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Original Article

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 2045 HV, an electrical conductivity of 5.3×10^3 S/m, a Young's modulus of 285 GPa and a 4-point bending strength of 162 MPa.

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

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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 sacrifical 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.

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 debinding process inherent to indirect processing. The fabrication process discussed in this text consists of four steps, as shown schematically in Fig. 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 µm) was dry blended with silicon carbide powder (α-SiC, Carborex BW F320, Washington Mills, purity = 99.2%, d_{50} = 29 µm) 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

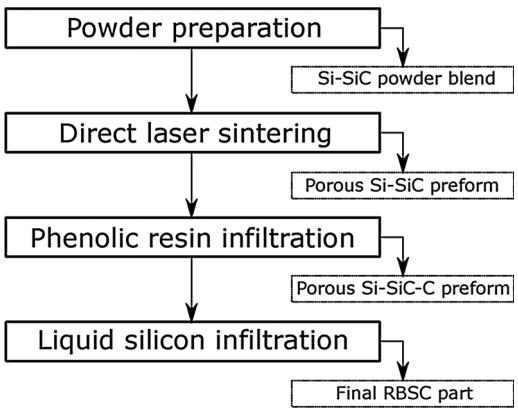

Fig. 1. The 4-step fabrication process for RBSC parts using laser sintering.

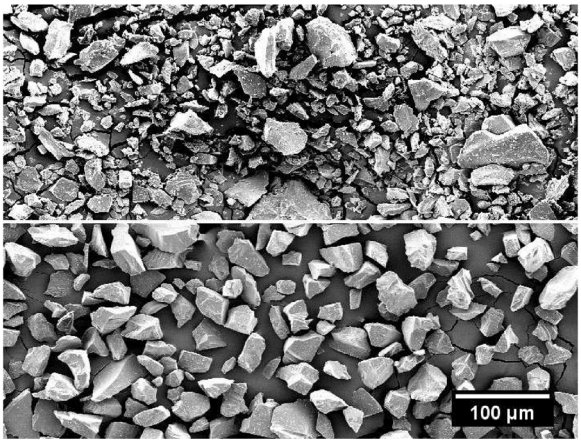

Fig. 2. Scanning electron microscopy image of the Si (Keyvest Simet 985, top) and SiC (Carborex BW F320, bottom) starting powder.

5 min were used. The morphology of the starting powders is shown in Fig. 2.

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 µm. Various batches of cubes (10 × 10 × 10 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 h 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 Fig. 3.

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 µm) 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