Si/SiC-Ceramic Prototypes via LS^{2}I -Process (Liquid Silicon Infiltration of Laser Sintered C-SiC Parts)

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Abstract

The liquid silicon infiltration of laser sintered C-SiC parts (LS^{2}I) is a solid freeform fabrication technique which allows the production of complex shaped Si/SiC prototypes. A mixture of SiC powder and reactive polymer binder is used in the laser sintering process to generate a porous green part. In the postprocessing, the porous green part structure has to be infiltrated with a precursor resin, carbonised and finally infiltrated with molten silicon. The infiltrated silicon reacts with the residual carbon to build β-SiC. Results generated by the use of reduced primary particle sizes as well as alternative infiltration materials and the use of other RP-techniques for the green part fabrication will be discussed in this paper.

Introduction

Up to now, several investigations on rapid prototyping ceramics have been performed worldwide. Most investigations have focused on ceramic filled SLA-resins, binder coated ceramic powders for SLS or 3D printing processing, ceramic filled sheets for LOM and other technologies such as laser induced generating by vapour deposition /1/,/2/,/3/,/4/,/5/,/6/. The post processes 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 presented technology relies on the debinding and sintering and is a combination of laser sintering, different infiltration and pyrolysis techniques /7/. In comparison to the other techniques, the polymeric binder is transformed to its residual carbon and must not be burnt out completely. The porous green part structure must be filled with precursors to increase the carbon yield after pyrolysis /8/,/9/. After the precursor infiltration, the binder system and the precursor are transformed in an inert pyrolysis reaction process to carbon. During pyrolysis the polymeric systems utilised result in a stable carbon binding structure penetrated by fine structured crack systems. 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 first investigations were carried out with an average SiC-powder particle size of about 70 µm and a powder density of 1.25-1.40 g/cm^3 (~39-44 % of full SiC density). Meanwhile the particle size was reduced to d_{50}=15µm and further investigations were done with d_{50}=1,5µm powder. The binder system, a dry powder resin, removes the need for the complex process of coating the SiC particles. Nevertheless first coating tests were carried out. A new powder resin shows a reduced melt viscosity and an improved wetting of the SiC particles. The binder content can be reduced from 18 %wt to 10-15 %wt. Therefore the shrinkage and warpage during the laser sintering of the green parts and during the pyrolysis was reduced. The complete process chain is shown in **figure 1**.

Post-infiltration with precursor

In the second step the open porosity of the laser sintered part is infiltrated with a precursor. Phenolic precursor resins must be pre-heated to get the lowest melt viscosity for the infiltration which takes place in a vacuum desiccator. Other precursor materials like PS or PAN have to be infiltrated in solution.

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 /10/,/11/,/12/.

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. In this process the shrinkage of the polymeric components 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 system can be influenced by different parameters such as SiC particle size, particle form, binder and precursor, infiltration and carbonisation process parameters.

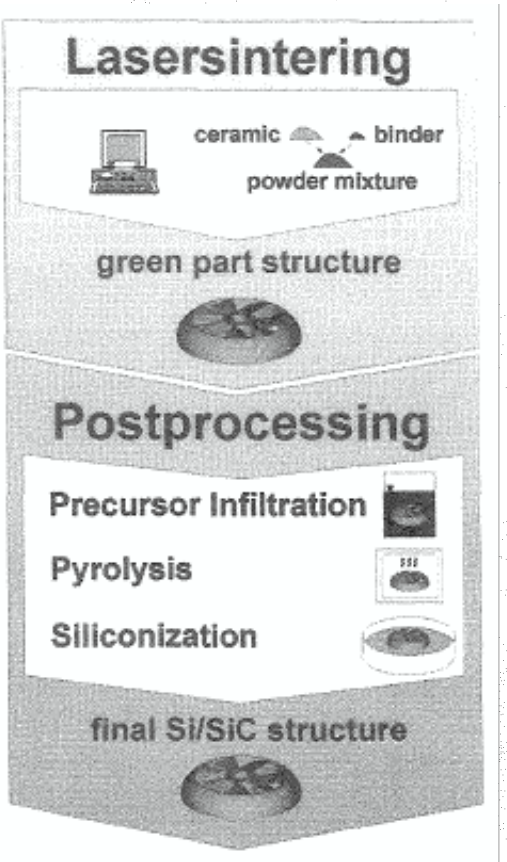

Figure 1: Process chain of the Si/SiC process

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 carbonized parts have to be placed

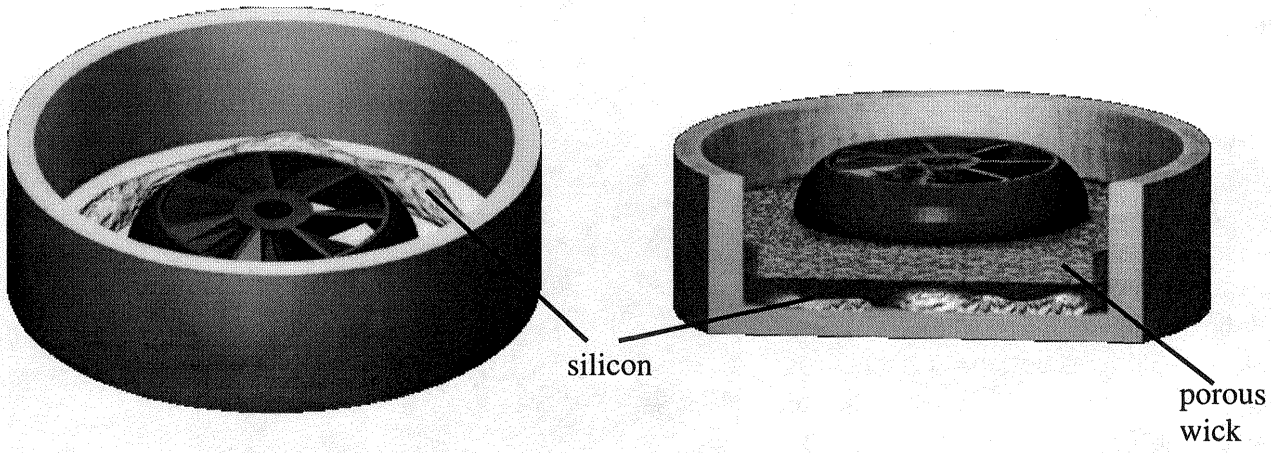

Figure 2: Left: Pyrolysed greenpart placed with silicon in bowl. Right: Pyrolysed greenpart placed on a porous wick panel

in a bowl or on a porous wick panel for a well dosed Si feeding **figure 2**. The removal of the parts after the siliconization can be simplified by placing the parts on additional weak supports. The degree of (**Si+C→SiC**) conversion during the siliconization can be controlled by the temperature profile. Therefore it is still one of the aims to realise a stoichiometric formation of the components to get a high yield of β-SiC. The infiltration height depends on the diameter of the crack capillaries and the infiltration time. The calculated infiltration heights for the Si infiltration are shown in **figure 3** /11/.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 green parts also improves the surface quality.

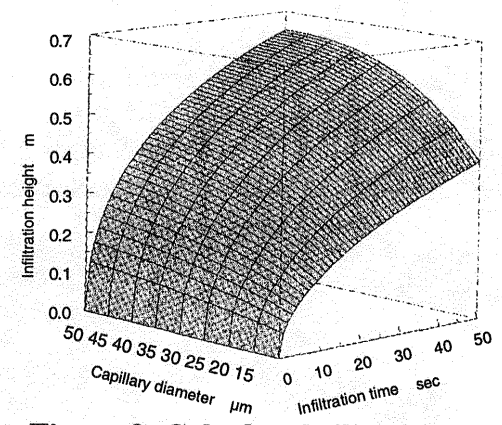

Figure 3: Calculated silicon infiltration height

Results of 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. With the modified machine particle sizes of 10-15µm can be used easily.

The reduction of the particle size is limited by the optical behaviour of the powder material. At the wavelength of the CO_2-laser SiC shows a very low absorption depth of approximately 5µm. To get a sufficient layer thickness the laser energy must be carried into the material by multi-reflection and heat transfer. The effect of multi-reflection depends on the

particle size. The smaller the particles the lower the energy transfer into the depth. Therefore the layer thickness must be reduced if smaller particle sizes should be realised. With a reduced particle size also the capillaries, necessary for the infiltration become smaller. The reduction of the particle size also reduces the maximum infiltration height **figure 3**.

Reduced particle size

The mechanical properties of ceramic parts depend on the ceramic structure and the surface quality of the parts. The strength primary depends on the fine-particle character and homogeneity of the structure. Each scratch or surface failure reduces the strength of the parts. The stairstep effects of layerwise building RP-systems are also surface failures reducing the mechanical strength. Therefore the ceramic structure and the surface quality must be improved by reduced SiC particle size and by reduced layer thickness. Additional finishing of the infiltrated green parts also improves the surface quality.

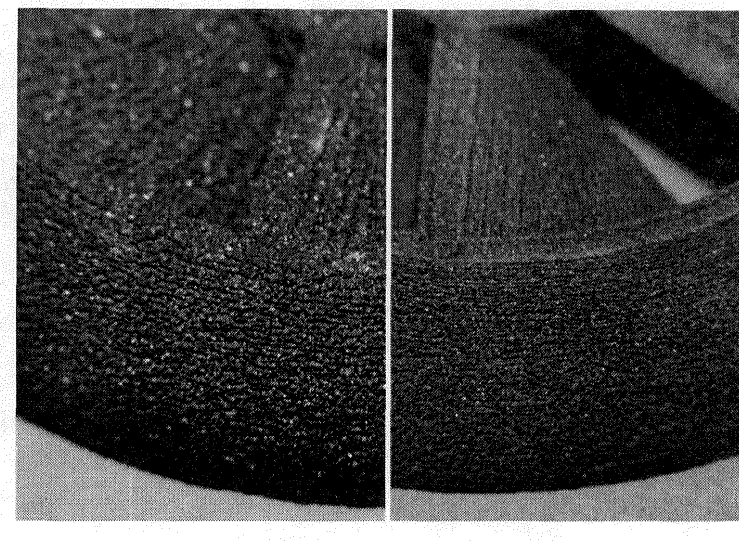

Figure 4: Left: Particle size 70µm, 200µm layers; right: particle size 15µm, 100µm layers

Figure 4 shows two samples processed with 70µm particle size, 200µm layer thickness on the left side and a sample with 15µm, 100µm layer thickness on the right side. The final structures with and without the precursor infiltration are shown in **figure 5.** The pictures show the structure for 15µm primary SiC particle size and for the rough 70µm powder.

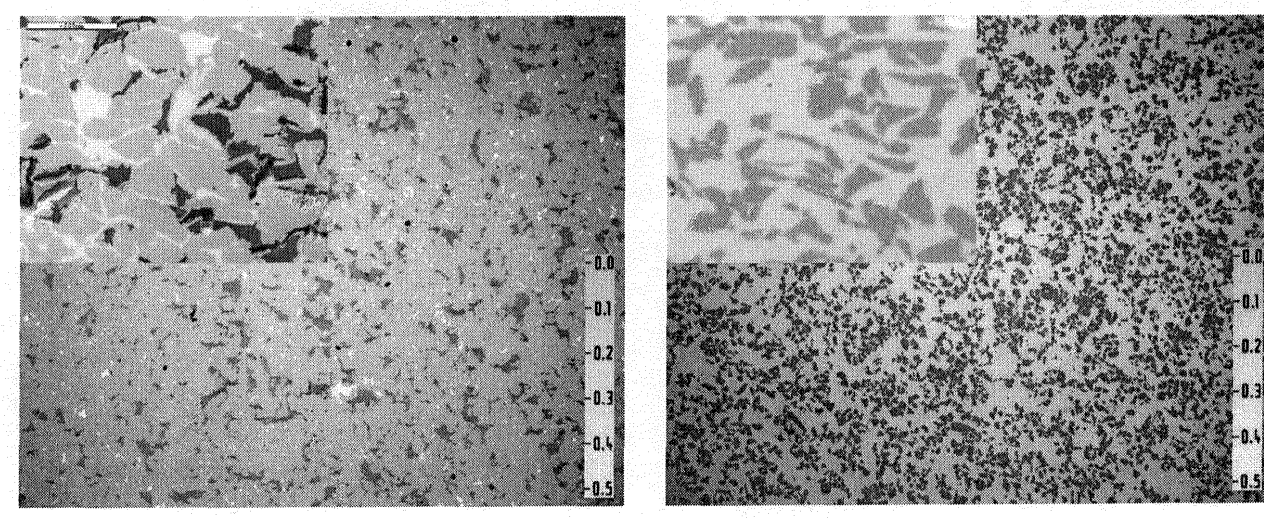

Figure 5: Left: Final Si/SiC structure with precursor infiltration. Right: Final structure without precursor infiltration. Primary particle sizes 15µm (70µm in u. l. corner)

Powder binder

The shrinkage and warpage during laser sintering of the green parts primary depends on the polymeric binder content. By the use of a new improved powder resin with a reduced melt viscosity the powder content is reduced to 10-15%wt. The warpage is eliminated almost completely. The parts can now be built without, or with very weak supports. The main problems of the new powder system are the reduced free-flowing properties. It is much more difficult to recoat in thin layers. But with a multi-recoating process the powder can be levelled very homogenously. The powder flow depends on the temperature and the humidity of the powder. Further on the lower melt viscosity reduces the resolution by the wider melting section.

Precursors

Phenolic resin was the first precursor system used in the investigations to increase the residual carbon content after the pyrolysis. Different phenol resins were tested. Phenolic resins show a good carbon yield and can be infiltrated easily into the porous green part structure

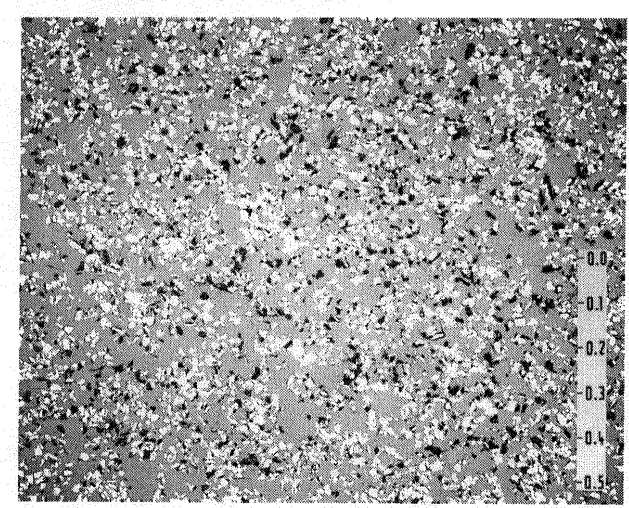

Figure 6: Green part structure infiltrated with phenolic resin

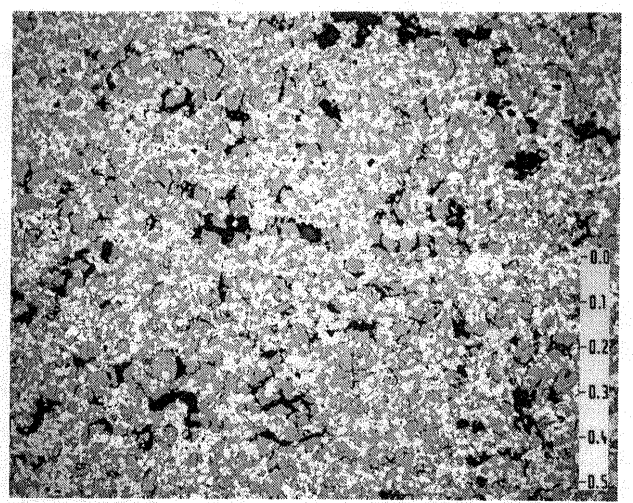

Figure 7: Final structure of a polysilazan infiltrated sample after pyrolysis

figure 6. But phenolic resins react in a polycondensation reaction by separating water. It is difficult to remove the water out of the structure without producing bubbles. Additional tests were carried out with polysilazan resin to directly form ceramic structures in the pyrolysis step. The final structure after pyrolysis and formation of the ceramic structure is shown in **figure 7**. Meanwhile other precursors like polystyrene were tested.

Test shapes and Examples

For the evaluation of the mechanical properties several test bars for bending tests were built. For the silicon infiltration via capillary action the samples have to be placed on support structures for easy removal of the buffer panel. **Figure 8** shows 7 bending test bars placed on a support panel for simplified removal of the bars after siliconization.

Also parts with overhangs undercuts and thin walls have been built successfully. With the new powder system, complex shaped green parts can be built up reliable and easily **figure 9**. All green parts were built up in the laboratory sinter station at IKP with 0.1mm slices.

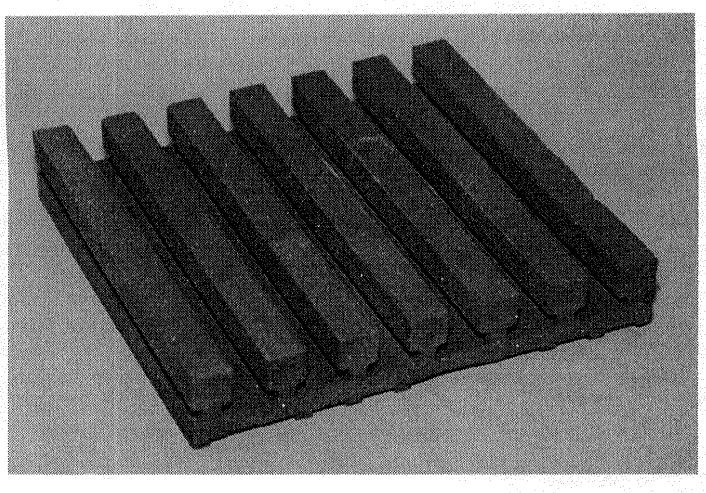

Figure 8: Test bars for bending tests with support

The lasersinter process is quite fast with a scan speed of 900 mm/sec., 0.2 mm hatch distance and up to 0.05-0.1 mm slices. Smaller slices are also possible for the adaption of smaller particle sizes. The post-curing and the precursor infiltration is done in approximately one day and depends on the chosen precursor system and processing. 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.

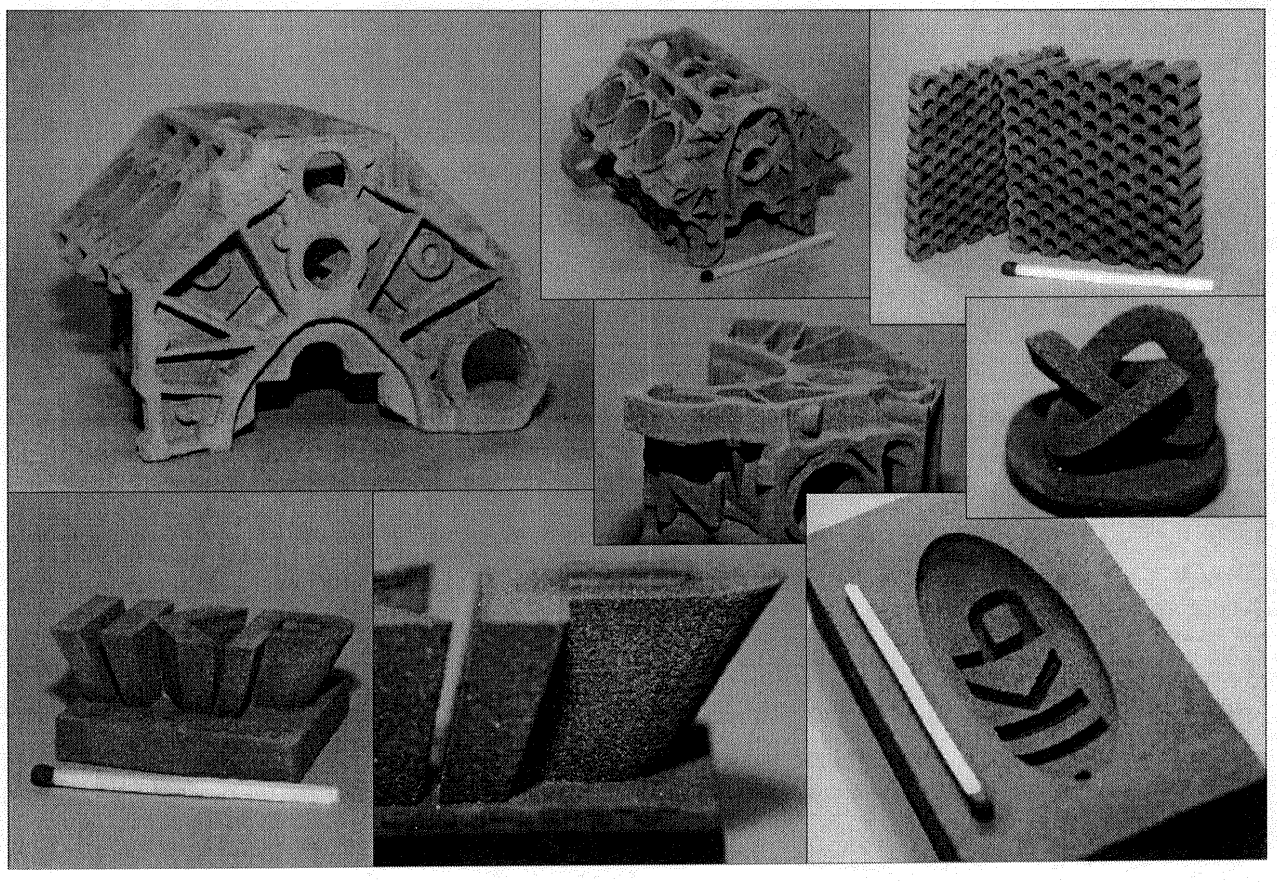

Figure 9: Complex test samples with overhangs, under cuts and inner sections like moulds and combs

Conclusion

Powders with smaller particle sizes were adapted successfully. The further reduction of the particle size is limited by the decrease of the optical absorption depth of the SiC-powder and the much more difficult layerwise recoating in the lasersinter process. Tests with agglomerated 1,5µm SiC powder showed good layerwise recoating conditions but inadequate absorption depths of the laser beam. Therefore only a small layer thickness can be realised.

The investigations must be focused on the further reduction of the particle size and higher powder packing densities. Therefore additional tests must be carried out with the laser operating at other wavelengths. First kick-off tests should be carried out with a Nd-YAG laser system also available at the IKP.

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.

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