Si/SiC-Ceramic
low process shrinkage - high temperature material for the Laser Sinter process

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Abstract

Actual RP-systems are very limited in producing adequate ceramic prototypes. In the presented process, the SiC-green part manufacturing by the laser sintering process in combination with special postprocessing allows the fast production of Si/SiC prototypes. A mixture of SiC powder and a reactive polymer binder system is used in the Laser Sinter process. In the following postprocessing the porous green part has to be infiltrated with a precursor resin, carbonised and finally infiltrated with molten silicon. In contrast to cold isostatic moulding or slip casting the shrinkage is very low (2-4 %). Experiments with suitable materials and process conditions were successful. This paper will show the state of and the possible further investigation into process.

Introduction

Up to now, there exists no commercialised Rapid Prototyping technique to directly generate ceramic parts without any post processing. All the known techniques require complex post processing such as debinding and sintering. Several investigations were carried out with ceramic filled SLA-resins, binder coated ceramic powders for SLS or 3D printing processing, ceramic filled sheets for LOM and other technologies like laser induced generating by vapour deposition /1/,/2/,/3/,/4/,/5/,/6/. Post processes such as debinding and sintering are necessary to obtain a high density ceramic structure. The theoretical maximum density of monomodal particles is 74 % with an increase in density during sintering to over 95 %, so, in existing processes, this leads to high shrinkage. The precise heating and cooling parameters used for debinding are very difficult to implement accurately.

The presented technology is also a combination of laser sintering and post processing techniques. But in opposite to the other techniques, the polymeric binder must not be burned out completely. The porous green part structure must be filled with special liquid phenol resin or any other infiltration materials with high carbon yield after pyrolysis /7/,/8/. After polymerisation of the infiltrated resin, the binder system and the infiltrated resin are transformed in an inert pyrolysis reaction process to carbon. During pyrolysis the polymeric systems utilised result in a stable carbon binding structure. Due to the shrinkage during pyrolysis the carbon regions show a fine structured crack system. In the final process the crack system has to be infiltrated with molten silicon. Because of the very low viscosity of the molten silicon and the capillary forces, the molten Si will fill the whole open porosity. The infiltrated silicon will finally react with the residual carbon to form β-SiC.

Si/SiC Processing with laser sintered pre-forms

Greenpart production by lasersinter process

The process technique for the green part production is similar to the well known direct croning process from EOS GmbH. The SiC powder has an average particle size of about 70 µm and a powder density of 1.25-1.40 g/cm^3 (~39-44 % of full SiC density). The use of a dry powder resin as binder removes the need for the complex process of coating the SiC particles. Coating SiC particles requires a complex procedure because of the very high abrasiveness of the particles. The particles scrape the coating chamber as well as the coating on other particles. The powder resin shows a very low melt viscosity and a good wetting of the SiC particles. Higher contents of binder increase the green part stability, but the greater the percentage of the binder contents, the more polymer is present between the SiC particles and therefore the higher shrinkage during pyrolysis.

Tests performed show that a powder mixture with a binder content of 18 %wt performs very well. The average open porosity of 55 % is very high but the green part strength is still good. The measured SiC-content in the green parts is about 31 % vol.. Recoating tests with the pure unbonded SiC powder showed densities of about 35 % in the powder bed. The complete process chain is shown in **figure 1**.

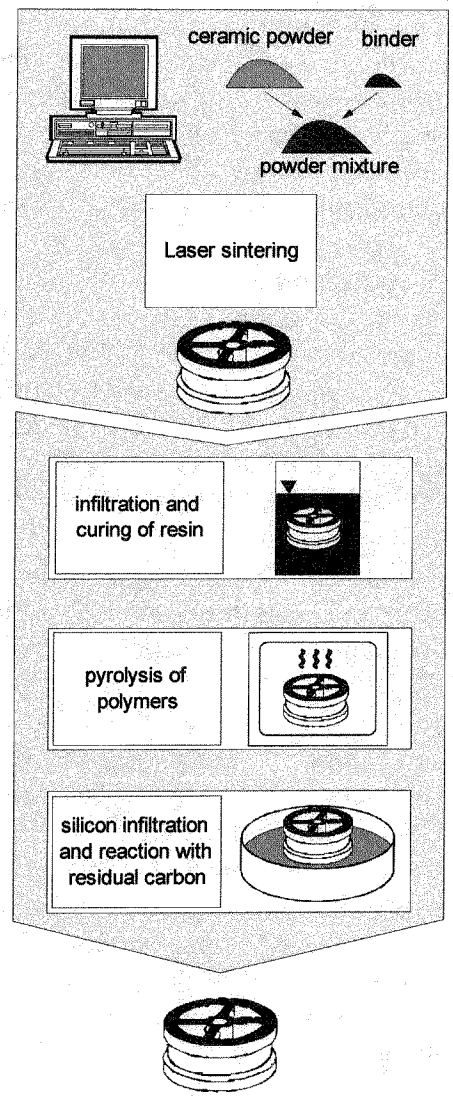

Figure 1: Process chain of the Si/SiC process

Post-infiltration with precursor resin

In the second step the open porosity of the laser sintered part is infiltrated with precursor resin. The resin must be pre-heated to get the lowest melt viscosity for the infiltration which takes place in a vacuum desiccator. Following the infiltration, the parts are put in a autoclave and the resin is cured under a pressure of 20 MPa and a temperature of approximately 170 °C. The weight increases by 50 % on average, and the open porosity is filled completely.

The following processing steps of pyrolysis and silicon infiltration are quite similar to the well known Liquid Silicon Infiltration Process (LSI) of the DLR for manufacturing fibre reinforced CMC materials /9/,/10/,/11/.

Pyrolysis of the polymeric components

The infiltrated and cured parts are now ready for the carbonisation process. During pyrolysis at a temperature of up to 900 °C under a nitrogen environment the polymer shrinks in an almost unrestricted manner in all directions, due to cracking of the compounds driving out the volatile components of the polymer and resulting in amorphous carbon. In this process the shrinkage of the resin during the

carbonisation is hindered by the SiC powder particles. Therefore a crack structure in the carbonised matrix is produced, which is necessary for the following silicon infiltration step. The crack structure is of interest for the infiltration and reaction dynamics during the silicon infiltration and therefore decisive for the resulting structure and the resulting material properties. The crack system can be influenced by different parameters such as SiC particle size, particle form, binder and infiltration resin, infiltration and carbonisation process parameters.

Silicon infiltration

During the last manufacturing step at temperatures up to 1600 °C, and in vacuum, the liquid silicon infiltrates the porous specimens due to the capillary forces, and reacts with the carbon of the residual matrix and forms to silicon carbide. The degree of conversion can be controlled by the temperature profile.
Therefore it is one of the main aims to realise a stoichiometric formation of the components to get a high yield of β-SiC. The resulting surface of the parts primarily depends on the surface of the green part. The surface quality can be improved by the use of smaller powder particles with a more uniform particle geometry.
Additional finishing of the infiltrated greenparts also improves the surface quality.

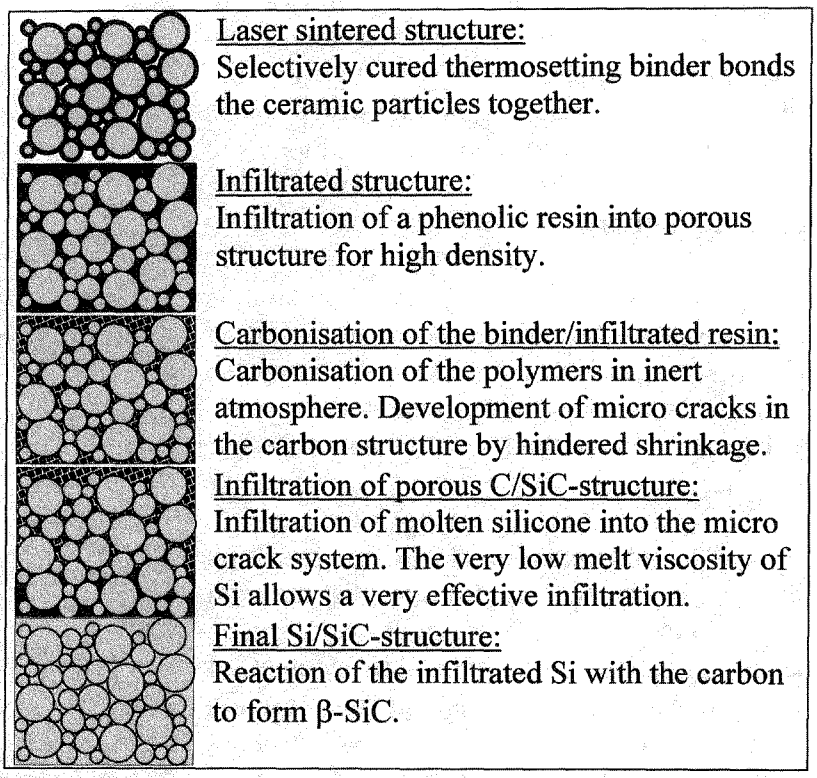

Figure 2: Modifications of the structure in each step of the process chain

Results of previous investigations

The aim of the first investigations was to show the feasibility of the process. Therefore a SiC-powder with a particle size of about 70 µm was chosen for easy powder recoating in the Laser Sinter machine. The mixture of the SiC-powder and the phenolic binder powder was varied in several steps. The phenolic powder resin melts between 70 and 110°C and is cured by condensation reaction. At temperatures higher than 150°C the included hexamethylene-tetramine degrades. A very high binder content of 18 %wt was applied because of the better stability for handling and the following post-infiltration process. The powder mixture can be processed with a laser energy density of about 50-90 mJ/mm^2. The phenolic binder showed a loss of weight of

approximately 4 % during laser induced curing. The single layers showed a thickness of more than 0.6 mm. Therefore there are no problems to build parts with 0.2 mm slices. It could be expected that the layer thickness decreases by increasing SiC-powder content. The parts taken out of the Lasersinter machine have to be post-cured with a low heating rate up to 200°C. Deformations during the post-curing can be prevented by placing the complex parts in a box with supporting SiC-powder (without binder).

Figure 3 shows a Si/SiC sample processed without infiltration of a precursor resin. The content of SiC (shown dark grey in figure 3) is low and the SiC phase is embedded into silicon with less connections between the SiC regions. The resulting porous structure has larger crack diameters and the conditions are therefore not optimal for capillary action induced infiltration.

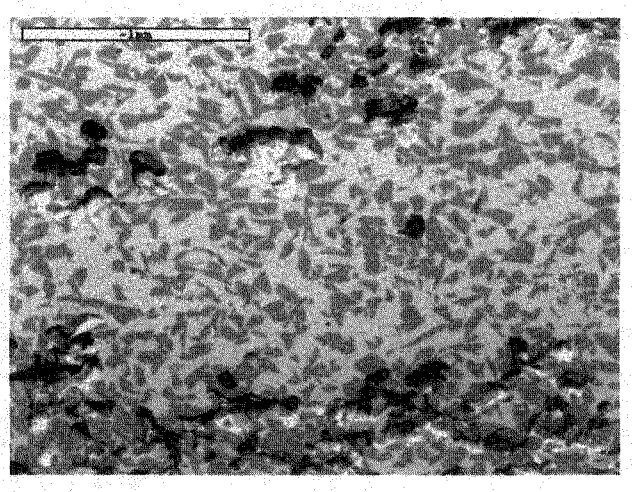

Figure 3: Si/SiC part processed without post-infiltration of precursor resin

Therefore the post-infiltration step is necessary to realise a higher content of carbon after the pyrolysis of the polymers. During the curing of the resin the specimen showed a shrinkage of 2% in thickness and about 1% in the other directions.

The infiltrated initial state for pyrolysis is shown in **Figure 4**. In this state, the material shows round about 5 % open porosity and a density of about 1.78 g/cm^3. The content of SiC powder (bright areas) in this section amounts to only 28 %. The powder packing density is very low and the particles are sharp edged. This oblong geometry prevent higher particle packing densities. With a more cuboid geometry the SiC-powder density can be increased up to more than 45 %.

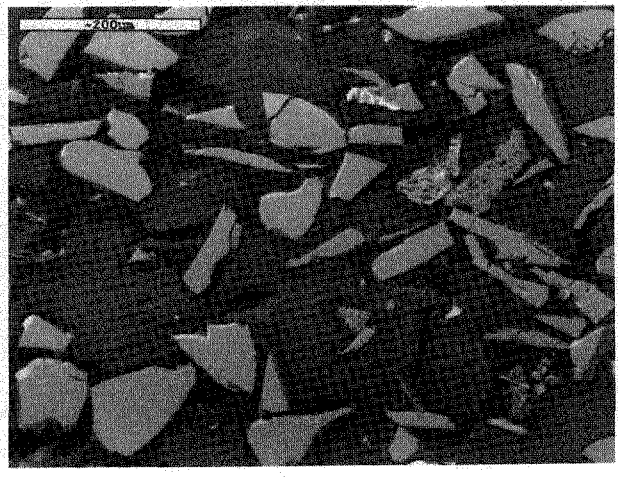

Figure 4: Part infiltrated with precursor resin

The structure of a carbonised sample is shown in **figure 5**. The mass loss during pyrolysis can be determined at about 18 % and the density at about 1.6 g/cm^3. As a result of mass loss and decreasing density the open porosity increases up to about 35 %. The SiC powder (bright areas) is now embedded in a highly porous carbon matrix (dark areas). With an average particle size of 70 µm, the crack system is not as fine structured as necessary to form SiC well.

Figure 5: Carbonised structure with crack system

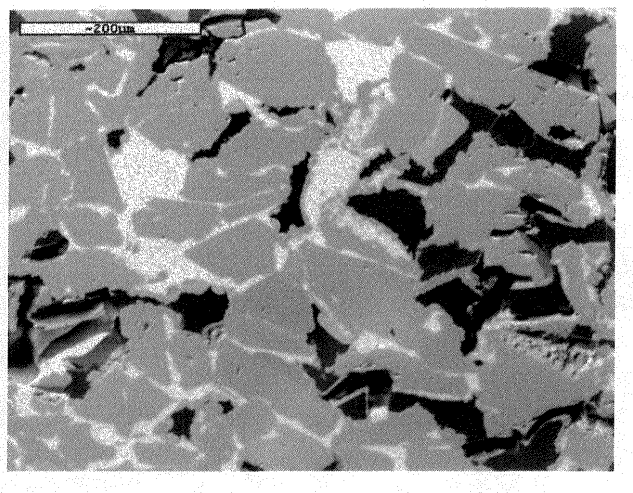

Figure 6: Final structure after Si infiltration

Figure 6 shows the final structure after the Si infiltration. The content of SiC (shown light grey) reaches 69 %, residual carbon 14 % (dark grey) and the residual silicon 13 % (bright). After siliconization mass increases up to about 15 % and the open porosity of the specimens decreases to approximately 4-6 %. The density increases to about 2.5 g/cm^3. The β-SiC content and structure must be optimised by a finer crack structure, a more regular dispersed carbon and a longer temperature dwell time during silicon infiltration. Therefore a smaller particle size and a higher particle packing density are the main keys for the further developments.

Test shapes and Examples

Figure 7 shows a selection of different precursor infiltrated test patterns. The flat plates on the left side were pyrolysed, siliconized and finally used for the 4 point bending test bars. The blades of the turbine wheel have a thickness of less then 1mm. The quality of the backside of the blades is also acceptable and shows no problematical overcure. The box on the right side of the picture has walls with different thicknesses to find the limitations in geometry. Also parts with 1mm walls have been built successfully. All greenparts were built up in the laboratory sinter station at IKP.

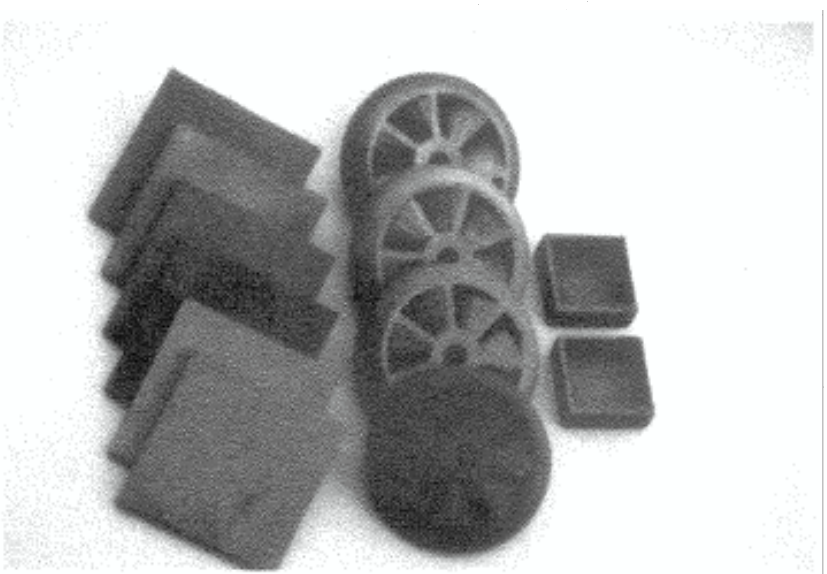

Figure 7: Selection of samples infiltrated with precursor

Figure 8 shows the test box with different walls in the three post-processing stages. The present limit in wall thickness with the 70 µm SiC powder is 1 mm. The shrinkage during the complete process is 2 %, measured along the walls of the box. The geometry also allows the estimation of the rounding of inner edges by the precursor resin and by the molten silicon by building a meniscus in the liquid phase. Whereas sharp edges normally must be avoided because of the high notch sensitivity of monolithic ceramics.

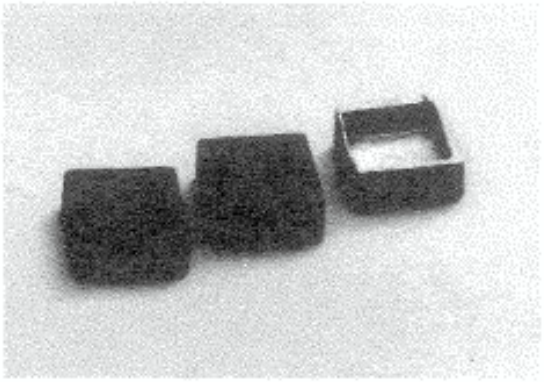

Figure 8: Sample box 25x25x10mm^3 (left: infiltrated with precursor resin; middle: pyrolysed; right: silicized).

The Lasersinter process is quite fast with a scan speed of 1000 mm/sec., 0.2 mm hatch distance and up to 0.2 mm slices. The post-curing and the precursor infiltration is done in approximately one day. The rapid pyrolysis requires two further days and the final silicon infiltration is also done in 2 days. The whole post-processing can be executed in 5 days.

Mechanical properties

Several test bars were tested in a 4 point bending test according to the EN 843-1 standard. The bars with a dimension of 45 x 3 x 4 mm were cut out of a flat sintered plate and were used directly in the tests without any further surface finishing. Therefore the measured strength values are low. The average bending strength of the first tested samples was 70 MPa, with a maximum strength of 99 MPa. Parts with a lower resin absorption show lower strength. Test bars made out of a plate produced with a 9 % lower resin absorption showed on average an 18 % decrease in strength. The strength of the test bars (surface quality of saw cut) cannot be compared with the values for Si/SiC found in literature. The next test series with improved material structures will be carried out with polished test bars for comparable results.

Conclusion

From these investigations we know that smaller particle sizes are of interest for structural β-SiC formation. Therefore further investigations must be focused on the reduction of the particle size in combination with a more regular particle shape for higher powder packing densities. The recoating system and especially the wiper blades of the sinter machine must also be adapted to the abrasive powder. The shrinkage during the precursor infiltration and curing must be reduced by a optimised binder content. The dimensions of the part are limited by the diffusion of water formed by the polycondensation of the phenolic precursor resin. Therefore the curing conditions of the precursor resin in the porous structure must be cleared. The parameters for the pyrolysis are of interest for an optimised porous crack structure. In conjunction with the parameters of the silicon infiltration, they specify the forming of the β-SiC and therefore the final structure.

Further investigations will also be made into the integration and combination of carbon fibre reinforced C/SiC strengthening elements into the RP-Si/SiC parts.

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