Rapid prototyping and manufacturing by gelcasting of metallic and ceramic slurries

Jürgen Stampfl *, Hao-Chih Liu, Seo Woo Nam, Katsuhiko Sakamoto, Hideaki Tsuru, Sangkyun Kang, Alexander G. Cooper, Alexander Nickel, Fritz B. Prinz

Stanford University, Rapid Prototyping Lab, Building 530, Room 226, Stanford, CA 94305, USA

Abstract

In this work an approach for rapid prototyping and manufacturing of metallic as well as ceramic parts is presented. By using Mold Shape Deposition Manufacturing (MoldSDM), a wax mold is fabricated which is filled with a slurry containing the final part material in powder form. The wax mold is manufactured by first decomposing the desired part geometry into machinable compacts. In a next step the mold is built up in a series of layers by machining either the wax or a sacrificial support material. The surface quality of the final mold is only limited by the abilities of the CNC machine. After casting a ceramic or metallic slurry, the wax mold is removed and the obtained green part debinded and sintered. In this work the mechanical and microstructural properties of the parts obtained by this method are presented. The materials which have been investigated are silicon nitride and stainless steels. Due to the high mold quality the process is suitable for a variety of applications in rapid prototyping and manufacturing where parts made of engineering materials are required. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A wide variety of commercially available systems for rapid prototyping (RP) enables the user to fabricate prototypes with almost any shape and in a large range of different sizes. The focus of most of these systems, like stereolithography (SLA) and fused deposition modeling (FDM), is to produce plastic prototypes with a high geometric quality. Most RP techniques put less emphasis on material issues, and if they do [1,2], it is not easy to switch between different materials. In this work we introduce an approach where an RP wax mold is fabricated in a first step. In a second step the wax mold is used to transfer the shape into the final part material. Mold Shape Deposition Manufacturing (MoldSDM) [3] is used to fabricate the wax mold, which is then filled with a metallic or ceramic gelcasting slurry. The main focus of this investigation is on parts made out of silicon nitride and stainless steel.

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* Corresponding author. Present address: Tu Wien, Inst. für Werkstoffkunde und Materialprüfung, Favoritenstrasse 9–11, A-1040 Wien, Austria. Tel.: +43-1-58801-30857; fax: +43-1-58801-30895.
E-mail address: juergen.stampfl@arcs.ac.at (J. Stampfl).

2. MoldSDM

MoldSDM [3] is an additive–subtractive layered manufacturing process for fabricating fugitive molds which can then be used to make parts using castable materials such as ceramic gelcasting [4,5] slurries and thermoset polymers [3]. Fig. 1(a) is an example process sequence for the fabrication of a simple part using MoldSDM. Molds are currently fabricated from a variety of waxes. These are deposited by casting and are shaped by either 3- or 5-axis computer numerical control (CNC) milling. The mold is constructed layer-by-layer in steps 1 through 8. Each step represents one material deposition and shaping cycle. The support material is removed in step 9 and the part material is cast in step 10. After removal of the mold in step 11 finishing operations, such as casting feature removal, are performed leaving the finished part in step 12. Processes such as sintering can be performed at any time after mold removal.

A typical cross section of a wax mold, which was made using MoldSDM, is shown in Fig. 1(b). The water-soluble support material has already been etched out.

Two features of the MoldSDM process are advantageous for the fabrication of complex structural ceramic components:

- all surfaces are either machined or replicated from machined surfaces resulting in smooth accurate geometry, and
- the part material is cast monolithically so there will be no layer boundaries, which are potential sources of defects, in the final part.

Both of these advantages are particularly important for flaw sensitive materials where surface roughness and internal defects can significantly reduce the part strength. Defects in the mold can arise from incomplete bonding between wax layers, or foreign particles or voids trapped at the layer boundaries.

3. Gelcasting

Gelcasting [4,6–8] is a molding technique for ceramic and metallic materials. The gelcasting slurry is obtained by mixing the part material in powder form into a liquid which consists of the following constituents: A solvent (either water or an organic solvent), one or several types of monomers, an initiator and in some cases an accelerator.

Fig. 1. Processing steps for MoldSDM (a) and section of wax mold (b).

3.1. Slurries

For this investigation three different base formulations for slurries were used. A water based formulation developed at Oak Ridge National Lab (ORNL) [4] and two solvent based formulations from Advanced Ceramics Research (ACR, Tucson, AZ) and SRI International (Menlo Park, CA), respectively. The solvent based formulations are proprietary, whereas the water based formulation from ORNL is patented [9] and published [6,10].

The water-based formulation was mainly used in combination with metallic powders. It can also be used for gelcasting of ceramics, but the interaction between water and the large surface of the ceramic particles decreases the shelf life of the slurries. For ceramic slurries the organic formulations are easier to use and give more easily reproducible results.

The casting procedures are similar for all types of slurries. After agitating the slurries for several hours to obtain a homogenous mix, initiator and/or accelerator are added to start the polymerization process. The slurry is then cast into an evacuated wax mold where the polymerization process continues until the liquid slurry is completely solidified. The wax is molten off to obtain the green part, which is then debinded and sintered.

Evacuation of the mold helps to avoid voids due to entrapped air and prohibits flaking of the green part surface. Flaking occurs if the slurry gets into contact with oxygen that can inhibit polymerization of the slurry. After drying, unpolymerized, "oxygen contaminated" layers of slurry peel off and leave the green part damaged. Many commercially available waxes contain antioxidants which can inhibit polymerization of the slurry, too. It is therefore necessary to choose a wax without polymerization-inhibiting additives. At the same time the wax must be machinable and the melting point should be between 80 and 100 °C. If the melting point is much lower, the mold can melt during gelling; if it is much higher, the green part can be damaged during melting off the wax mold. The waxes used in this work were supplied by Kindt–Collins (Cleveland, OH). For most parts a wax blend which was derived from Kindt–Collin's Master File-a-wax and Master Protowax gave good results. Both wax types were used without antioxidants or coloring agents.

In general the ceramic slurries are less viscous at the same solid loading than the metallic slurries. They are therefore easier to cast. Settling of the powder particles is also more critical in the case of metallic slurries (due to the higher density of most metals). But with the right precautions (correct solid loading, fairly short gelling time) this problem can be avoided for metals too.
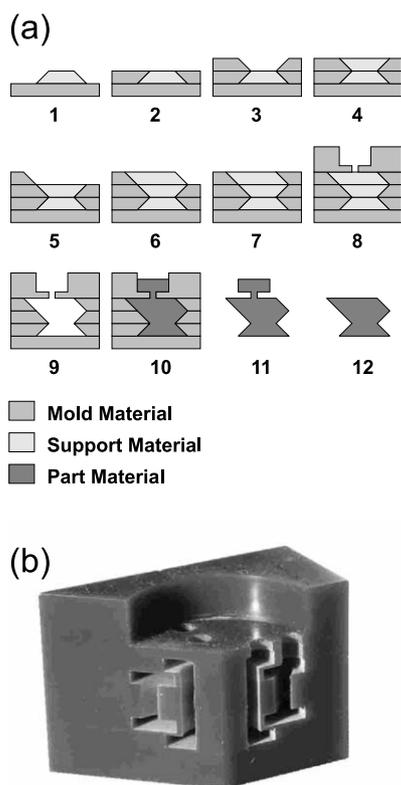
Table 1
Chemical composition of 17-4PH stainless steel

Element	C	Ni	Cr	Mo	Si	Mn	Cu	S	Nb	O	P	Fe
Weight %	0.04	4.21	16.06	0.01	0.41	0.11	3.73	0.01	0.26	0.54	0.01	BAL

For the metallic slurries, gas atomized powder of a precipitation hardening steel (17-4 PH, composition see Table 1) was used. Two different types of slurries were prepared: one with a 20 μm powder, and one with a 44 μm powder. In both cases similar solid loadings of around 50vol.% were achieved.

The ceramic slurries were composed of 88wt.% Si_3N_4, 9wt.% Y_2O_3 and 3wt.% Al_2O_3. The fairly high content of oxide ceramics simplifies the sintering process. At the same time the high oxide content will degrade the mechanical properties at elevated temperatures [11]. To achieve a higher solid loading, a bimodal silicon nitride powder (obtained from UBE, Japan) with $D_{50} = 0.5$ μm and $D_{50} = 0.7$ μm was used. Of each powder type, the same amount was weighed in. The overall solid loading for the silicon nitride slurries was 52vol.%. At this solid loading, a viscosity of 12.8 Poise was measured at room temperature (shear rate 60 rpm). The linear shrinkage during sintering is around 18% [5], and the tolerances due to irregular shrinkage can be kept in most cases at variations lower than 1% of the final dimensions. An example of a green and sintered ceramic turbine is shown in Fig. 2.

The metallic parts were debinded under nitrogen and further sintered in a mixture of argon and hydrogen at temperatures up to 1250 °C. The ceramic parts were debinded in air and sintered in nitrogen at 1750 °C.

3.2. Microstructure

Especially in the case of silicon nitride, the control of the microstructure is crucial for the quality of the final part. Since for applications in RP most surfaces of the sintered part cannot be further machined or ground to get the net-shape, the surface microstructure has to be considered in addition to the bulk microstructure. The final surface roughness of the sintered part is determined by two factors: The original particle size and the amount of grain growth of the β-needles which build up during the α–β-phase transformation. By adjusting the sintering atmosphere in a way that inhibits the grain growth on the surface, the surface roughness can be kept low. At the same time the phase transformation can occur in the bulk material to achieve the needle-like microstructure which determines the mechanical strength and toughness of the material.

In Fig. 3, scanning electron microscopy (SEM) micrographs of the bulk and surface microstructure are shown. The bulk microstructure, which was prepared by etching a polished sample in liquid sodium hydroxide (Fig. 3(a)) shows the typical β-needles in a glassy matrix. Due to the inhibited grain growth at the surface (Fig. 3(b)), the individual powder particles sinter together to form a fairly smooth surface. The root mean square (RMS) surface roughness of the final part is between 0.5 and 1.8 μm [5]. This value was obtained by using a profilometer (Federal Surf Indicator).

3.3. Micromachined molds

Progress in the field of macro-manufacturing (CNC machining, RP,...) and micromachining (plasma etching, lithographic techniques) is beginning to close a gap that was once very large. The macro-world (part or feature size > 1 mm) usually deals with a wide variety of materials in complex shapes whereas the micromachined parts are made out of a limited number of materials (mostly originating from semiconductor processes) in fairly simple shapes. Since gelcasting can be used in combination with macromachined as well as with micromachined molds, it is the ideal method to
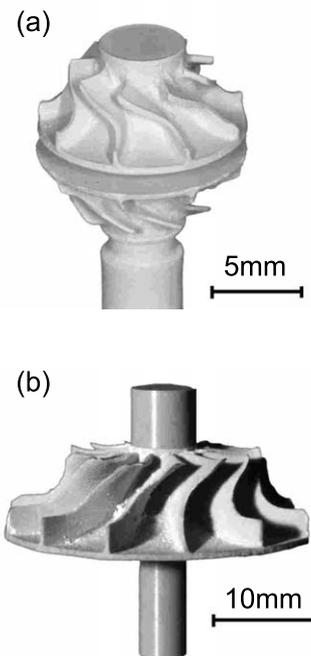

Fig. 2. Green (a) and sintered (b) silicon nitride turbine.
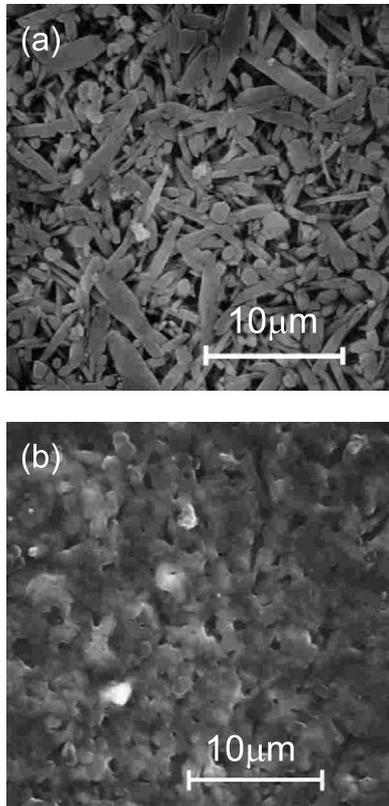
Fig. 3. Microstructure of sintered silicon nitride in the bulk material (a) and on the surface (b).

transfer mold-shapes with a wide size-spectrum into a large number of engineering materials [12].

Fig. 4 shows two parts obtained by gelcasting into a micro-mold (plasma etched silicon). After the slurry had solidified, the mold was removed chemically. The resulting parts replicate the original patterns very well, and the surface smoothness is only limited by the size of the utilized powder particles (as can be seen in Fig. 4(a)). Compared to most conventional manufacturing techniques used for fabrication of microsystems (lithography, plasma etching, electroplating), gelcasting expands the design space due to its ability to fill molds of arbitrary shape, including undercut and non-prismatic shapes. In this work, only simple molds with prismatic and non-undercut features are presented. To fabricate micro-molds with non-prismatic shapes and undercuts, concepts like using water-soluble support material, would need to be addressed in the context of micromachining.

4. Mechanical properties

Since the slurries utilized for this work contain commercially available powders which are sintered according to standard schedules, it can be expected that parts made by gelcasting [13] have similar properties to parts

fabricated by powder injection molding [14]. Table 2 gives a summary of the mechanical properties of 4-point-bend samples (Si_3N_4) and tensile specimens (stainless steel). Due to the ductility of the metallic samples and the brittleness of ceramic samples, the specific surface condition of the tested sample is less critical for metallic specimens than it is for ceramic samples.

In order to get a more complete description of the behavior of ceramic samples, Si_3N_4-beams were tested in the polished and unpolished state (see Table 2). All Si_3N_4-samples were sintered at 1750 °C in nitrogen atmosphere. The specimen size was $3 \times 4 \times 45$ mm. As expected, the polished and gas pressure sintered sam-
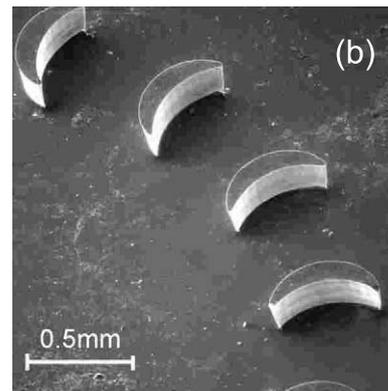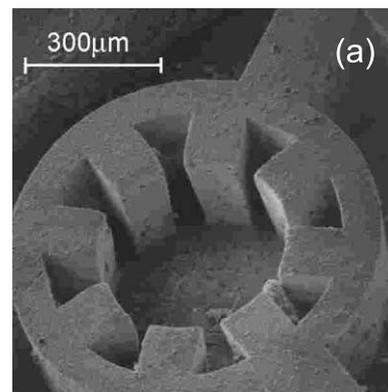

Fig. 4. Sintered test structure (a) and green turbine wheel (b) made out of gelcast silicon nitride.

Table 2
Mechanical properties

Material	Strength (MPa)	Density (%)
Si_3N_4 unpolished	414	97
Si_3N_4 polished	950	97
Si_3N_4 gas press. sint., polished	983	99
17-4 PH stainless steel	900	95

The values for Si_3N_4 were measured in 4-point-bending. The value for stainless steel is the tensile strength.

Table 3
Influence of mold surface quality on the mechanical properties of Si_3N_4

Sample	Slurry	Average strength (MPa)	Maximum strength (MPa)
Polished	ACR	930	1020
Unpolished parallel scallops	ACR	414	600
Unpolished perpend. scallops 0.001 mm	ACR	406	500
Unpolished perpend. scallops 0.005 mm	ACR	416	495
Unpolished perpend. scallops 0.01 mm	ACR	288	360
Unpolished perpend. scallops 0.1 mm	ACR	231	257
Unpolished parallel scallops	SRI	428	550

Fig. 5. Sintered stainless steel impeller (left) and polyurethane impeller (right).

ples yield the highest strength. All polished samples, independent of the sintering conditions, are stronger than the unpolished samples. Variations of the surface condition (surface roughness, surface microstructure) are therefore more relevant for the overall strength than variations in the bulk structure.

To quantify the influence of the surface roughness, several samples with defined grooves on the surface have been prepared. By machining scallops of defined height into the wax molds, the surface roughness of the final beam can be adjusted. The scallops were machined parallel or vertical, respectively, to the load line of the beam. Table 3 summarizes these results. The beams with the highest average strength are those with parallel scallops. The perpendicular scallops serve as notch and therefore decrease, as expected, the strength. The larger the scallop height, the more the strength decreases. But even the beams with parallel scallops have a significantly lower strength than polished beams. Two types of gels were used for this test; most beams were fabricated using the ACR gel. A second batch of beams, prepared using SRI gel, showed similar results (Table 3).

We can, therefore, conclude that two parameters in addition to the bulk properties determine the final mechanical properties of silicon nitride samples:

- The surface quality of the mold is transferred into the final part. The higher this surface roughness, the lower the final mechanical strength. The defects in the mold surface can cause notches which lead to stress concentrations in the final part. Depending on the applied load, these stress concentrations decrease the strength.
- Even in the case of a perfectly smooth mold surface, the difference between bulk microstructure and surface microstructure has to be considered when describing the mechanical properties of silicon nitride parts. The highest strength that could be achieved with unpolished samples (Table 3) is around 600 MPa, well below the 1020 MPa maximum strength of polished samples.

5. Conclusion

Gelcasting in combination with MoldSDM is capable of producing parts with complex shapes and well-defined microstructural and mechanical properties. By using gelcasting, very small parts with fine features can be fabricated (see Fig. 4) as well as fairly large parts (Fig. 5). Due to the decomposition into machinable compacts, almost any engineering design can be manufactured using MoldSDM. In combination with gelcasting, a wide variety of materials is available. In this work it could be shown that gelcasting offers viable routes for fabricating stainless steel and silicon nitride parts.

The mechanical and microstructural properties of these parts are comparable to those obtained by conventional manufacturing techniques. The materials used for MoldSDM (waxes, water soluble support material) are fully compatible with gelcasting and the combination of these two techniques opens new routes for the short-term fabrication of prototypes and small-scale production quantities of metallic and ceramic parts.

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