DIRECT SELECTIVE LASER SINTERING OF REACTION BONDED SILICON CARBIDE

Sebastian Meyers*, Jean-Pierre Kruth*, Jef Vleugels **

* KU Leuven, Department of Mechanical Engineering, division PMA, Celestijnenlaan 300, 3001 Heverlee, Belgium
** KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium

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Abstract

Three-dimensional reaction bonded silicon carbide (SiSiC or RBSC) parts have been produced by direct selective laser sintering (SLS). Unlike previously investigated processing routes, which make use of a sacrificial polymer binder to form green parts, the parts in this work are built by scanning subsequent layers composed of a mixture of silicon and silicon carbide powders. A fibre laser is used to selectively melt the silicon under an inert argon atmosphere, resulting in porous preforms of sufficient strength for further handling and processing. After impregnation with a graphite suspension and infiltration with liquid Si at 1450°C, highly dense reaction bonded silicon carbide parts are obtained.

Introduction

Silicon carbide is an engineering ceramic which is difficult to manufacture by most conventional powder processing routes [1]. Reaction bonding, however, is a process that allows for near net-shape production of SiC materials at lower processing temperatures and in shorter times [2]. It relies on silicon infiltration of a carbon-containing preform and the subsequent reaction to SiC. The final product is reaction bonded silicon carbide (RBSC), i.e., a matrix composite containing primary SiC, secondary (reaction formed) SiC and residual Si. This residual Si is the main drawback of the processing route, since it limits the maximum service temperature of the material (Si melts at 1420°C). Nevertheless, RBSC has some interesting properties like high hardness, good thermal conductivity, chemical resistivity and low thermal expansion, which make it suitable for industrial applications.

In order to facilitate the production of RBSC for industrial applications, additive manufacturing techniques can be used. Selective laser sintering (SLS) and selective laser melting (SLM), for example, are powder bed fusion layered manufacturing techniques which can produce complex 3D parts [3]. The selective laser sintering of RBSC using a sacrificial polymer binder has already been extensively studied. Vail et al. [4] produced polymer encapsulated SiC particles and fabricated green parts with good strength and relative densities of 48 – 51%. Further research by Evans et al. [5] [6] focussed on using a char-yielding binder in order to provide residual carbon in the structure. The residual carbon could then react with molten Si during infiltration to form a secondary SiC phase. This approach resulted in highly dense RBSC parts. However, Stevinson et al. [7] observed that the surfaces showed liquid Si over-extrusions after infiltration. Hon et al. [8] performed selective laser sintering of SiC-polyamide powder mixtures. The effect of the SLS parameters, energy density and the initial powder blend composition on the produced parts were studied.

Some authors have also attempted to produce RBSC parts without using a sacrificial polymer binder. Birmingham et al. [9] showed that selective laser (reaction) sintering of Si powder beds in a C_2H_2 gas atmosphere could result in single- and multilayer shapes with high SiC content. Streek et al. [10] used laser micro sintering to process both SiSiC with a q-switched laser and pure SiC powders with a continuous (cw) laser. Finally, Vacuher et al. [11] did not focus on RBSC, but produced aluminium – SiC metal matrix composites by selective laser sintering blended powder mixtures with an Nd:YAG q-switched laser. This resulted in final parts with porosities of 40-60%.

In the present work, porous preforms were produced by direct selective laser sintering blended Si-SiC powder mixtures without using a sacrificial polymer binder. Partial melting of the silicon acted as the powder consolidation mechanism. After SLS, the preforms were impregnated with a graphite suspension to provide a carbon source during subsequent liquid Si infiltration. This allows for in situ formation of secondary (reaction formed) SiC. After Si infiltration, highly dense SiSiC parts are obtained. A schematic of the process is shown in Figure 1. Density measurements and microscopy imaging are used to examine the final quality of the products.

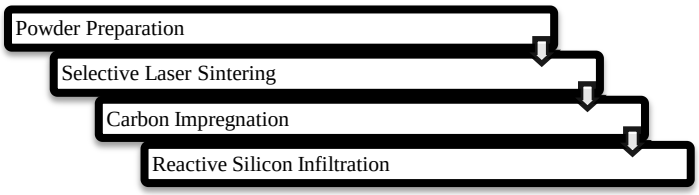

Figure 1: processing schematic: direct SLS of SiSiC.

Experimental Procedures

Powder Preparation

Powder mixtures were prepared by mixing 67 weight% silicon carbide (SiC, CARBOREX BW F320, Washington Mills, purity = 99.2%, d_{50} = 29 µm) and 33 weight% silicon (Si, SIMET 985, Keyvest, purity = 98%, d_{50} = 45 µm) in a polyethylene container on a Turbula mixer for 6 hours at 75 rpm. The mixing was done dry and resulted in a homogeneous SiSiC powder that could subsequently be loaded into the SLS machine. The starting powders are shown in Figure 2.

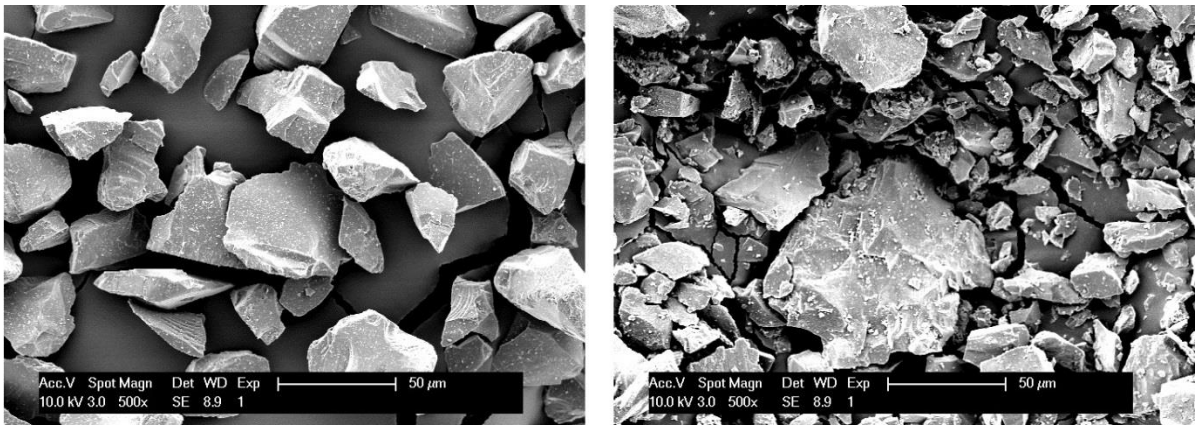

Figure 2: Washington Mills SiC powder (CARBOREX BW F320, left) and Keyvest Si powder (SIMET 985, right).

Selective Laser Sintering

Selective laser sintering was done on a commercial Concept Laser Mlab cusing machine, equipped with a 100 W continuous (cw) fibre laser with a spot size of 50 µm. The parts were built in various batches of several 10x10x10 mm^3 cubes. The scanning parameters were varied across these cubes in order to obtain an optimal parameter set. Laser powers were varied between 10 – 95 W and scanning speeds from 30 – 800 mm/s. The scanning was done continuously with a 90 degree rotation between layers. The powder layer thickness was fixed at 60 µm and no preheating was used.

Carbon Impregnation

In order to impregnate the SLS preforms with carbon, a graphite-acetone suspension was used. To this end, 20 vol% of graphite powder (C, Dragon Seal Graphite MF2/99.5-99.9RG, NGS Naturgraphit GmbH, purity = 99.5-99.9%, d_{50} = 2µm) was suspended in acetone (C_3H_6O, Nyssens Graphics, purity = 99%) and mixed using a magnetic stirring device for 30 minutes. After this, impregnation was accomplished by dipping the preforms in the suspension twice for 5 minutes with an intermediate drying step.

Reactive Silicon Infiltration

After graphite impregnation, the preforms were transferred to a graphite crucible. The crucible was lined with graphite paper on the inside and contained silicon wafer chunks (Imec, Leuven) on the bottom. The preforms were placed on top of the silicon wafer chunks. The crucible containing the preforms was transferred to a hot press (FCT Systeme , model W100/150-2200-50 LAX) for high temperature silicon infiltration under vacuum (10^{-1} mbar). The temperature was increased to 1450°C at a heating rate of 50°C/min. A dwell time of 30 minutes was applied at 1450°C and the crucible was subsequently cooled down to room temperature.

Measurements

After fabrication, different measurements were done to evaluate the quality of the cubes. Density measurements were done on the porous preforms and the final RBSC composites using the Archimedes method (Acculab atilon ATL-244-1). X-ray diffraction measurements (Seifert 3003 TT) were carried out to gain information on the phase composition of the preforms. Scanning Electron Microscopy (SEM, FEI XL30-FEG) was done on the top and side surfaces of the porous preforms, and finally light microscopy (Leica DMILM HC) was performed on the final RBSC composites to assess the microstructure and SiC content.

Results & Discussion

Selective laser sintering was done with different parameter sets. High power – high scanning speed sets were used at the start, but resulted in fragile and dimensionally unstable preforms. More robust and dimensionally accurate preforms were obtained by using parameter sets with reduced laser power and scan speed. Parameter sets can be compared by expressing the laser energy density:

$$E = \frac{P}{v * s * l}$$

With:

- E = laser energy density in J/mm³
- P = laser power in W
- v = scanning speed in mm/s
- s = scan spacing or hatch spacing in mm
- l = powder layer thickness in mm

Preforms built with similar laser energy densities, but with a higher P and v, were found to be of lower quality than preforms with a lower P and v, as illustrated in Figure 3. The dimensions of the preforms were as-defined.

Figure 3: High power - high scanning speed (P = 40W, v = 200 mm/s, left) versus low power - low scanning speed (P = 20W, v = 100 mm/s, right) with comparable E ≈ 43 J/mm³.

The effect of scan spacing was investigated by investigating top surfaces of different preforms with scanning electron microscopy. A comparison of two preforms with different scan spacings is presented in Figure 4. The preform on the left was made using a scan spacing 2 times higher than the preform on the right. The surface shows some protrusions, which can be linked to the scan tracks (arrows, with 90 degree rotation). The preform with smaller scan spacing does not show these features, but clearly still contains some porosity.

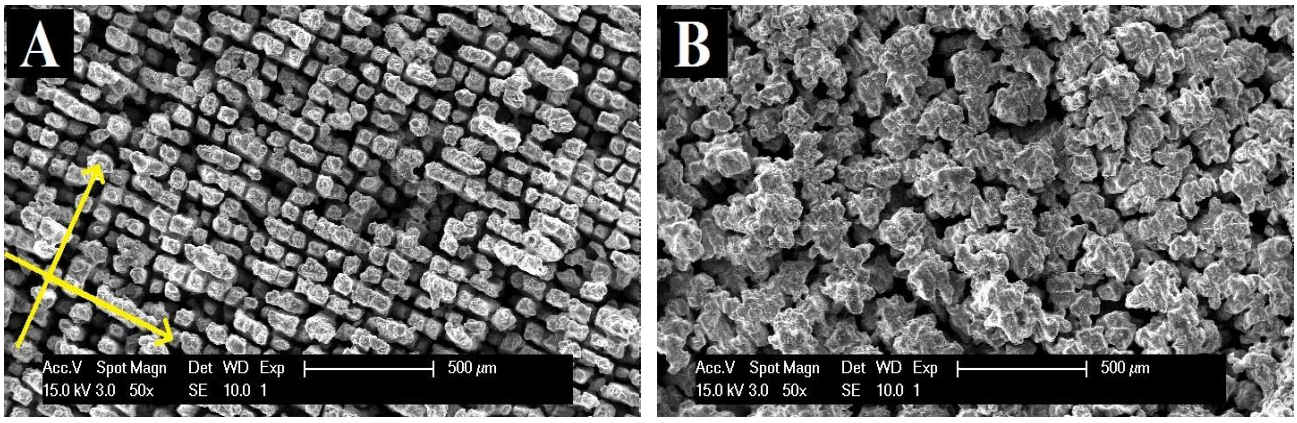

Figure 4: SEM images of SLS preform top surfaces with P = 20W, v = 90 mm/s (a: s = 77 µm, b: s = 35 µm).

In order to quantify the porosity, the density was measured according to the Archimedes method. These measurements showed that the densities vary between 40 and 50% of the theoretical density and decrease when the laser energy density increases. This leads to the conclusion that low laser energy densities (30-100 J/mm³) in combination with low laser powers and scanning speeds lead to better preforms. These preforms, although porous, are dimensionally accurate and strong enough to be processed further.

X-ray diffraction (XRD) was performed in order to identify the phases present in the fabricated preforms. The measurements showed that the preforms consist of silicon carbide (α-SiC, polytype 6H) and silicon. A typical XRD pattern is shown in Figure 5.

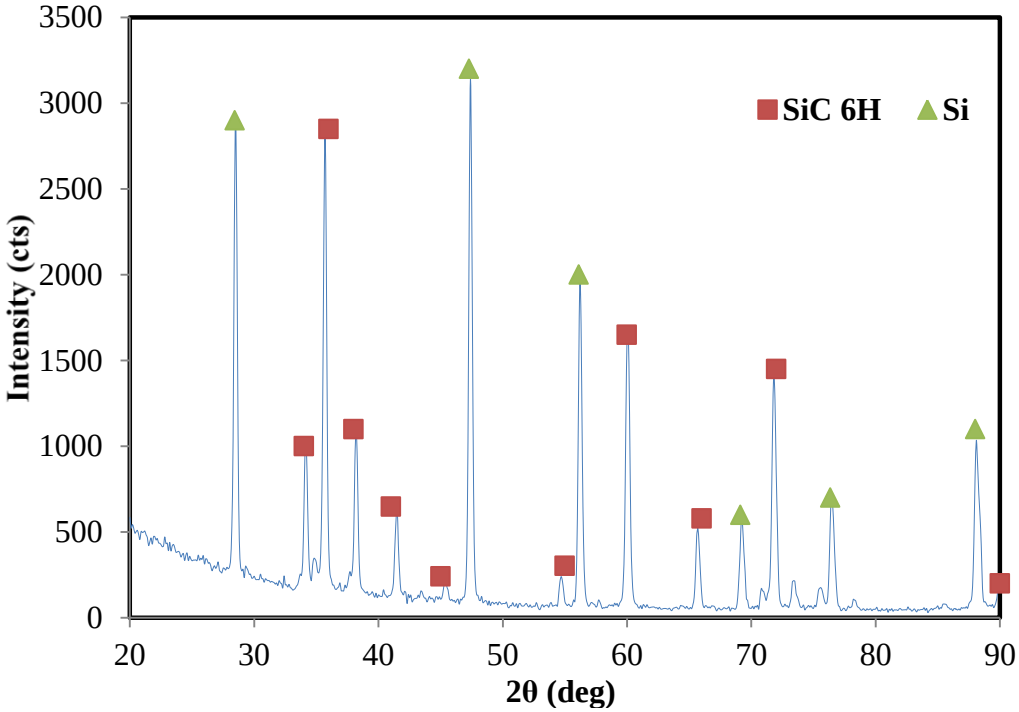

Figure 5: XRD spectrum of a Si/SiC composite after SLS.

After impregnation with a graphite suspension and infiltration with liquid silicon at 1450°C, RBSC cubes were obtained. These cubes showed some surface protrusions of infiltrated silicon (over-infiltration). However, they appeared to be highly dense. The final microstructure is shown in Figure 6. The part was scanned with parameters comparable to the one from Figure 4.a, albeit with a slightly lower scanning speed (P = 20W, v = 70 mm/s, s = 77 µm). The bright matrix phase is silicon, whereas the grey contrast phase is α-SiC starting powder. Around the α-SiC, a dark grey border of reaction formed SiC can be seen. This is shown in higher magnification on Figure 7. The reaction formed SiC is a result of the reaction between the liquid Si and the impregnated graphite (C) during infiltration:

$$Si\ (l) + C\ (s) \rightarrow SiC\ (s)$$

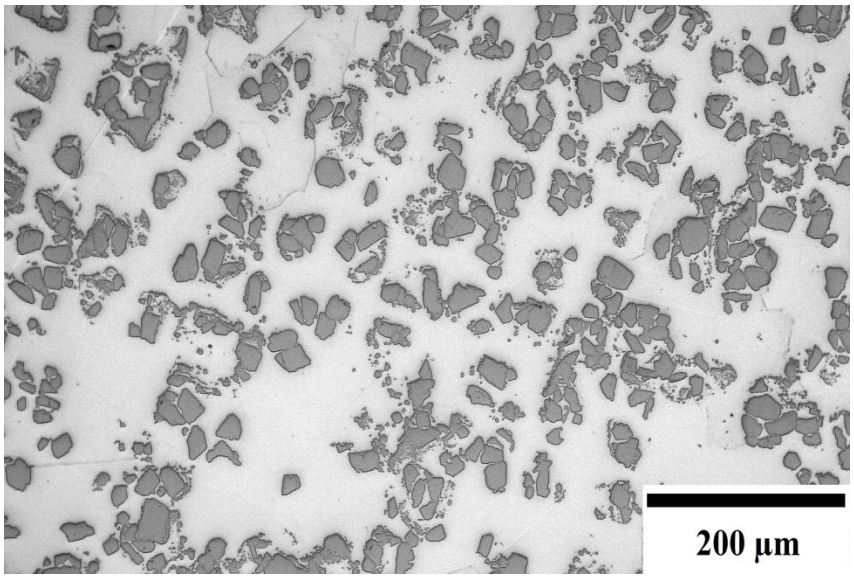

Figure 6: Typical microstructure of a RBSC part produced by SLS and subsequent post-processing.

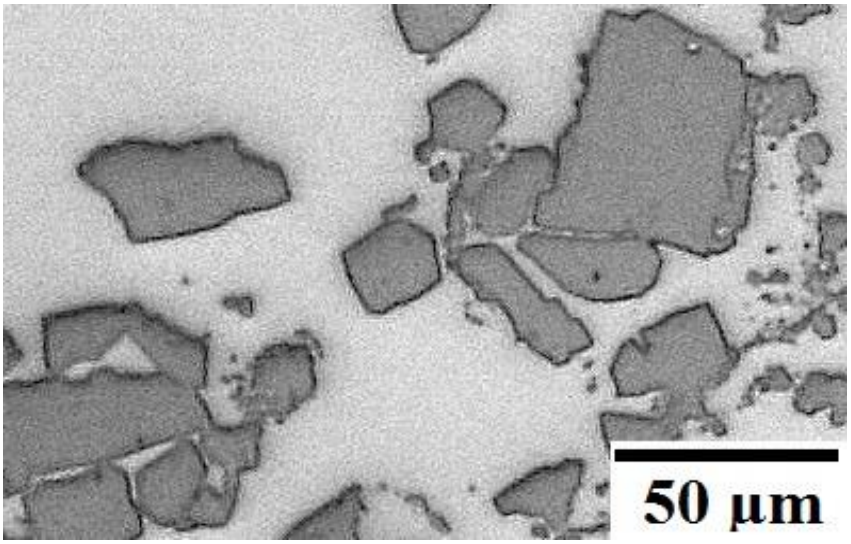

Figure 7: Detailed view of the dark grey reaction formed SiC around the primary SiC grains.

Clearly, the final RBSC cubes still contain a high amount of silicon. This is due to a too low amount of carbon in the preform after graphite impregnation. This issue can be addressed in one of the following ways:

- Carbon impregnation under external pressure should yield a higher carbon content in the fabricated preforms;
- Impregnation with a phenolic resin and subsequent de-binding could result in an increased carbon content;
- Carbon could be added to the base powder mixture so that the preforms after SLS contain a certain amount of carbon, or better yet a higher amount of silicon carbide thanks to the reaction of molten silicon with free carbon.

In order to quantify the current amount of SiC, image analysis software was used on 10 different light microscopy images. This showed that the cubes scanned with a high scan spacing of 77 µm contain only 35-40% SiC. From this, a theoretical density of 2.66 g/cm³ can be calculated. Cubes scanned with a lower scan spacing of 50 µm contain more SiC (60%), resulting in a theoretical density of 2.85 g/cm³.

The densities of the infiltrated RBSC shapes were compared to the calculated theoretical density and found to depend on the used laser scan spacing. A larger scan spacing resulted in relative densities of 95%, whereas a lower scan spacing yields significantly lower final densities of 70%. These lower densities are possibly caused by a large volume of closed porosity in the middle of the part, which effectively inhibits liquid silicon infiltration. A cross section of a low scan spacing part is shown in Figure 8. The lighter grey parts are infiltrated with molten Si. Clearly, a core-shell like structure was obtained. The silicon could successfully infiltrate the edges of the part, but did not enter the core.

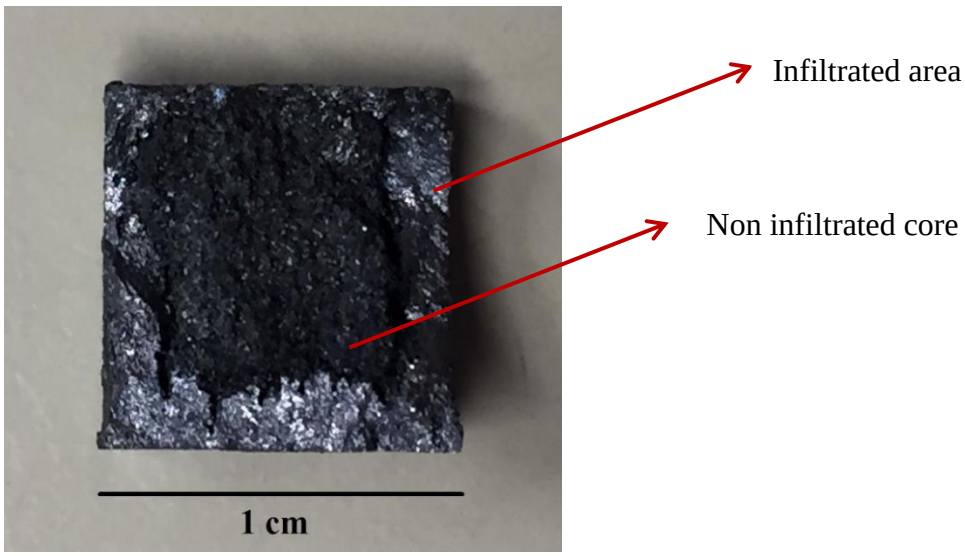

Figure 8: Cross section of a Si-infiltrated low scan spacing SLS part with shell-like structure.

The dimensions of the final infiltrated Si-SiC cubes were, again, as-defined. This means no shrinkage occurred during post processing, which was to be expected since there was no polymer de-binding step involved.

Conclusions & Suggestions

RBSC parts have been produced without the use of a sacrificial binder by direct selective laser sintering. During direct SLS, melting and re-solidification of the silicon could act as a binder mechanism. High laser power – high scanning speed SLS parameter sets failed to produce successful parts. However, low laser power – low scanning speed parameters resulted in Si-SiC preforms of sufficient strength for further handling. After carbon impregnation and liquid silicon infiltration, highly dense (~95%) RBSC parts were obtained. These parts contained a high amount (~60%) of residual silicon, but strategies to resolve this issue were proposed and are currently under investigation.

Acknowledgements

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