

Silica moulds built by stereolithography

C. ESPOSITO CORCIONE, A. GRECO, F. MONTAGNA, A. LICCIULLI, A. MAFFEZZOLI

Department of Innovation Engineering, University of Lecce, Via Monteroni 73100, Lecce, Italy

E-mail: carola.corcione@unile.it

In this work the production of ceramic moulds for aluminium casting using a stereolithographic apparatus is presented. Suspensions of silica powders in a photoreactive resin were used in standard STL equipment in order to build green parts. UV curable pre-ceramic suspensions have been studied using photocalorimetric and rheological characterizations. Thermogravimetry was used to analyse the behaviour of the pre-ceramic green during thermal treatment. Stereolithography apparatus (SLA) was modified in order to fabricate ceramic green. Silica objects were obtained by pyrolysis of the organic binder and subsequent sintering at high temperature. A characterization of mechanical properties of the green and sintered ceramic materials was performed. Finally moulds for investment casting of aluminium were built by stereolithography and used for casting as a green as well as after sintering. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Conventional ceramic forming techniques are based on powder filling of a negative mould and subsequent powder compaction at high pressure and temperature. The outlay of moulds is the major costing factor especially for the production of complex shape prototypes. The use of Rapid Prototyping (RP) processes can reduce the costs and time for the production of single objects or of very limited series [1]. Since the mid 80's the need of fast automatic fabrication techniques lead to the development of many additive RP technologies [1]. This new fabrication concept allowed the construction of complex parts, starting from a 3D-CAD model, without using a mould. In RP, the object is obtained bonding, layer by layer, its sections by an additive process rather than cutting or "sculpturing" the parts from a homogeneous block. The key point of RP is given by the direct link between the CAD model and the solid object, generated in few hours suggesting that tailor made or single functional parts can be fabricated, for example, for prosthetic fabrication in a very short time. Traditionally, most of the RP processes are used to produce polymeric objects. However, over the last decade, several solid free-form fabrication (SFF) methods have been investigated as techniques to fabricate metal or ceramic parts [1] directly from computer 3D projects. In particular SFF of ceramics is aimed to produce high performance, near net-shape structural [2, 3] and/or functional [4–6] ceramic parts. The interest in this fabrication process arises from different application fields: ceramic materials are needed as prototype for functional tests and pre-series production tests, ceramic moulds in unique copy are needed in metal casting, e.g. jewellery, ceramic cores are needed in investment casting of hollow objects. Since ceramics are good

biomaterials, either inert or bioactive implants are made by alumina, zirconia, carbon, hydroxyapatite, bioglass. Many applications are possible with the convergence of three distinct technologies: medical imaging (computer assisted tomography CT, Magnetic Resonance Imaging MRI), CAD and computer graphics for image processing and edge detection, rapid prototyping of ceramic implant.

Only recently the significant efforts devoted to the development of technologies of RP based on non-polymeric materials lead to the market equipments based on the selective laser sintering of metallic powders, but the RP of ceramic parts is still at laboratory scale [7–13].

In this work the production of ceramic objects using a stereolithographic apparatus is presented. Laser Stereolithography (STL) [14] represents the most assessed process for rapid prototyping and can be adapted to building of ceramic objects. In STL the objects are obtained curing a low viscosity liquid resin layer by layer. The shape and the dimensions of the parts are directly transferred from a three dimensional CAD system to the stereolithography equipment where a laser beam (usually He-Cd or Ar) polymerises the different sections. Suspensions of ceramic powders in a photoreactive resin can be also used in standard STL equipment in order to build green parts [3, 15]. A candidate ceramic stereolithography suspension must satisfy several requirements. It must have high reactivity in order to minimize the build time, its viscosity must be comparable with that of commercial SLA resins [3] and high volume loading of ceramic powder is required to obtain properly sintered ceramic.

In a previous work [15], the photo activated resin was loaded with alumina powders and ceramic objects

were obtained using an experimental stereolithography set-up. Mechanical properties of sintered products were comparable with those of traditionally sintered ceramics. Some differences were observed, probably due to the residual porosity, not less than 10%. Nevertheless, the high loading of alumina powders results in lower values of cure depth, D_p [14], associated with the scattering of light from ceramic particles. In this work alumina powders have been replaced by silica powders, to increase the cure depth, as better explained in the results and discussion section.

The preliminary development of suspensions was performed using photocalorimetric and rheological characterizations. Thermogravimetry has been used to analyse the behaviour of the pre-ceramic green during pyrolysis. A stereolithography apparatus, SLA-250 (3D System, Valencia, CA) has been modified in order to fabricate ceramic green. Ceramic objects have been obtained by pyrolysis of the organic binder and subsequent sintering of the green at high temperature. A characterization of mechanical properties and microstructure of the samples has been performed. Finally, the silica suspension has been used directly in the stereolithographic apparatus to build moulds of different shapes for aluminium casting. Both green and sintered ceramics moulds were used.

2. Experimental

2.1. Materials

The adopted suspensions are prepared using a proprietary mix of commercially available multifunctional acrylic and silicone acrylate monomers. The resins mix is loaded with an amorphous silica powder (average particle size $5 \mu\text{m}$) from Sibelco. In every formulation 3% by weight of Irgacure 184 (1-hydroxy-cyclohexyl-phenyl-ketone) from Ciba, as photoinitiator, is added. A very homogeneous slurry when mixing is performed in a planetary ball mill (Ceramic Instrument). The properties of this formulation were compared with those of SL5170, a commercial stereolithographic epoxy based resin from Ciba.

2.2. Investment casting

Metal castings were performed using ceramic green moulds (i.e. non sintered mould) and ceramic moulds sintered at different temperatures in order to obtain different degree of densification. Aluminum was melted in alumina crucibles at 800°C and poured in the moulds. In the case of sintered ceramic mould the preheating was applied to improve the casting process.

2.3. Characterisation techniques

The suspensions have been characterized in terms of UV reactivity and of viscosity. The green and sintered components were studied with thermal analysis, and the mechanical properties and microstructure of sintered parts were analysed. The techniques used for materials characterization are the following:

- Differential Scanning Calorimetry (DSC). The cure of the resin was carried out in a nitrogen

atmosphere at 25°C in a DSC Perkin Elmer DSC-7. The DSC is modified for irradiation of the sample using transparent quartz windows. The light reaching the sample, produced by a 300 W Xenon lamp Cermax LX 300, is limited to a wavelength interval of $325 \pm 4 \text{ nm}$ using a monochromator, in order to simulate the irradiation band of a He-Cd laser beam. The beam is focused on the sample using a system of lenses and a mirror.

- Rheology. The viscosity of suspensions at 25°C , as a function of the amount of filler loaded, is measured using a strain controlled rheometer (Ares Rheometric Scientific) with a cone and plate geometry and in a shear rate range between 0.1 and 100 s^{-1} .
- Thermogravimetry (TGA). The weight changes of the preceramic green samples during pyrolysis of the organic binder and sintering is studied using TGA, Netzsch STA 406.
- Mechanical testing are performed using a dynamometer, Lloyd LR5K. Three point bending test of green and sintered ceramic bars are performed according to UNI EN 843 (specimen dimension: $50 \times 5 \times 3 \text{ mm}$).
- The values of porosity (P), apparent (T) and bulk density (B) for the sintered samples have been obtained according to ISO 10545-3.

3. Result and discussion

3.1. Formulation of suspensions

Different formulations of base resin for ceramic suspension have been prepared with the aim of maximizing the reactivity and minimizing the viscosity. The use of an organofunctional silane is considered a key factor in order to improve the dispersion of the alumina powder in a hydrophobic resin. Furthermore the silane can provide a solid residue of silica after pyrolysis of the organic binder of green. This residual silica is thought to reduce shrinkage and improve sintering. The modified differential scanning calorimeter described above was used to compare the rate of reaction of the formulations with that of the commercial epoxy based resin SL5170. The kinetic properties of SL5170 are considered as a benchmark for the use in STL.

The DSC measurements have been used to monitor the polymerization by assuming that the heat evolved during reaction is proportional to the fraction of reactive groups consumed. Following this approach the degree of reaction, α at a certain time t is defined as:

$$\alpha(t) = H(t)/H_{\text{tot}} \quad (1)$$

where $H(t)$ is the partial heat of reaction developed during a DSC experiment and H_{tot} represents the total heat of reaction measured when the reaction is completed. The reaction rate, $d\alpha/dt$, is thus obtained from the heat flow dH/dt as:

$$d\alpha/dt = 1/H_{\text{tot}}(dH/dt) \quad (2)$$

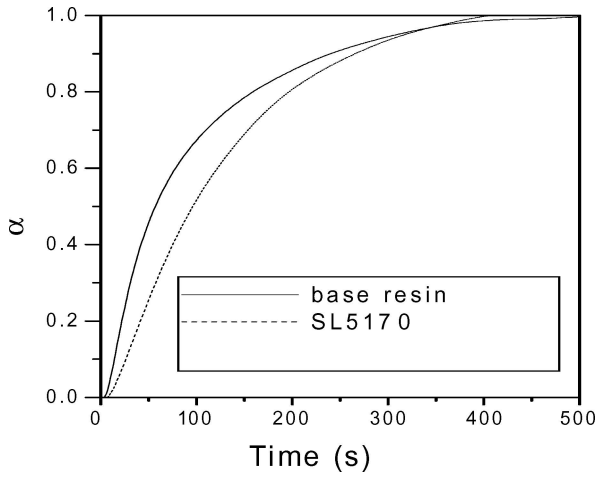


Figure 1 Time dependence of the degree of reaction for the acrylic based resin compared with that of the STL resin SL 5170.

The time dependence of the degree of reaction calculated by DSC for the base resin is compared in Fig. 1 with that of the STL resin SL 5170. As shown in Fig. 1, the time to reach full conversion for the base resin is lower than that of SL 5170. This suggests that the same conversion can be obtained with lower energy dose.

The reactivity of a STL resin is also characterized by two parameters relating the cure depth (C_d) i.e. the thickness of gelled resin with the energy dose at the vat surface (E_0) [14]:

$$C_d = D_p \ln \frac{E_0}{E_c} \quad (3)$$

where the working parameters D_p and E_c , are the penetration depth and critical energy respectively. E_c represents the minimum value of energy needed to promote polymerization on the suspension surface, while D_p is a characteristic parameter proportional to the gelled thickness. A good resin for stereolithography is characterized by low values of E_c , in order to start the reaction with low energy dose, and by high values of D_p , in order to maximize the cured thickness.

For typical stereolithography resins, attenuation of UV radiation intensity through the resin thickness occurs almost entirely by absorption and it can be modeled with Beer's law [16]:

$$E = E_0 \exp(-\gamma L) \quad (4)$$

relating energy density (E) to depth (L) through the extinction coefficient (γ). Using Equations 3 and 4, the cure depth can be described by:

$$C_d = \frac{1}{\gamma} \ln \left(\frac{E_0}{E_c} \right) \quad (5)$$

The extinction coefficient links cure depth to laser intensity and scan speed and it is a key parameter for stereolithography.

Ceramic powders behave as scattering centers, significantly increasing the UV radiation intensity attenuation. Halloran *et al.* [16] used the Beer's law expression

of ultraviolet radiation in a concentrated suspension of scattering particles to model the depth of cure for a suspension of ceramic particles in a medium of photocurable monomers. They demonstrated that for ceramic volume fractions above about 10%, the cure depth is predominantly controlled by the scattering of the UV radiation. They also reported that the cure depth of a ceramic suspensions can be modeled accurately with the following equation:

$$C_d = \frac{2\langle d \rangle}{3Q\Phi} \frac{n_0^2}{\Delta n^2} \ln \left(\frac{E_0}{E_c} \right) \quad (6)$$

where $\langle d \rangle$ is the average particle size, Q is the scattering efficiency term, ϕ is the solid volume fraction, Δn ($n_0 - n_1$), where n_0 and n_1 are the index of refraction of the liquid resin and of the ceramic particles respectively. This equation is a Beer's law expression with an extinction coefficient, $\gamma_{\text{eff}} = \frac{3Q\Delta n^2}{2\langle d \rangle n_0^2}$.

The addition of ceramic powders strongly influences C_d , and consequently D_p at a given exposure dose when there is an high difference in refraction index between resin and powders. In this work, adequate C_d values were obtained using silica powders characterized by lower values of the Δn than those of alumina powders, previously studied [15]. The lower index of refraction of silica ($n_1 = 1.56$) compared with that of alumina ($n_1 = 1.7$) should lead to higher C_d values, according to Equation 6. "Windowpanes test parts" [14] were built in order to determine the working parameters E_c and D_p for the different formulations. The results are reported in Table I. As expected silica filled resin shows higher values of D_p and lower values of E_c compared to the alumina filled resin [15]. Further, the silica filled suspension shows lower values of E_c even compared to the commercial resin, SL5170. In order to better understand the effect of E_c and D_p on the cured thickness, the alumina [15] and the silica filled suspensions were irradiated at 325 nm at a constant energy (dose) of 2600 mJ/cm². The value of C_d , reported in Table I for the silica suspension is higher than that of the alumina suspension, and comparable with that of the commercial resin. The results obtained for D_p and E_c suggest that the silica suspension is more suitable for stereolithography than the alumina suspension.

According to Equation 6 the scattering efficiency Q for alumina and silica suspensions was calculated, using the experimental values of E_c , D_p and C_d reported in Table I. The results are also reported in Table I. The

TABLE I Comparison between the working parameters of alumina and silica suspensions and that of the commercial resin

Composition	E_c (mJ/cm ²)	D_p (mm)	C_d (mm) $E_0 = 2600$ mJ/cm ²	Q
Epoxy resin	13.5	0.121	0.341 ± 0.017	–
Base resin + 45% vol alumina	32.8	0.0527	0.121 ± 0.0048	0.0037
Base resin + 50% vol silica	12.7	0.137	0.323 ± 0.016	0.0012

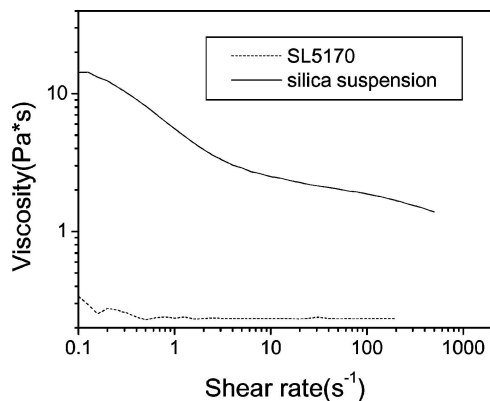


Figure 2 Viscosity vs. shear rate measurements for the silica loaded suspension compared with that of the STL resin SL 5170.

silica filled suspension shows lower values of Q as compared to alumina suspension.

Moreover the ceramic based formulation should be capable to auto-level during recoating of the vat surface in the stereolithography apparatus essentially for the construction of supports [14]. Such a requirement is difficult to be fulfilled when high solid loaded suspensions are used. In this case, a low viscosity of the base resin is extremely important, reducing the final viscosity of the ceramic filled suspension. The use of an organofunctional silane is also a key factor to allow the dispersion of the powder in the hydrophobic resin and reduce the viscosity. In addition the silane provide a solid residue of silica after pyrolysis of the organic binder of green. This residual silica can contribute to reduce shrinkage and improve sintering.

Viscosity vs. shear rate measurements are reported in Fig. 2 for the SL5170 resin and the silica loaded suspension at 50%. Measurements were performed in the range between 0.1 and 100 s^{-1} .

In order to be used in SLA equipment, the ceramic suspension viscosity must be of the same order of that of conventional resins. The viscosity limit reported by Halloran *et al.* is 3 Pa * s [3]. As it can be seen in Fig. 2, this value of viscosity for the ceramic suspension is obtained at about 4 s^{-1} , which is a value much lower than that occurring during recoating (typically 100 s^{-1}).

In Fig. 3 the effect of silica loading on the viscosity of suspension is shown for two different values of shear rate. The two values of shear rates were chosen,

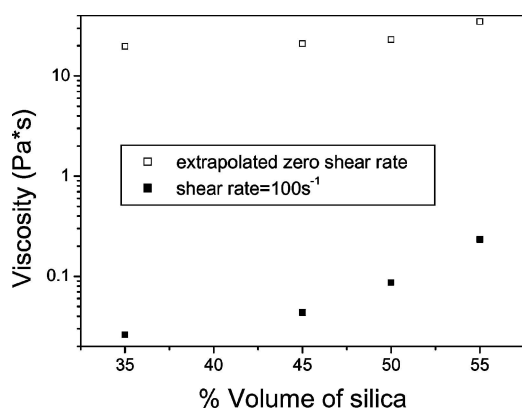


Figure 3 Effect of silica loading on the viscosity of suspension for two different values of shear rate.

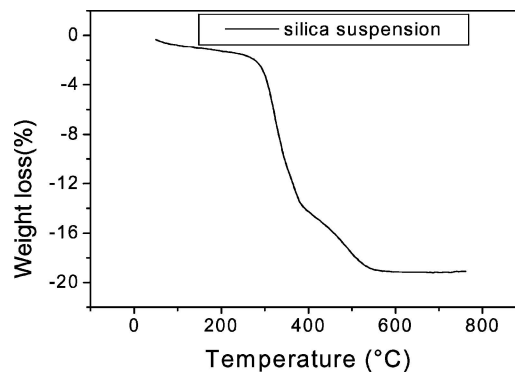


Figure 4 Weight loss of the silica loaded suspension vs. temperature.

corresponding to the very high value encountered during recoating, and to the low value typical of the auto-leveling phase. In order to achieve auto-leveling properties, zero shear rate viscosity was calculated from experimental data according to Cross model [17]. As it can be observed, the viscosity increases with silica loading for the two values of shear rate following an exponential trend at 100 s^{-1} .

TGA analysis has been used to identify the temperature intervals where pyrolysis takes place and evaluate the solid yield of the ceramic suspensions. The weight loss of the suspension is shown in Fig. 4. In the case of ceramic suspension the resin burn out occurs up to 550°C with a weight loss of about 19%. Two degradation steps are detected in Fig. 4. The first can be attributed to the degradation of acrylates and the second to silicone acrylate monomers. At higher temperatures the weight of the sample remains constant and no other degradation phenomena is observed. The silica content of the suspension corresponds to about 77% by weight. The difference between this value and the one experimentally obtained (81%) is attributed to silica residual after resin burn-out of organic binder.

Following the indications of TGA experiments the resin burn out between 200 and 550°C must be very slow, because in this phase the strong shrinkage can determine thermal stresses.

The overall thermal treatment has then been divided into three steps:

Post-cure: the green ceramic part is held in a furnace at 160°C for 100 min, in order to allow a complete reaction of the resin eventually not fully reacted at the end of the laser exposure. The resulting pre-ceramic green is characterized by the typical mechanical properties of a mineral filled

- **Pyrolysis:** heating at about 60°C/h to 500°C.
- **Sintering:** heating from 500°C to 1100°C or 1250°C at 120°C/h. The high temperature treatment increase the strength but also the shrinkage of the material.

Three points flexural test were carried out on green sample, made out with the ceramic suspension on the SL250. The typical stress-strain curve is shown in Fig. 5. The flexural modulus and the strength are reported in Table II.

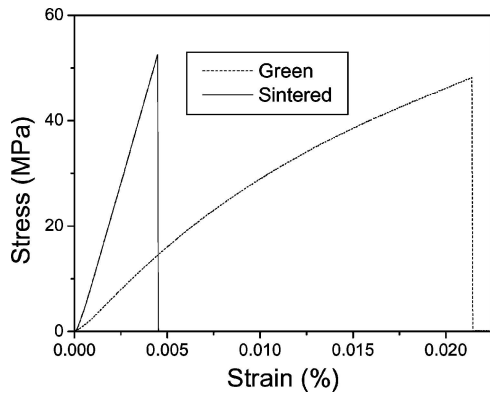


Figure 5 Results of three points flexural test for green and sintered samples built with the silica-loaded suspension.

The strength is 49 ± 0.3 MPa for the green sample and 53 ± 2.6 MPa for the sintered sample. The sintered sample shows a value of strength comparable to that of the sintered silica powders. Whereas the value of the flexural modulus is much lower than that of the traditionally sintered silica powders (65–75 GPa).

The values of porosity (P), apparent (T), bulk density (B) and shrinkage for the sintered samples of the silica suspension is reported in Table III. These values have been obtained according to ISO 10545.3. The values reported in Table III indicate that the low modulus measured during flexural tests can be attributed to the high porosity of the sintered samples.

TABLE II Flexural modulus and the strength of ceramic green and sintered samples

Sample	σ_{\max} (MPa)	E (GPa)
Green	49 ± 0.3	2.4 ± 0.1
Sintered	52.5 ± 2.6	10.2 ± 0.5

TABLE III Values of porosity (P), apparent (T) and bulk density (B) and shrinkage for the sintered samples of the silica suspension obtained according to ISO 10545-3

Sample	P (%)	T (g/cm ³)	B (g/cm ³)	(%)
Green	0	1.97	1.97	0
Sintered at 1100°C	40	2.51	1.23	3
Sintered at 1250°C	33.3	2.48	1.65	5

3.2. Mould fabrication

The silica suspension has been used directly in the stereolithographic apparatus to build moulds of different shapes for aluminium casting. Both green and sintered ceramics moulds were used. One of the green moulds fabricated with the SLA250 is shown in Fig. 6.

The low viscosity and the high reactivity of the suspension allows the fabrication of quite complex shapes, such as those shown in Fig. 7. Nevertheless, the building times of the suspension were still higher than those of the commercial resin, thus suggesting that a further increase of reactivity (lower building times) and

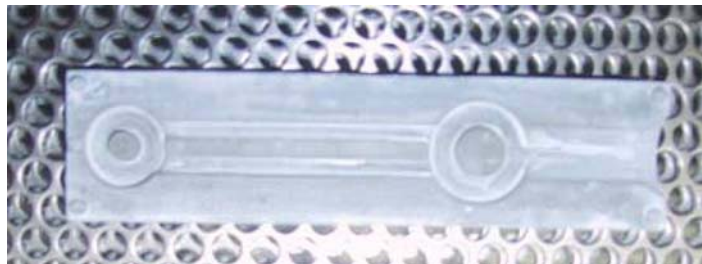


Figure 6 Photograph of a green mould obtained with the silica suspension.



Figure 7 Photograph of a mechanical part obtained by aluminium casting in a ceramic green mould.

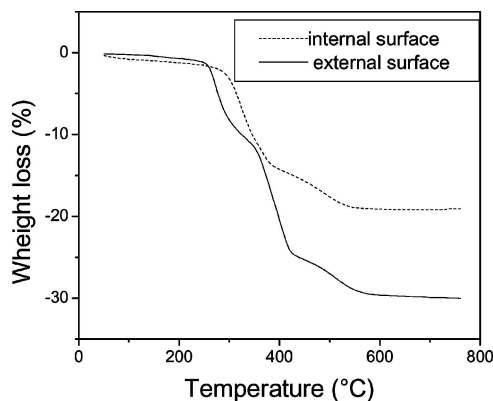


Figure 8 Comparison between the results of TGA analysis on the in-mould part (the part of the green in contact with the aluminium during casting) and the outmould part.

a reduction of viscosity (lower z-wait time [14]) should be achieved. The aluminium casting was successful as shown in Fig. 7.

TGA analysis was performed on the internal part, in contact with the aluminium during casting, and the external surface of the green mould after three castings. The results reported in Fig. 8 show that some significant differences can be observed between the two zones of the mould. In particular, the weight loss at the end of TGA scan is lower for the mould material in contact with aluminium during casting. This indicates that pyrolysis of the organic resin occurred during the moulding phase, because of the high temperature of molten aluminium (about 700°C). The mould was used for three casting experiments before severely and extreme cracking was observed.

Successful casting was also performed using mould sintered at different temperatures. The main advantage deriving from sintering of the mould is given by the possibility to preheat the mould before casting. As a consequence, lower viscosity of the aluminium, delayed solidification during casting and reduced the thermal shock can be significantly reduced. On the other hand, with sintered mould, it was not possible to perform multiple casting, since defects observed after sintering are responsible of severe cracking.

4. Conclusions

Ceramic moulds for metal casting have been obtained from photoactivated ceramic suspensions using an STL apparatus (SLA250). The photoreactivity and the viscosity are the key properties in the forming process efficiency, whereas their thermal behaviour and ceramic content are the relevant properties during the sintering phase, determining the structural properties of the final ceramic. Thanks to the low difference in refraction index between resins and silica powders a good re-

activity and cure was obtained whereas in a previous paper [15] the use of alumina powders lead to very low reactivity and cure depth, D_p , associated with scattering of light from ceramic particles. Two mould types have been prepared. The green mould, the unsintered one, slowly degraded after each casting. Similarly to the sand mould of lost wax processes it is destroyed to remove the metal cast. The limited isotropic shrinkage during sintering need to be compensated by producing bigger green moulds. The high strength mould can be used without big damage for several casting but requires special sintering additives much care in the thermal curing process and design.

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References

1. R. KNITTER, W. BAUER, D. GOHRING and P. RISTHAUS, Fabrication of Ceramic Microcomponents by Process Chain, Euro RP 2001.
2. A. GRECO, A. LICCIULLI and A. MAFFEZZOLI, *J. Mater. Sci.* **36** (2001) 99.
3. G. A. BRADY and J. W. HALLORAN, *ibid.* **33** (1998) 45.
4. D. J. WALLER and A. SAFARI, *J. Amer. Ceram. Soc.* **75**(6) (1992) 1648.
5. H. L. MARCUS and D. L. BOURELL, *Adv. Mater. Proc.* **9** (1993) 28.
6. A. LICCIULLI, C. ESPOSITO CORCIONE, A. GRECO, and A. MAFFEZZOLI, *J. Europ. Ceram. Soc.* **24** (2004) 3769.
7. M. L. GRIFFITH and J. W. HALLORAN, *J. Amer. Soc.* **79**(10) (1996) 2601.
8. C. HINCZEWSKI, S. CORBEL and T. CHARTIER, *Rapid Prototyp. J.* **4** (3) (1998) 104.
9. J. W. HALLORAN, *et al.* US Patent (2000).
10. G. A. BRADY and J. W. HALLORAN, *Rapid Prototyp. J.*, **3**(2) (1997) 61.
11. S. G. T.-M. CHU, J. W. HALLORAN, J. HOLLISTER, and S. E. FEINBERG, *J. Mater. Sci.: Mater. Med.*, in press (2000).
12. G. T.-M. CHU and J. W. HALLORAN, *J. Amer. Ceram. Soc.* **83**(10) (2000) 2375.
13. T. CHARTIER, C. CHAPUT, F. DOREAU and M. LOISEAU, *J. Mater. Sci.* **37** (2002) 3141.
14. P. F. JACOBS, "Rapid Prototyping and Manufacturing" (SME, Dearborn, USA 1992).
15. C. ESPOSITO CORCIONE, A. GRECO, A. LICCIULLI, M. MARTENA and A. MAFFEZZOLI, "Advanced Manufacturing Systems and Technology," edited by E. Kuljanic (CISM Courses and Lectures No. 437, Springer Wien New York, 2002) p. 731.
16. M. L. GRIFFITH and W. HALLORAN, *J. Appl. Phys.* **81**(6) (1997).
17. M. CROSS, *J. Colloid. Sci.* **20** (1965) 417.

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