and powder. After reaching the sintering temperature range (about 125°C) of the PS-powder the temperature is held until a sufficient firm sintering is reached. As silicone is a bad heat conductor the sintering time is widely dependent of the thickness and the silicone used.

After sintering the mold is taken out of the oven, covered with cold PS-powder and a weight placed on top. During the cooling the weighted powder prevents the shrinking mold from curling and guarantees an exact molding of the silicone model. The advantages of that sintering concept are obvious: no staircase effect, better surface quality and the opportunity to produce as many molds as required.

4.3 DEMOLDING TECHNIQUES

As mentioned before there exist two demolding principles: mechanical and chemical demolding.

4.3.1 MECHANICAL DEMOLDING

The first green bodies were demolded mechanically by carefully paring the sintered layers with a scalpel. With this the major problem are the sintering parameters. A hard sintered mold with high strength is difficult to demold because the layers hold together to much, whereas a soft sintered mold is easy to peel but contains defects which can precipitate an intrusion of slurry into the mold or at worst a fracture of the mold. Furthermore, experiment showed that this demolding strategy is unapplicable on complex geometries.

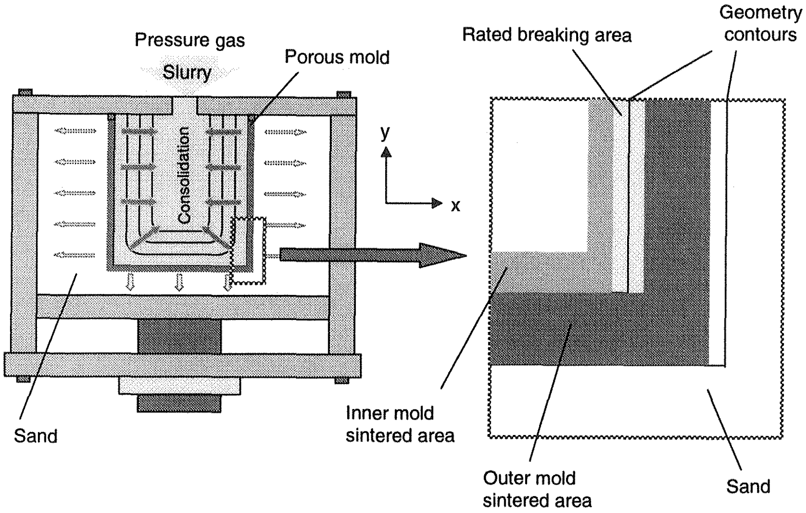

Figure 4: Double mold production with rated breaking area

On this account an improved sintering concept for mechanical demolding was developed (figure 4). The produced part consists of a thin inner and a stabilizing outer mold separated by an unsintered region in the layer (x-direction) direction. In the building direction (y-direction) there is no unsintered area applied because on one hand, only an unsintered region of layer thickness is possible which causes problems in the sintering process, on the other hand the layers can easily be separated by paring with a scalpel. As the geometries of inner and outer mold have to be constructed at a tangent to each other, the rated breaking point between them is reached by implementing a bigger hatch compensation (0,6 - 0,8 mm) for the laser scanning parameters than usual. After the slurry is cast in the mold, the outer mold is removed with a scalpel and then the inner mold with a thickness about 1,5 mm can be peeled from the ceramic cake.

4.3.2 CHEMICAL DEMOLDING

As experiments showed that mechanical demolding is complicated and labour-intensive, dissolvers were tried to dissolve the polystyrene molds. After casting the mold was placed in a dissolver filled, closed exicator with a magnetic mixer. After some hours the polystyrene mold is dissolved and the ceramic green body lies demolded in the bath. The gypsum coating still adheres to the cake and as the gypsum binds to water, it mainly prevents toluene from penetration in the slurry. The part is taken out of the toluene bath and immersed in clean PS-free toluene. After that the wet green body is taken out and cautiously dried. Before sintering, remnants of gypsum and PS have to be remotely rubbed off with a stiff paint-brush.

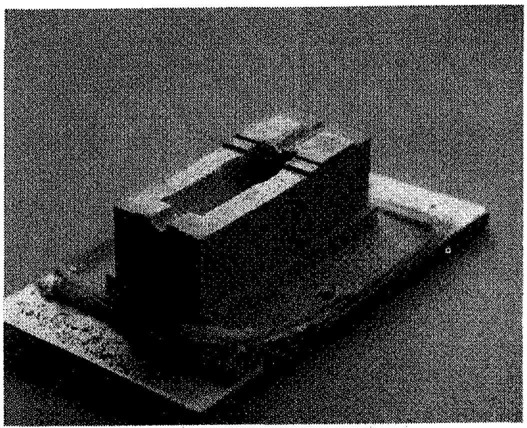

Figure 5: Green body after demolding with Toluene

5 RESULTS

Specimens fabricated with this new processing achieved a high sintered density of > 97% of the theoretical value, as shown in Tab.1. All the samples were cast using the slurries with a solid volume fraction of 0.31. The value for the sample PSC (pressure slip casting) is a mean value of many samples.

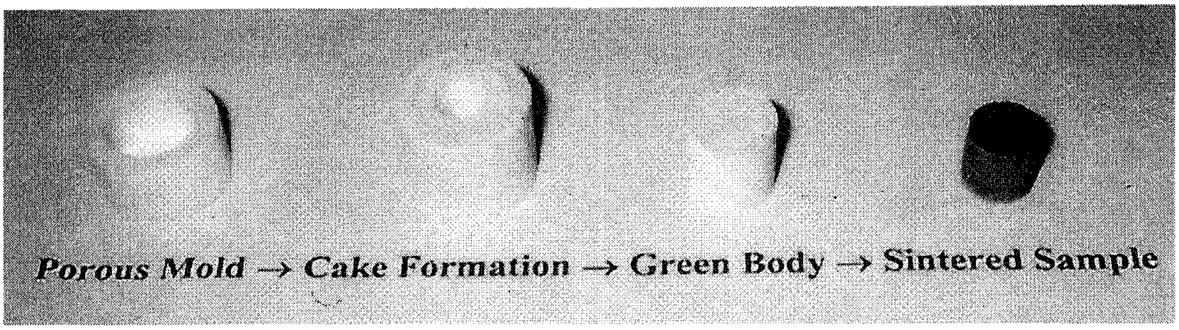

Figure 6: Steps of the process

There is a correlation between the green density and the final sintered density. It should be noted that the green density appeared to be the most important parameter for the final product and it depends strongly on the properties of the slurry in this process. The remaining porosity within the samples is, in general, very small, and well dispersed throughout the matrix.

Sample	Green density (% of theor.)	Sintered density (% of theor.)	Linear shrinkage (%)	Note
PSC	57.2	97.6	radial ΔΦ: 18.5 Δh: 18.5	pressure slip casting with homogeneous slurry
CIP	56.0	96.0	radial ΔΦ: 18.4 Δh: 18.4	cold isostatic pressing (600MPa)

Tab.1: Green and sintered densities and the shrinkage of Si_3N_4 samples

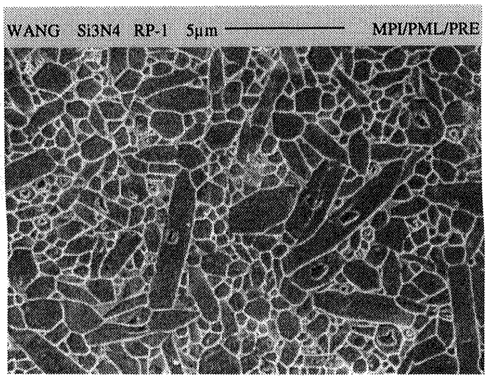

Figure 7: SEM mirograph of a polished specimen (plasma etched) showing the grain structure of sintered Si_3N_4

In order to investigate the sinterability, a sample prepared by cold isostatic pressing with the same composition was also sintered at the same sintering conditions. The Si_3N_4 parts produced by this new technology has the highest relative density (Tab.1). The β-Si_3N_4 phase with homogeneous microstructure is very well developed (as shown in Fig. 7). The glass phase is also uniform. From Tab.1 we know that the linear shrinkage after sintering both in radial and high directions of the simple cylinder specimen is nearly the same. No inhomogeneous shrinkage could be detected. This means that the green density before sintering is very uniform, just like the specimen produced by cold isostatic pressing.

6 ACKNOWLEDGMENT

This work is supported by the state of Baden-Wuerttemberg under contract 07-105-406 in cooperation with Bertrandt Fahrzeugtechnik GmbH, Cardenas GbR, Oxidkeramik J. Cardenas GmbH and VEPA GmbH.

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