

Solid freeform fabrication of ceramic parts from filler loaded preceramic polymers

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Abstract

Manufacturing of ceramic parts was achieved by selective laser treatment of a preceramic polymer (polysiloxane) loaded with ceramic filler powder (alumina). Thin layers of polymer/filler powder mixture were sequentially cured with a CO₂-laser ($\lambda=10.6\ \mu\text{m}$) thereby generating the geometrical shape of the part. Subsequently, the cured thermoset part was annealed in nitrogen atmosphere at 600 to 1000 °C to convert the compact into a Si-O-C/Al₂O₃ micro-composite material. Dimensional changes upon pyrolysis ($\Delta l/l_0 \approx 3\%$) can be controlled by adjusting the polymer-to-filler ratio and the heat treatment conditions. The new process is called Selective Laser Curing (SLC).

1. Introduction

Various solid freeform fabrication techniques for manufacturing of ceramic parts have been developed, including Selective Laser Sintering, Stereolithography, Laminated Object Manufacturing, Fused Deposition Modelling and a variety of printing techniques [1-10]. All of these techniques use a polymeric binder phase to stabilise the shape of a ceramic powder part. Prior to high temperature sintering, however, the binder has to be removed and a high porosity of typically 30-50 % gives rise for pronounced dimensional changes. The selective laser sintering process offers the possibility to compact the powder directly by local heating [11]. Alternatively a porous template can be produced which may be infiltrated subsequently with porcelain slurry [12] or silicon melt [13]. The selective laser sintering techniques require a high temperature in the laser spot to trigger local sintering processes. Due to high temperature gradients residual stresses can cause local thermal shock failure and interlayer crack formation. In the selective laser curing process, however, significantly lower temperatures are applied (< 300 °C) and thermal gradient induced damaging is expected to be significantly reduced and dimensional accuracy will be improved.

Preceramic polymers suffer from a pronounced shrinkage up to 30 % (linear) upon pyrolysis due to the difference between the density of the polymer precursor ($\rho_{\text{polymer}} 1.0\text{-}1.3\ \text{g/cm}^3$) and the ceramic residue ($\rho_{\text{ceramic}} > 2\text{-}3\ \text{g/cm}^3$). The shrinkage associated with the polymer to ceramic conversion can be reduced down to 0 % when the polymer is loaded with active or inert fillers [14]. Active fillers react with the decomposition products of the polymer to form a rigid network of carbide or oxide product phases which results in a pronounced reduction of shrinkage.

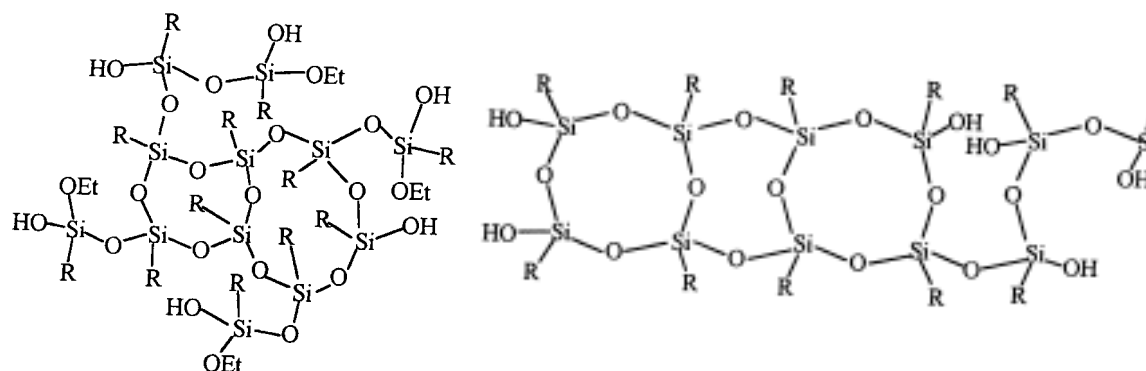
The aim of the present work was to study the novel selective laser curing process for shaping of a polysiloxane loaded with 50 vol.-% alumina powder as an inert filler.

Polysiloxanes offer a high ceramic yield (> 80 wt.%), are stable in ambient environment and show a high transmission for laser light of 85 % (relative) to achieve volumetric heating. The alumina filler was applied to reduce shrinkage during subsequent thermal processing. During laser curing the filler offers control over the processing window by means of its transmittance for laser radiation, heat capacity and heat conductivity.

2. Experimental Procedure

2.1 Materials

A Poly(methylsilsesquioxane) (PMS) $[(\text{CH}_3)_{0.96}(\text{OH})_{0.036}(\text{OC}_2\text{H}_5)_{0.004}\text{SiO}_{1.5}]_n$ with $n \approx 9000$ (Festharz MK, Wacker Chemie Burghausen, FRG) was mixed with 50 vol.-% alumina powder (Gilox 63, Alcoa, FRG) with a mean particle size of 20 μm . The PMS is a white powder with a medium particle size of 8.5 μm and a melting point of 50 $^\circ\text{C}$. The elemental composition is 42 wt.-% Si, 36 wt.-% O, 18 wt.-% C and 4 wt.-% H. Si-OH and Si-OC₂H₅ functional groups in the partially crosslinked molecular structures, Fig. 1, give rise for a condensation curing reaction when the polymer is heated to 150 - 250 $^\circ\text{C}$. H₂O and C₂H₅OH are the main condensation products to be released upon curing. 1 wt.-% of Aluminium-acetylacetonat (C₁₅H₂₁AlO₆) was added as a catalyst to accelerate the curing reaction.



R = CH₃, reactive side-chains: OH and OEt = OC₂H₅

Fig 1: Supposed molecular structure of polymethylsilsesquioxane [15].

The powder was prepared by dry mixing polymer, catalyst and filler in a ball mill equipped with polyethylene lining for 16 h with approximately 60 rpm. The polymer and the filler were dried prior to the mixing step, alumina at 130 $^\circ\text{C}$ and PMS at 40 $^\circ\text{C}$ under reduced pressure of 10³ Pa. The weight loss of the polymer after drying was 0.07 wt.-%. For FTIR- and wetting measurements the plain polymer powder (without filler and catalyst) was used.

2.2 Laser curing and pyrolysis

The curing experiments were carried out with a 200 W cw-CO₂-laser (wavelength 10.6 μm) in a standard Selective Laser Sintering machine (M 250, EOS Munich, FRG). The focused gaussian beam diameter was 400 μm and the scanning speed of the laser was adjustable from 0 m/s up to 3 m/s. Parts composed of up to 40 single layers were manufactured with a single layer thickness of 100 μm . Table 1 summarises the processing variables.

Process variable	Investigated range of values
Scan velocity [v_{scan}]	80 – 200 mm/s
Laser power [$E_{laser\ beam}$]	6.9 W
Line energy $\left[E_{line} = \frac{E_{laser\ beam}}{v_{scan}} \right]$	34 – 86 Ws/m
Hatching distance [h_s]	200 μm
Layer thickness [p_a]	100 μm

Tab 1: Range of process variables varied in the selective laser curing experiments.

After the selective laser curing the parts were subsequently pyrolysed under flowing nitrogen atmosphere with a flow rate of 0.2 l/min in an electrically heated tube furnace. The specimens were placed in a steel insert and the maximum pyrolysing temperature was 1000 °C.

2.3 Characterisation

The structural rearrangement reactions associated with the thermal processing were analysed by infrared spectroscopy (FT-IR) (Impact 420, Nicolet). Wetting of the alumina filler by the molten polymer was examined by measurement of the wetting angle according to the sessile drop method in a microscope (Leitz, Wetzlar, Germany) equipped with a heater. Dense alumina plates served as the substrates and the temperature was varied in the range from 70 to 110 °C in air. The linear dimensional change during heating of the cured part was measured with a differential dilatometer (Netsch - Dilatometer 1600, Netsch Gerätebau, Selb, FRG) using a Quartz-glass rod as a reference.

The degree of curing was determined by a thermo-barometric analysis technique [16, 17]. For this purpose the gaseous curing products (ethanol and water) leaving the polymer during the curing reaction were collected in a closed reaction tube which was evacuated prior to the specimen heating. The degree of curing, α_{cur} , was normalised to the maximum pressure, P_{max}^{cur} , where the gaseous reaction products, C_2H_5OH and H_2O , are supposed to have completely left the polymer.

$$\alpha_{cur} = \frac{P^{cur}}{P_{max}^{cur}} \quad (1)$$

Accordingly, the degree of pyrolysis, α_{pyr} , was correlated with the amount of gaseous decomposition species released upon pyrolysis heating.

$$\alpha_{pyr} = \frac{P^{pyr}}{P_{max}^{pyr}} \quad (2)$$

Fig. 2 shows α_{cur} and α_{pyr} of the PMS as a function of temperature.

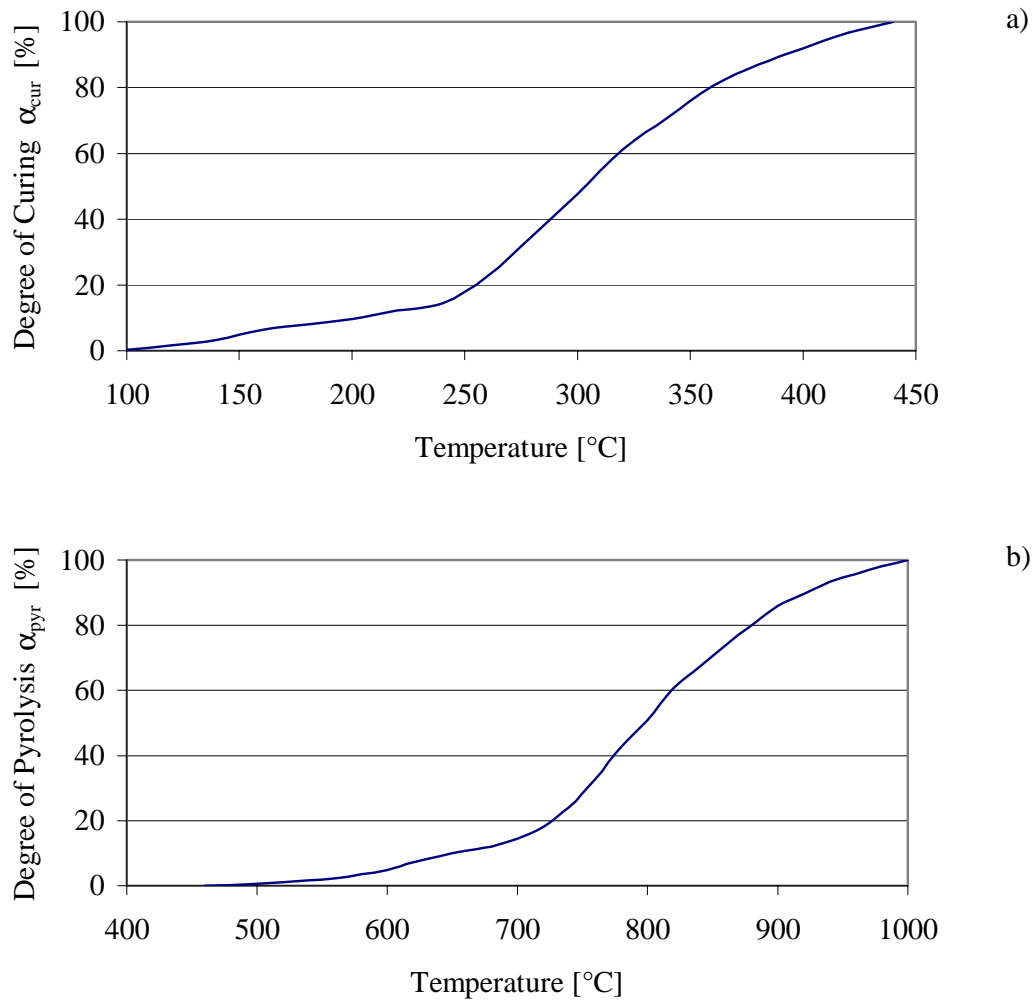


Fig. 2: Degree of curing a) and of pyrolysis b) as derived from thermo-barometric gas analysis for poly(methylsilsesquioxane).

3. Results

3.1 Laser heating

The extension of the heat affected zone was estimated by exposure of one trace on the powder bed with the CO₂-laser (6.9 W, 125 mm/s scan-velocity), Fig 3. The width of the trace was measured to be 500 μm and the depth 160 μm .

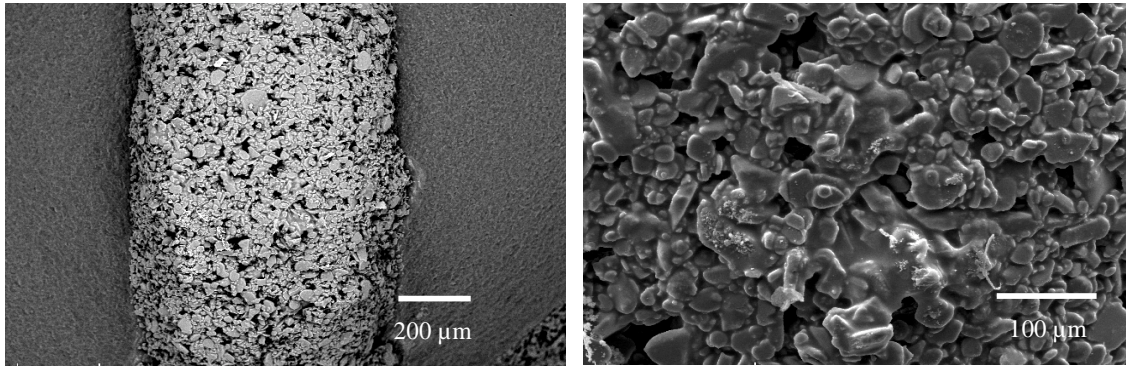


Fig. 3: Laser cured trace and microstructure of the polymer wetted filler material.

Most important for the distribution of the laser energy in the powder bed is a volumetric laser energy absorption and heating [18-22]. FT-IR was used to get results for the coupling of laser radiation with a wave length of 10.6 μm to Poly(methylsilsequioxane). The relative transmission of Festharz MK is 85 % and the transmission of alumina is given in literature [23] and is better than 97 %. Due to high transmission of the polymer the energy can couple in the surface of the filler powder. Depending on the size, shape and concentration of the filler in the polymer matrix the local heating conditions can be varied in a wide range. Fig. 4 shows the results of a FE simulation of the SLC process with different coupling depths. A comparison of simulation and the laser cured traces is described in [23].

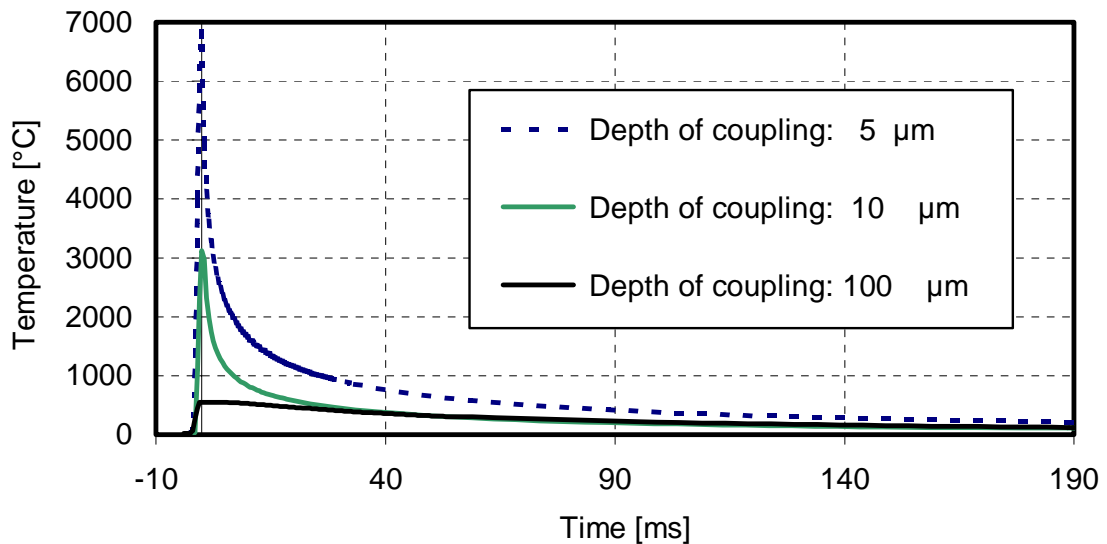


Fig. 4: Peak temperatures in the polysiloxane/alumina mixture as calculated by FE simulation for three different coupling depths.

3.2 Wetting and curing

When the laser interacts with the polymer/powder mixture melting of the PMS-polymer starts at 50 $^{\circ}\text{C}$. With increasing temperature a decrease of the wetting angle of the polymer melt on alumina from $> 40^{\circ}$ at 70 $^{\circ}\text{C}$ to $> 10^{\circ}$ at 130 $^{\circ}\text{C}$ was observed, Fig. 5.

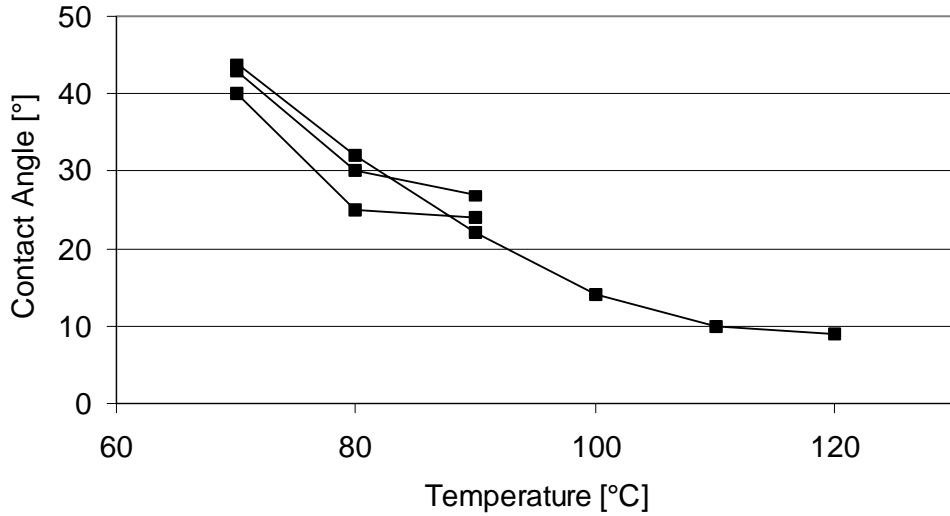
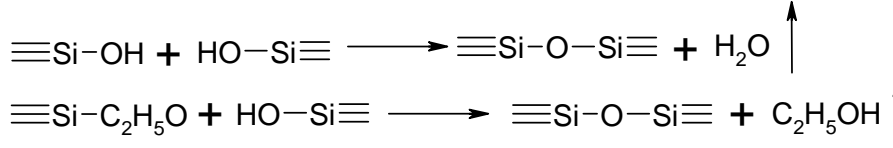


Fig. 5: Wetting angle of Poly(methylsilsesquioxane) on dense alumina in air.

Further heating above 120 °C triggers the curing reactions:



Water and alcohol may leave the thin layers (< 100 μm) without extended formation of porosity. With increasing temperature and time the degree of curing increases reaching a maximum of approximately 0.42 at a line energy of 86 Ws/m, Fig. 6. The laser power was kept constant and the different line energies were realized by different scanning velocities. A degree of curing of at least 35 % was found to be necessary to maintain the geometrical shape of a laser cured part.

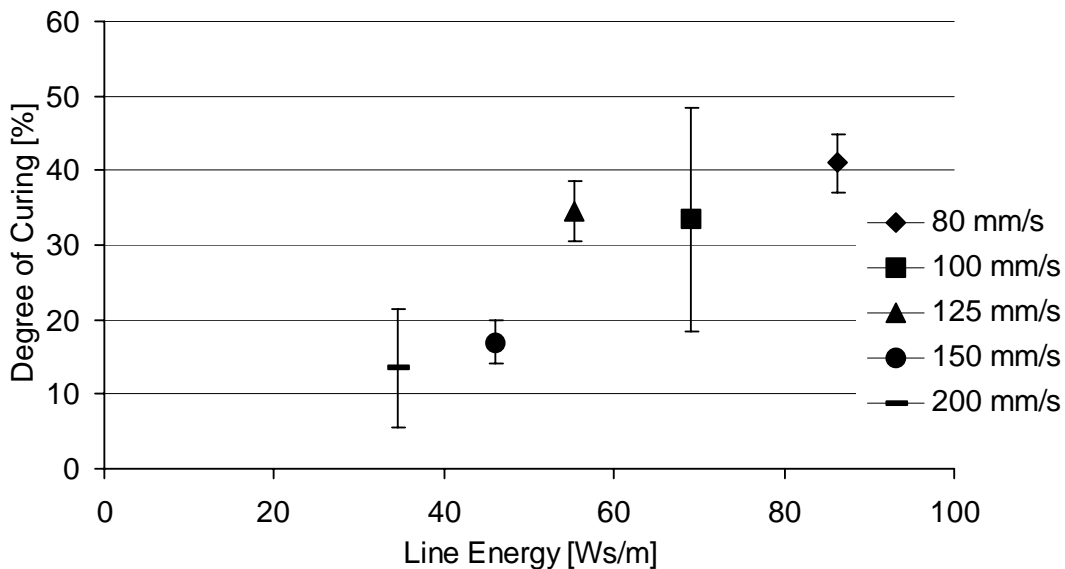


Fig. 6: Degree of curing vs. line energy at different scanning velocities at 6.9 W laser power.

A downscaled turbine wheel was manufactured with a line energy of 46 Ws/, a hatching distance of 200 μm and a layer thickness of 100 μm , Fig. 7. After laser curing the part was pyrolysed at 700 $^{\circ}\text{C}$. A heating and cooling rate of 300 $^{\circ}\text{C}/\text{h}$ and a dwell time of 4 h were applied.



Fig. 7: Demonstration part, a downscaled turbine wheel fabricated by selective laser curing and subsequent pyrolysis of poly(methylsilsesquioxane)/alumina precursor powder.

4. Conclusion

Selective Laser Curing is a novel process for solid freeform fabrication of ceramic parts from laser light curable preceramic polymers. Poly(methylsilsesquioxane) loaded with Al_2O_3 filler was converted to a Si-O-C/ Al_2O_3 micro composite ceramic. A low dimensional change (< 3 %) and a wide range of possible polymer and filler compositions make this novel process particularly interesting for ceramic based rapid prototype manufacturing.

5. Acknowledgements

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6. Literature

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