Direct Laser Sintering of Reaction Bonded Silicon Carbide with Low Residual Silicon Content

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Abstract

Additive manufacturing (AM) techniques are promising manufacturing methods for the production of complex parts in small series. In this work, laser sintering (LS) was used to fabricate reaction bonded silicon carbide (RBSC) parts. First, silicon carbide (SiC) and silicon (Si) powders were mixed in order to obtain a homogeneous powder. This powder mixture was subsequently laser sintered, where the Si melts and re-solidifies to bind the primary SiC particles. Afterwards, these SiSiC preforms were impregnated with a phenolic resin. This phenolic resin was pyrolysed yielding porous carbon, which was transformed into secondary reaction formed SiC when the preforms were infiltrated with molten silicon in the final step. This resulted in fully dense RBSC parts with up to 84 vol% SiC. The optimized SiSiC combined a Vickers hardness of 2045HV, an electrical conductivity of $5.3 \cdot 10^3 S/m$, a Youngs modulus of 285GPa and a 4-point bending strength of 162MPa.

Keywords: Additive Manufacturing, Laser Sintering, Silicon Carbide, Reaction Bonding

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1. Introduction

Silicon carbide (SiC) ceramics are interesting candidate materials for various applications thanks to their excellent mechanical and thermal properties. They are, however, difficult to manufacture using conventional methods that make use of solid state or liquid phase sintering. Different sintering aids are needed in order to come to a somewhat satisfactory result since grain growth is usually dominant over densification [1]. Due to the very high hardness of SiC, component shaping is only possible with expensive diamond tooling and mainly limited to grinding operations. An alternative, cheaper and faster way to produce near-net-shape SiC materials is reaction bonding. In reaction bonding, a porous preform consisting of SiC and carbon (C) is infiltrated with molten silicon (Si). The Si melt reacts with the carbon and forms a secondary SiC [2]. The end result is a reaction bonded Silicon Carbide (RBSC) composed of primary α -SiC, secondary or reaction formed β -SiC and residual Si. The amount of residual Si should be kept to a minimum in order to maximize performance, mechanical and thermal properties of the final part.

Porous preforms for reaction bonding of SiC can be made in different ways. There are two groups of conventional techniques for producing RBSC preforms. One group of techniques makes use of a binder material which is pyrolysed in order to obtain a SiC/C preform. Amongst these techniques are slip casting, injection moulding and tape casting. Another group of fabrication methods works without binder materials. It consists of uniaxial and isostatic pressing, but these techniques can only be used for the production of simple shape RBSC parts. Complex RBSC parts can be obtained by injection moulding, requiring expensive moulds, or slip casting. As a result, these processes are only feasible for large series. For the economical production of small series or prototypes of complex RBSC parts, additive manufacturing techniques have major advantages over conventional techniques. Amongst these, laser sintering is particularly suitable for the production of complex, net-shape parts. Laser sintering (LS) is a

powder bed fusion technique [3] in which a powder is first paved into a thin layer and then scanned by a laser which selectively fuses the particles together. A new layer is then paved on top of the previous one and the process repeats until a 3D part is obtained.

Laser sintering can be done indirectly or directly. In indirect LS, a sacrificial binder material is used which is later removed by debinding. This process was patented in 1993 by Barlow et al. [4] and facilitates processing of materials with high melting points and/or low thermal shock resistance, like ceramics. The binder, usually a polymer, melts during laser scanning and fuses the ceramic particles together. Subramanian et al. [5] mixed polymer powders with alumina particles and laser sintered green parts. Shahzad et al. [6] used a phase inversion technique to produce spherical alumina-polymer composite microspheres. After laser sintering, debinding and furnace sintering, alumina parts with relative densities of about 50 % were obtained. The density was increased to up to 89 % by introducing additional post-processing steps like suspension infiltration and isostatic pressing [7]. Indirect LS of RBSC was first performed by Vail et al. [8], who produced green parts with relative densities of 48-51 %. Evans et al. [9] introduced the use of a char-yielding binder. During Si infiltration, the Si and the carbon react to form SiC. In this way, highly dense RBSC parts were produced. However, local over-extrusions were present and resulted in a poor surface quality [10]. These were attributed to the expansion of Si during solidification by Stevinson et al. [11] in a later study.

Direct laser sintering does not use a sacrificial binder material, instead the base material or part thereof is melted directly by the laser. Birmingham et al. [12] performed selective laser reaction sintering by scanning a silicon powder bed in a reactive acetylene (C_2H_2) atmosphere. The acetylene served as a carbon source and reacted with the silicon powder to form silicon carbide. The end result were porous single and multi-layer parts with high SiC content. Another process, termed laser micro sintering, was used by Streek et al. [13] to produce

Si-SiC parts with a q-switched laser and pure SiC parts with a continuous (CW) laser.

Figure 1: The 4-step fabrication process for RBSC parts using laser sintering.

This paper investigates direct laser sintering of Si-SiC powder blends. Compared to indirect laser sintering, as used by Evans et al. [9] [10], direct laser sintering does not make use of a binder material during processing. This reduces the risk of phenomena such as crack formation, shrinkage and slumping which can occur during the time-consuming de-binding process inherent to indirect processing. The fabrication process discussed in this text consists of four steps, as shown schematically in figure 1. In the first step, silicon and silicon carbide powders are mixed in order to obtain a homogeneous powder blend. This powder blend is then selectively laser sintered in the second step. The silicon melts and re-solidifies, acting as a consolidation mechanism during the LS process. This results in porous Si-SiC preforms which are then impregnated with a carbon-yielding phenolic resin in the third step. After pyrolysis of this resin, high amounts of carbon are left in the porous preform. In the final step, the carbon reacts with silicon during Si-infiltration to form a secondary (reaction formed) silicon carbide. The end result is a fully dense Si-SiC part with high SiC content and promising mechanical properties.

2. Experimental Techniques

2.1. Powder Preparation

Silicon powder (Si, Simet 985, Keyvest, purity = 98%, $d_{50} = 45 \mu\text{m}$) was dry blended with silicon carbide powder (α -SiC, Carborex BW F320, Washington Mills, purity = 99.2%, $d_{50} = 29 \mu\text{m}$) in a 40:60 vol% ratio in a pan mixing device (Eirich 1-Liter Mixer EL1, Maschinenfabrik Gustav Eirich GmbH & Co KG). A mixing speed of 2400 rpm and time of 5 minutes were used. The morphology of the starting powders is shown in figure 2.

Figure 2: Scanning electron microscopy image of the Si (Keyvest Simet 985, top) and SiC (Carborex BW F320, bottom) starting powder.

2.2. Laser Sintering

Magics software (v18, Materialise, Belgium) was used to prepare and slice build files for the laser sintering process. Laser sintering was performed on a commercial Mlab cusing R machine (Concept Laser, GmbH) equipped with a 100 W continuous (CW) fibre laser. This laser has a wavelength of 1064 nm and a spotsize ($1/e^2$) of $50 \mu\text{m}$. Various batches of cubes ($10 \times 10 \times 10 \text{ mm}^3$) were

scanned in order to find the optimum processing window. Laser powers (P) of 12 to 21 W and scanning speeds (v) from 50 to 500 mm/s were used, while the layer thickness was kept constant at 30 μm and the scan spacing at 77 μm . The scanning was done in a continuous zig-zag pattern and rotated by 90 degrees between layers. An inert argon atmosphere was used to prevent oxidation of the powder.

2.3. Phenolic Resin Impregnation and Pyrolysis

In order to increase the SiC content in the final parts, the preforms obtained after laser sintering were impregnated with a phenolic resin. The resin is of the resole type, as formulated by Mainzer et al. [14]. The resin yields a high amount of porous carbon after pyrolysis due to the use of β -naphthol combined with phenol and formaldehyde in the preparation stage. Two different resin impregnation approaches were used. For the first approach, the resin was infiltrated into the Si-SiC preforms with a pipette until no more resin was absorbed, and then cured in an oven at 150°C. The infiltration and curing was repeated three times in order to fill up as much of the pores as possible. Afterwards, pyrolysis was performed in nitrogen atmosphere with a heating rate of 2°C/min and a dwell time of 2 hours at 700°C. This approach is termed phenolic impregnation treatment I1. The second approach, phenolic impregnation treatment I2, is the same as I1 but adds another phenolic resin infiltration, curing and pyrolysis. Both approaches are shown schematically in figure 3.

Figure 3: Phenolic resin impregnation treatments I1 and I2.

2.4. Reactive Silicon Infiltration

For the silicon infiltration, the phenolic resin infiltrated Si-SiC samples were loaded into a graphite crucible coated with boron nitride (BN). Si wafer chunks (Imec, Leuven) or powder (RsSiTec, purity = 99%, $d_{50} = 5 \mu\text{m}$) were used underneath the sample for infiltration. The crucible was heated in a graphite element resistively heated hot press furnace (W100/150-2200-50 LAX, FCT Systeme, Frankenblick, Germany) in a vacuum of 0.1 mbar. The temperature was increased within 5 minutes to 452°C , the onset temperature of the pyrometer reading. The heating rate was then controlled at $20^\circ\text{C}/\text{min}$ up to 700°C , where it was held for 1 hour in order to pyrolyse the remaining phenolic resin in the preforms. The temperature was further increased at a rate of $50^\circ\text{C}/\text{min}$ to 1450°C with a dwell time of 1 hour. This is above the melting temperature of silicon and allowed the melt to infiltrate the Si-SiC samples. After naturally cooling down the furnace to room temperature, dense Si-SiC parts were obtained.

2.5. Measurements & Mechanical Testing

The morphology of the raw powder material was studied using scanning electron microscopy (SEM, FEI XL30-FEG). The flowability, i.e. angle of repose, of the powders and mixtures was investigated on a home-made angle of repose measurement set-up available at the department of Chemical Engineering of KU Leuven, similar to the Granudrum equipment (Granutools, Belgium). The laser sintered parts were analysed by means of SEM and X-ray diffraction measurements (Seifert 3003 TT, Germany) in order to gain knowledge on the phases present in the material. The phenolic resin was subjected to a thermogravimetric analysis (TGA, SDT Q600, TA Instruments) in order to assess the pyrolysis behaviour at elevated temperatures in a nitrogen atmosphere.

The finished parts were ground, polished and subjected to optical microscopy (Leica DMILM HC). The images were used to study the final SiC content using image analysis software (ImageJ). SiC content was double checked by doing

an XRD Rietveld analysis and by etching away the residual Si in a mixture of 50 vol% hydrofluoric acid (HF, 48% (w/w)) and 50 vol% nitric acid (HNO₃, 65% (w/w)). Densities of laser sintered and finished parts were assessed by the Archimedes method (Acculab atilon ATL-244-1). The Vickers hardness, $HV_{0.3}$, was measured on a hardness tester (Model FV-700, Future-Tech Corp., Japan) with an indentation load of 2.94 N. Si-SiC beams (3x4x45 mm³) were fabricated for mechanical testing. These were laser sintered with a laser power of 15 W and a scanning speed of 100 mm/s, then impregnated with phenolic resin and pyrolysed according to treatment I2, and finally infiltrated with Si. Afterwards they were ground to final dimensions as per ASTM C1161-13. The beams were used to measure the Young's Modulus using the impulse excitation technique (IET, RFDA, IMCE, Belgium) and resistivity (Resistomat, type 2302, Burster, Germany). Finally, four-point bending tests (ElectroPuls E10000, Instron) were performed according to ASTM C1161-13.

3. Results & Discussion

3.1. Powder Characterization

The starting powder used for laser sintering consists of 40 vol% Si and 60 vol% α -SiC powders. Both powders are angular and sharp, as shown in figure 2, as opposed to conventional powders used in laser sintering, which are usually spherical or at least have rounded edges. The angular morphology could cause problems in layer deposition, as it increases inter-particle friction. During preliminary single layer testing, however, it was apparent that the Si-SiC powder blend could successfully be deposited in layers of 30 μ m.

The flowability was quantified using the dynamic angle of repose, a generally accepted characterisation technique to measure flowability of powders [15]. The in-house test setup uses a rotating cylinder (3 rpm, 2 min) that is filled with

Figure 4: The angle of repose data for the Si-SiC powder blend.

Figure 5: The angle of repose data for the Si and SiC powders.

12.5 ml of powder. The angle of repose is then obtained as the angle of the rotating powder mass relative to the horizontal plane. This angle is measured frame by frame using a camera and a matlab script, as a function of rotation time. A typical profile is shown in figure 4, where the data represents the de-

tected slope of the powder bed as a function of time. As can be seen, the angle increases and then suddenly decreases when the powder 'avalanches' or tumbles down. The average angle of repose obtained from this test was 46 degrees for the Si-SiC powder blend, which is high but acceptable. An angle of repose below 40 degrees is considered to characterise a powder with good flowability. The angle of repose profiles for the starting powder materials are shown in figure 5. The SiC powder clearly shows a better flow behaviour than the Si powder. This can be concluded by looking at the average angle of repose of the powders (dashed lines on figure 5) but even more so by inspecting the maximum peak values ('avalanche angles'), which are much higher for the Si powder. Comparing the angle of repose curves of the starting powders and their blend allows to conclude that the flowability of the SiSiC powder blend is better than that of the Si starting powder.

3.2. Laser Sintering

The purpose of laser sintering is to form dimensionally accurate porous preforms of sufficient strength that are suitable for subsequent infiltration. In order to find the right parameter set, laser power and scanning speed were varied and different batches of cubes were produced, as shown in figure 6. High power (P) and scanning speed (v) sets resulted in fragile parts that crumbled upon handling. Low power and scanning speed sets resulted in accurate and more robust preforms. An optimal parameter set range was defined using density measurement and dimensional accuracy as criteria. Successful results are obtained with laser powers of 14-21 W, scanning speeds of 50-200 mm/s, a hatch spacing of 77 μm and layer thickness of 30 μm .

The laser sintered parts were subjected to scanning electron microscopy in order to assess the porosity and structure of the material. Figure 8 shows a high magnification image of a laser sintered preform. Resolidified Si can be observed (light grey) covering the α -SiC (darker grey) originating from the starting powder and binding the SiC particles together. The structure of the top surface

Figure 6: A set of laser sintered cubes (the areas marked with an x contained failed parts).

of a preform is shown in figure 7. A characteristic pattern can be identified, with needle-like protrusions in tracks parallel to the scanning directions of the laser, which rotates with 90 degrees between layers. This pattern originates from the scanning strategy and the hatch spacing, i.e. the distance between two parallel scan tracks, which likely causes the observed porosity between scan tracks. Decreasing the hatch spacing results in a higher overlap between two subsequent parallel scan tracks, and should eliminate this pattern, as illustrated in figures 9 and 10, where parts scanned with a hatch spacing of $77 \mu\text{m}$ and $50 \mu\text{m}$ are compared. However, the porosity is still present, albeit in a more random pattern.

Density measurements showed porosities of 45-55 %, for both the low and high hatch spacing parts. The theoretical density used to calculate these relative values was 2.86 g/cm^3 , i.e. based on the powder blend mixing ratio of 40 vol% Si and 60 vol% SiC. The porosity was filled with phenolic resin and silicon in subsequent post-processing steps. The dimensions of the cubes were as pre-defined, i.e. $10 \times 10 \times 10 \text{ mm}^3$.

The density of cubes for three different scanning speeds and laser powers ranging from 12 to 21 W at a fixed scan spacing of $77 \mu\text{m}$ and a powder layer thickness

Figure 7: SEM image of a laser sintered preform, top view, low magnification, with a characteristic porosity pattern ($P = 15$ W, $v = 100$ mm/s, $s = 77$ μ m).

Figure 8: SEM image of a laser sintered preform, top view, with Si that has been molten and re-solidified, and α -SiC starting powder.

Figure 9: SEM image of a laser sintered preform scanned with a hatch spacing of 77 μ m, resulting in a characteristic porosity between scan tracks (arrows).

Figure 10: SEM image of a laser sintered preform scanned with a lower hatch spacing of 50 μ m, resulting in a more random porosity pattern.

of 30 μ m are summarised in figure 11. The influence of laser power and scanning speed, the two parameters that were varied during the experiments described here, can be more easily understood by defining the laser line energy (LLE) delivered to the powder bed:

$$LLE = \frac{P}{v} \quad (1)$$

with P the laser power in W and v the scanning speed in mm/s. The laser energy therefore increases with increasing laser power P and decreasing scanning

Figure 11: Density versus laser power for cubes fabricated with scanning speeds of 50, 100 and 200 mm/s.

speed v . Cubes made with a laser power below 13 W were not consolidated, except at the lowest scanning speed of 50 mm/s. This is caused by a lack-of-fusion issue due to insufficient laser energy being delivered to the powder bed to melt the silicon. Cubes made with laser powers higher than 21 W crumbled and lost their geometrical accuracy. Some of the silicon in the powder bed likely started to evaporate at these higher laser energy densities and the SiC in the powder bed decomposed into Si and C. Good results were obtained with laser powers between 13 and 21 W. Concerning the effect of the scanning speed, higher scanning speeds resulted in lower densities. Again, this can be explained by a lack-of-fusion: the higher scanning speeds lead to a decrease in laser energy delivered to the powder bed and thus insufficient melting of the Si. For a scanning speed of 50 mm/s, the laser power hardly influenced the density. However, for higher scanning speeds the density decreased with increasing laser power. The reason for this is likely local overheating and evaporation of Si or de-composition of SiC, although it is not clear why this phenomenon does not occur at a scanning speed of 50 mm/s.

The density after SLS is correlated to the final α -SiC content in the Si

Table 1: Post SLS density versus final SiC content ($P = 15$ W, different scanning speeds) after Si infiltration without phenolic resin.

Scanning speed (mm/s)	50	100	200
SLS density (%)	54	50	47
Final SiC %	32.4	30	28.2

infiltrated parts. The higher the density, the more α -SiC is present in the preform, which leads to a higher α -SiC content in the final part. A comparison is made in table 1 for cubes scanned with a laser power of 15 W, a scan spacing of $77 \mu m$ and a layer thickness of $30 \mu m$ at different scanning speeds. Note that these laser sintered parts were not infiltrated with phenolic resin, only with Si. Phenolic resin infiltration will cause a massive increase in SiC content due to the added reaction-formed β -SiC. This will be further discussed in subsection 3.3. XRD analysis, presented in figure 12, revealed that the laser sintered preforms consisted of Si and α -SiC, as expected based on the starting material.

Figure 12: XRD data of a laser sintered ceramic, with peaks corresponding to Si (square, red) and α -SiC (square, black).

In order to prove the viability of the process for the production of complex objects, some demo parts were made. These were scanned with a laser power of 15 W and a scanning speed of 100 mm/s. This scanning speed is used as a trade-off between post-SLS SiC content and production speed, as scanning speeds of 50 mm/s lead to very long build times. Figure 13 presents a heat sink component with cooling ribs after SLS and after liquid silicon infiltration. Figure 14 presents a laser sintered and a liquid Si infiltrated gear.

Figure 13: A porous, as-laser sintered (left) and a dense, finished heat sink (right).

Figure 14: A porous, as-laser sintered (left) and a dense, finished gear (right).

The dimensions of the finished part were as defined, with the exception of some dross formation due to liquid Si infiltration. Roughness measurements were carried out and showed a mean roughness of $12.5\mu m R_a$ for the laser sintered part and $10.3\mu m R_a$ for the finished part.

3.3. Phenolic resin impregnation and pyrolysis

The phenolic resin was infiltrated into the laser sintered preforms and pyrolysed to yield porous carbon. In order to gain information on the temperature range for the pyrolysis of the resin, a thermogravimetric analysis was performed, as shown in figure 15. A first weight loss occurred around $100^\circ C$ and corresponds to the water evaporation from the resin. The subsequent steady weight loss virtually levels off around $600^\circ C$. The carbon yield at that point amounts to about 60 wt% of the original weight of the resin. This leads to high amounts of porous carbon being present in the impregnated Si-SiC preform, as can be seen on the SEM pictures of impregnated preforms (treatment I2) in figures 16 and 17. This is important for the formation of reaction-formed SiC during the liquid silicon

infiltration.

Figure 15: TGA analysis of the phenolic resin used for impregnation of the porous Si-SiC.

Figure 16: Preform fabricated according to phenolic impregnation treatment I2, with a high amount of carbon resulting from resin pyrolysis, low magnification.

Figure 17: Preform fabricated according to phenolic impregnation treatment I2, with a high amount of carbon resulting from resin pyrolysis, higher magnification.

The reaction taking place during liquid silicon infiltration is:

From this, the theoretical amount of carbon needed to reach a 100% pure SiC part starting from a 40:60 Si:SiC preform with a density of 50% can be

calculated. This is summarized in table 2 and compared to the actual measured values of carbon impregnated in the preform using phenolic impregnation treatments I1 and I2. From the measured weights of added carbon, a theoretical assessment was made concerning the expected final amount of SiC in the part, assuming that the added carbon is fully converted to β -SiC. The weight values in the table are based on a preform (and final part) volume of 1 cm³. Values in bold are measured.

Table 2: Calculated theoretical amounts of carbon needed for a full conversion of Si into β -SiC and measured values and their theoretical effect on the final SiC content. Calculations made based on a total preform and part volume of 1 cm³, $\rho_{SiC} = 3.21$ g/cm³, $\rho_{Si} = 2.33$ g/cm³, $\rho_C = 2.267$ g/cm³.

		No β -SiC	Max β -SiC	Measured, I1	Measured, I2
Preform	SiC (vol%)	30	30	29.4	29.4
	Si (vol%)	20	20	19.6	19.6
	pores (vol%)	50	50	51	51
Resin & Si infiltration	Add. C (g)	0	0.673	0.39	0.52
	Add. C (vol%)	0	29.7	17.2	22.9
	β -SiC (vol%)	0	70	40.6	54.1
Final Part	SiC (vol%)	30	100	69.9	83.5
	Si (vol%)	70	0	30.1	16.5
	pores (vol%)	0	0	0	0

3.4. Liquid silicon infiltration

Liquid silicon infiltration leads to fully dense reaction bonded silicon carbide material, as illustrated in figure 18 for the parts that were scanned with a laser power of 15 W, a scanning speed of 100 mm/s, a scan spacing of 77 μ m and a powder layer thickness of 30 μ m. Image analysis techniques were used to study light microscopy images and analyse the amount of silicon carbide in the final structure. If the phenolic resin impregnation step is omitted, no β -SiC is formed

since there is no carbon for the Si melt to react with. This leads to microstructures as shown on figure 18a, with darker grey α -SiC grains embedded in a light grey Si matrix. The structure is dense, but the SiC content is only about 35 vol%.

Figure 18: Light optical micrographs of a dense SiSiC part after Si infiltration without (a) and with (b) phenolic resin impregnation.

The SiC content can be increased by performing phenolic resin impregnation. This provides porous carbon in the laser sintered preform, which reacts with the silicon during infiltration to form β -SiC. The final microstructure obtained after phenolic resin impregnation treatment I2 is shown in figure 18b. Again, the light grey matrix is Si, which is present in much smaller amounts compared to figure 18a. The dark grey grains are α -SiC originating from the starting powder that was laser sintered. The lighter grey phase inbetween is β -SiC which results from the reaction between the Si melt and porous carbon from the phenolic resin. The SiC content is up to 84.9 vol%, based on image analysis.

The final SiC content and thus microstructure and properties of the produced Si-SiC material mainly depend on whether or not carbon impregnation was performed. Furthermore, the amount of carbon impregnation cycles has an effect. A comparison between 3 cubes with different post-processing cycles is

made in table 3. These cubes were all laser sintered with a scan spacing of $77\text{ }\mu\text{m}$ and a layer thickness of $30\text{ }\mu\text{m}$. Cube 1 (figure 18a) was not subjected to carbon impregnation, cube 2 was subjected to phenolic resin impregnation treatment I1 and cube 3 (figure 18b) underwent phenolic resin impregnation treatment I2. It is clear that the additional impregnation and pyrolysis results in the formation of an additional 21 vol% SiC after Si infiltration.

Table 3: A comparison between Si-SiC cubes made with different post-processing strategies.

	Cube 1	Cube 2	Cube 3
Laser Power (W)	15	15	15
Scanning speed (mm/s)	100	100	100
Carbon impregnation & pyrolysis	none	I1	I2
SiC content (final, vol%)	34.7 ± 0.7	64.0 ± 2.6	84.9 ± 1.3

An XRD measurement was performed on cube 3 to confirm that the phases seen in light microscopy were indeed Si, α -SiC and β -SiC, as presented in figure 19. Peaks for Si are visible, as well as coinciding peaks for α -SiC and β -SiC. The presence of these phases was quantified using Rietveld analysis, yielding 27.5 vol% α -SiC, 56.1 vol% β -SiC and 16.4 vol% Si. This points to a SiC content of 83.6 vol%, which is close to the 84.9 ± 1.3 vol% measured by light microscopy image based analysis on the same sample and the composition predicted in table 2.

3.5. Material properties of the produced RBSC

Material properties investigated include electrical resistivity, Young's modulus and flexural strength. The tests were done on $8\text{ }3\text{x}4\text{x}45\text{ mm}^3$ beams. These beams were laser sintered with a laser power of 15 W, a scanning speed of 100

Figure 19: XRD pattern of a RBSC cube (resin impregnation treatment I2), with peaks corresponding to Si, α -SiC and β -SiC.

mm/s, a scan spacing of $77 \mu\text{m}$ and a powder layer thickness of $30 \mu\text{m}$. The resistivity of the beams was $2.0 \pm 0.7 \times 10^{-4} \Omega\text{m}$. The conductivity σ , calculated as the inverse of the resistivity, is $5.3 \pm 0.9 \times 10^3 \text{ S/m}$. These values point to a moderate conductivity.

The impulse excitation technique (IET), a non-destructive test, was performed in order to accurately measure the Young's modulus of the produced RBSC. The Young's modulus amounted to $285 \pm 5 \text{ GPa}$. Afterwards, four-point bending tests were performed. The flexural strength was $162 \pm 7 \text{ MPa}$. Stress-strain curves are shown in figure 20. Finally, Vicker's hardness was measured with an indentation load of 2.96 N and amounted to 2045 ± 252 . A summary of the properties of the obtained Si-SiC material can be found in table 4, where they are also compared to those of a similar material, IntrinSiC by Schunk GmbH (Germany) [16]. An increase in Young's modulus and flexural strength is expected when increasing the SiC content or decreasing the α -SiC particle size. The latter, however, is not straightforward, as a decrease in powder size will have a negative influence on the layer paving during laser sintering.

Table 4: Properties of laser sintered Si-SiC (P = 15 W, v = 100 mm/s, l = 30 μm , s = 77 μm).

	Si-SiC	IntrinSiC (Schunk)
SiC content (<i>vol%</i>)	84.9 ± 1.3 ⁰	80.4
Resistivity (Ωm)	$2.0 \pm 0.7 * 10^{-4}$	-
Young's Modulus (<i>GPa</i>)	285 ± 5	360
Flexural Strength (<i>MPa</i>)	162 ± 7	150
Hardness (<i>HV</i>)	2045 ± 252 ¹	2800

Figure 20: Stress-strain curves obtained from 4-point bending tests on laser sintered RBSC.

The Schunk process is comparable to the process described in this work and the properties of the produced materials are very similar. Both processes

⁰As measured using image analysis software. XRD Rietveld analysis yields a SiC content of 83.6 vol%, etching points to a SiC content of 82.5 vol%.

¹ $HV_{0.3}$

are a sequence of 4 steps (powder/binder preparation, additive manufacturing, carbon impregnation, liquid silicon infiltration). In the Schunk process [17], carbon is impregnated through a sequence of 2-4 carbon suspension infiltration steps with intermittent drying steps, similar to the phenolic resin impregnation with intermittent crosslinking and pyrolysis. Binder jetting is used as an AM technique, starting from coarser SiC powder (70-200 μm) and using higher layer thicknesses (up to 500 μm). This leads to lower processing times in comparison with laser sintering. However, laser sintering is more suited for the production of fine features, since the layer thicknesses are lower (30 μm) and the laser spot is very small (50 μm). The process presented here is therefore complementary to the already industrially viable Schunk process, i.e. laser sintering for smaller intricate parts with fine details and the IntrinSiC binder jetting process for a faster production of larger scale parts.

4. Summary

This paper describes how laser sintering was used as a shaping technique for reaction bonded SiC preforms starting from Si and SiC powders. During laser sintering, consolidation is achieved when the Si melts and re-solidifies, effectively binding the SiC particles together. Post-processing consisting of phenolic resin impregnation and liquid Si infiltration yielded dense parts. The viability of the process for complex parts was demonstrated by fabricating and infiltrating a number of complex shape components. The material properties of the produced material depend on the final SiC content. Density after laser sintering has a small effect on the final SiC content of the parts, while the phenolic resin impregnation has a large effect, since it fills the residual porosity with carbon which later reacts to β -SiC during liquid Si infiltration. A double resin impregnation + pyrolysis cycle (treatment I2) resulted in Si-SiC parts with up to 84 % SiC, a Young's modulus of 285 *GPa* and a flexural strength of 162 *MPa*.

Acknowledgements

This work was supported by the Research Foundation Flanders (FWO) under project FWO-G.0956.14N, and the research fund of KU Leuven through project GOA/15/012-SUMMA. The authors would like to thank Michael Van den Eynde for his assistance with the angle of repose measurement set-up and Dr. Thomas Lapauw for his contribution on Rietveld analysis.

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