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Advanced Laminated Object Manufacturing (LOM) of SiSiC Ceramics

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Abstract

Carbon sheets were used as a starting material for fabrication of SiSiC composites by advanced LOM. This approach consists of three steps: First a preform was fabricated form phenolic resin coated carbon paper with a LOM-device. Second the preform was turned into a carbon preform by pyrolysis in N_2-atmosphere. Third pressureless reactive melt infiltration of silicon into the as fabricated carbon preform, which finally yielded a dense SiSiC composite. SEM analysis revealed a microstructure consisting of uniformly dispersed β-SiC grains in a matrix of silicon. The LOM fabricated material exhibited an average four point bending strength and Youngs modulus of 115 MPa and 165 GPa, respectively.

Introduction

SiC-based ceramics exhibit superior mechanical properties, high temperature resistance, chemical stability and oxidation resistance from ambient to peek operation temperatures required for advanced applications ranging from automotive to aerospace uses [1-5]. The manufacturing of SiC-based ceramic composites by reactive infiltration of C/SiC-powder or carbon fiber reinforced carbon preforms with liquid Si at temperatures between 1450-1600°C in vacuum (LSI-process) represents an established processing route. Nearly dense interpenetrating or fiber reinforced ceramic composite materials with a variable amount of excessive Si are obtained. Well known materials are REFEL SiC [6] and SILCOMP SiC/Si [7] as well as carbon fiber reinforced SiC-CMCs [8]. The LSI-process is also capable for manufacturing near net-shape ceramic composites for structural applications [9, 10]. SiC can be manufactured by rapid prototyping technologies, such as selective laser sintering [13], three dimensional printing [14] or laminated object manufacturing (LOM) [11,12].

LOM produces three-dimensional objects with sheets of paper, polymer, metal or a combination thereof [15]. It can be considered as a hybrid between "subtractive" and "additive" processes: the parts are indeed built up in the layer by layer approach ("additive" processes), but each layer is individually cut by a special tool ("subtractive" processes) in the shape of the cross section of the part. Each layer is bonded to the previous layer with an adhesive coating on the bottom side of the sheets (e.g., paper), that is activated by a heat or pressure during the LOM process [15]. A convenient way to fabricate advanced structural ceramics by LOM includes use of ceramic based tapes processed by tape casting. The ceramics obtained include Al_2O_3 [16], monolithic ZrO_2 and ZrO_2/Al2O3 [17], SiC and SiC/SiC [11,12] and Si_3N_4 [18].

The intention of the present work was to demonstrate the fabrication of dense SiSiC laminar composites by Laminated Object Manufacturing.

Experimental procedure

Processing included preparation of carbon sheets coated with a suitable adhesive, LOM processing and final post-processing with liquid Si infiltration into the porous carbon component. Carbon sheets made from pitch fibers as shown in Fig 1 (Sigratex PE204, Thickness ~ 200 µm, SGL Carbon Group, Meitingen, Germany) were laminated to a heat activated adhesive film containing phenolic resin and butyl nitrile rubber,(Tesa HAF 8410 Tesa AG, Thickness ~ 60 µm, Hamburg, Germany). After lamination at120°C a carbon sheet coated with a phenoly butyl nitrile rubber heat activated adhesive film on one side and a thickness of 250 µm was LOM processed in a LOM device (Kira PLT A4, Kira Corporation, Japan). Fig. 2 shows the processing scheme applied. Lamination was carried out at 180 °C for 60 s and was adopted to the curing cycle of the adhesive layer. Sample bars which consisted of 20 individual layers each with an overall sample height of 5 mm and a density of 0.42 ± 0.01 g/cm³ were prepared.

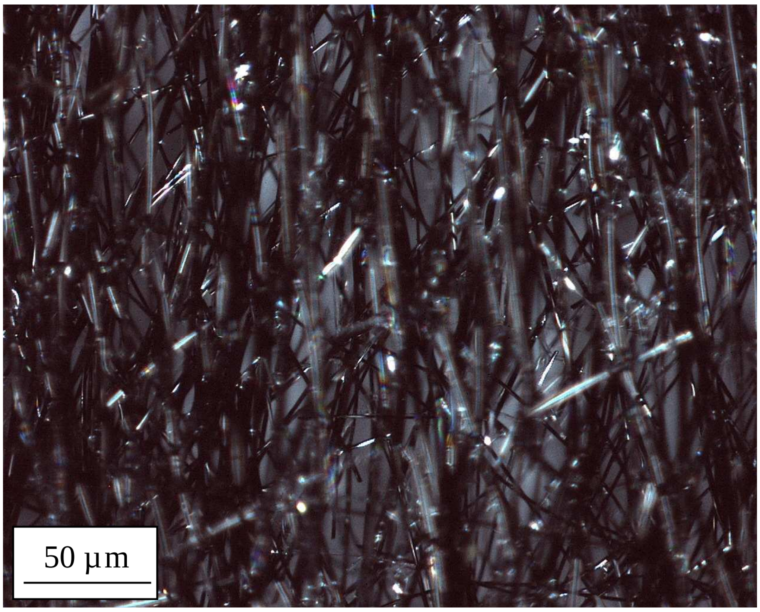

Figure 1 Microstructure of the carbon sheets,

The porous layered samples were pyrolysed in an electrically heated furnace (Gero GLO 40, Gero, Germany) in nitrogen atmosphere. The heating cycle was optimized using differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). A heating rate of 1 °C min^{-1} up to 350°C with a holding time of 1 h was applied to avoid cracking and curling of the sheet during pyrolysis. Further heating up to 800°C was continued with a rate of 2 °C min^{-1}. After 1h exposure at 800°C the samples were cooled to room temperature with a cooling rate of 5°C/min. The porous carbonised samples were then infiltrated with liquid silicon in vacuum at 1500°C for 1h.

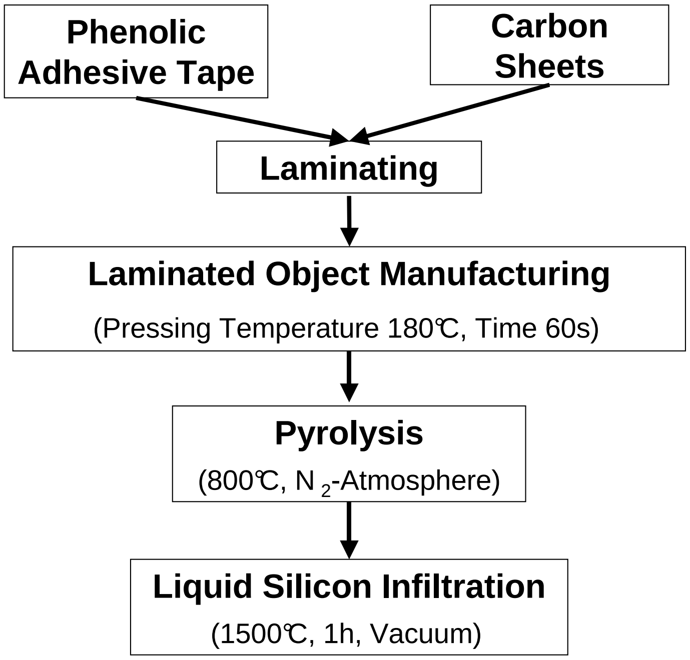

Figure 2: Processing scheme.

The weight loss and shrinkage upon thermal treatment and post-infiltration were determined. Densities were measured geometrically and by Archimedes method using water as the immersion medium. The strut density of the carbonised samples was measured using He-pycnometry analysis. X-Ray diffraction (XRD) analysis (Kristalloflex D 500, Siemens, Karlsruhe, Germany) was conducted using monochromatic Cu-Kα radiation at a scan rate of $0.75°\text{min}^{-1}$. Microstructure and micro chemical composition of the as-pyrolysed and the SiSiC samples were analyzed by scanning electron microscopy (SEM, Quanta 200, FEI, Germany) equipped with an energy-dispersive spectrometer (EDS, Inca x-sight, Oxford Instruments, UK). The samples for SEM/EDS analyses were ground and polished to a 3 μm diamond finish. At least five different spot analyses were conducted to obtain the average composition of a given phase.

The dependence of fracture strength on the fiber orientation of the fabricated SiSiC bars ($3\times4\times45$ mm^3) was evaluated in four-point bending with the loading direction normal to the layer extension using spans of 40 and 20 mm according to ASTM standard C1211-92. The tensile surfaces of the samples were polished to a 3 μm diamond finish prior to loading. The tests were performed using an universal testing machine (Instron 4204, Instron corp. Canton, MA USA) with a crosshead speed of 0.5 mm/min. The Youngs modulus was determined using the impulse excitation technique (Buzz-o-sonic, BuzzMac Software, Glendale, MI, USA) according to ASTM E1876 and C1259.

Results and discussion

Fig. 2 shows the cross section of the LOMed multi layer prior to post-infiltration with Si. The individual layers of the carbon sheets and the phenolic butyl nitrile rubber adhesive can be distinguished in Fig 3a. Fig. 3b shows the microstructure of the pyrolysed body. The properties of the carbonized LOMed samples are summarized in Table I.

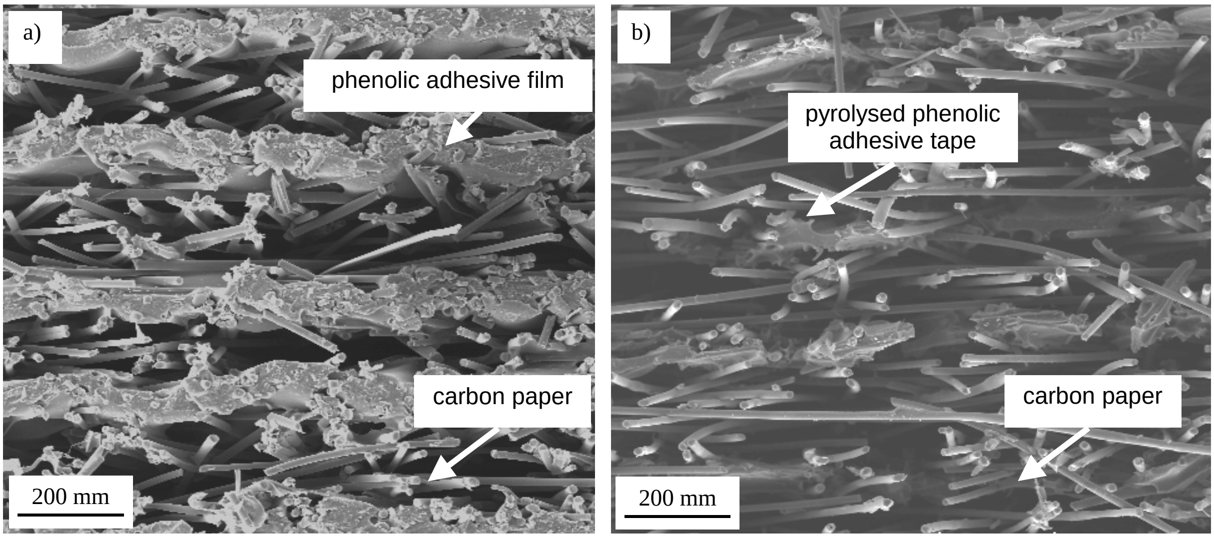

Figure 3: Multilayer structure of a LOMed sample: a) as LOMed, b) after pyrolysis.

Table I: Properties of the carbonized LOMed samples.

Mass loss	43.7± 1.7%
In plane shrinkage (x-, y-direction)	0.5 ± 0.4 %

Out of plane shrinkage (z-direction)	0.7 ± 0.6 %
Total porosity	85.6 %
Geometrical density	0.24 g/cm³
Strut density (composite)	1.68 g/cm³

The mass loss during pyrolysis was caused by the phenolic butyl nitril rubber adhesive. According to the results of the DSC and TGA measurements the butyl nitrile rubber starts to decompose at 275°C and the phenolic resin decomposes at 350°C.

After infiltration with Si, the geometrical shape of the preforms was preserved and no further shrinkage was observed. Thus, the presented approach can be considered as a near-net-shape forming process of ceramic parts [19].

XRD analysis after reactive infiltration revealed the presence of only two crystalline phases, Si and β-SiC. The as-infiltrated SiSiC laminar composites had a density of 2.3 ± 0.02 g cm^{-3}. According to the SEM micrographs presented in Fig. 4 the porosity was completely infiltrated with Si, however, a substantial amount of unreacted carbon still remained. The phase composition after infiltration as obtained from stereological analysis of the SEM micrographs (Image C Intronic GmbH, Germany) was approximated to 18.3 vol% SiC, 75.4 vol% Si and 6.3 vol% of residual carbon.

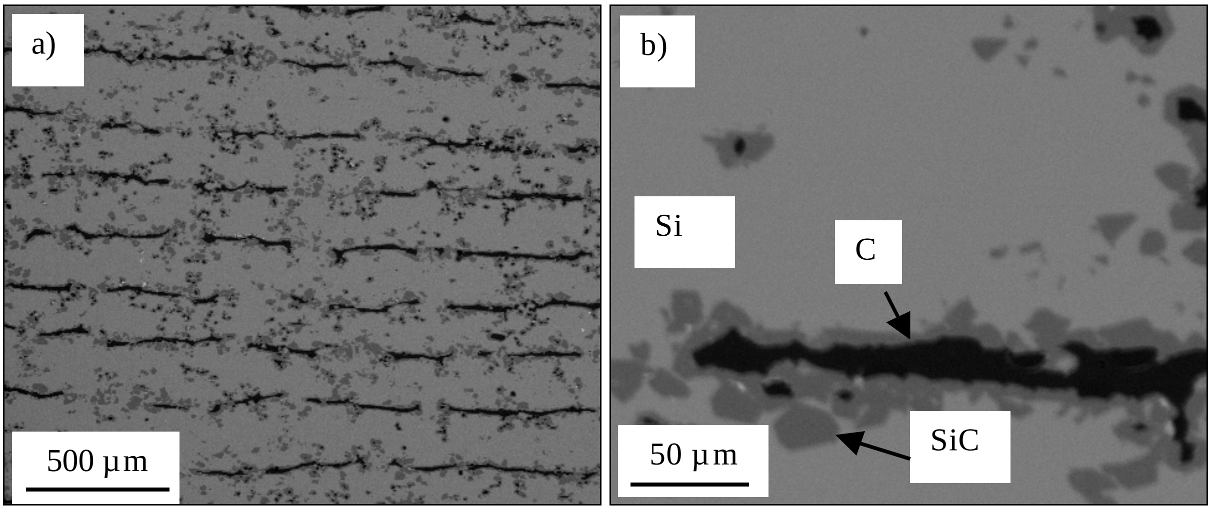

Figure 4: Microstructure of the SiSiC composite infiltrated 1h at 1500°C and annealed for 1h.

The Youngs modulus for the specimen infiltrated at 1500°C for 1h was determined as 165 ± 7 GPa. The measured values of the elastic modulus of the fabricated SiSiC composites are in good agreement with the predicted values for the composite materials [20]:

$$E_{comp} = \sum_i E_i V_i$$

where E_i is the elastic moduli of the constituents and V_i is the volume fractions. Using the date for the plain phases (E_{Si} =167 MPa [20], E_{SiC} = 414 MPA [21] and $E_{GlassyC}$ = 20 GPa [22]) a Youngs modulus of 200 GPa is estimated, which is slightly higher than the experimental one due to a higher amount of residual carbon than obtain by image analysis.

The infiltrated SiSiC composites obtained an average bending strength of 115 ± 15 MPa, which is in the same range as other SiC-material manufactured LOM of cast SiC-tapes [11,12]. Fig. 5 shows the correlation between the four point bending strength and the fiber orientation of the specimen. A fiber orientation of 0° represents a loading direction (tensile stress) parallel to the fiber elongation, whereas an orientation of 90° denotes a loading direction perpendicular to the fiber. A fiber orientation of 0/90° was created by alternatively stacking layers with fiber orientation of 0° and 90°. The bending strength remained almost invariant with changing the fiber orientation which might be announced with the high amount of Si and the low fraction of SiC giving rise for a quasi isotropic mechanical behavior. Hence further development will be focused on reducing the fraction of Si and unreacted carbon.

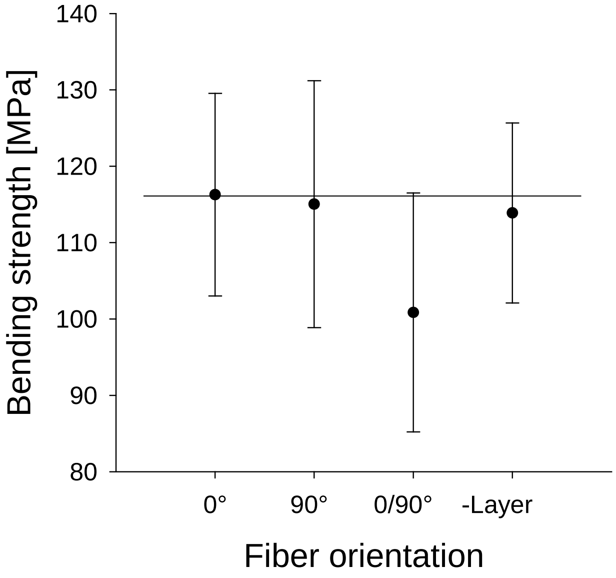

Figure 5: Bending strength vs. fiber orientation.

Fig. 6 shows the rise in flexural strength with increasing SiC content. According to Fig 7 which show the influence of the preform porosity on the phase composition of the component, the maximum SiC content is reached with a preform porosity of 42.7 vol%. The focus of further research is on decreasing the preform porosity by infiltration resins with high carbon yield or SiC-slurries into the as LOMed components, to increase the SiC- content and improve the mechanical properties.

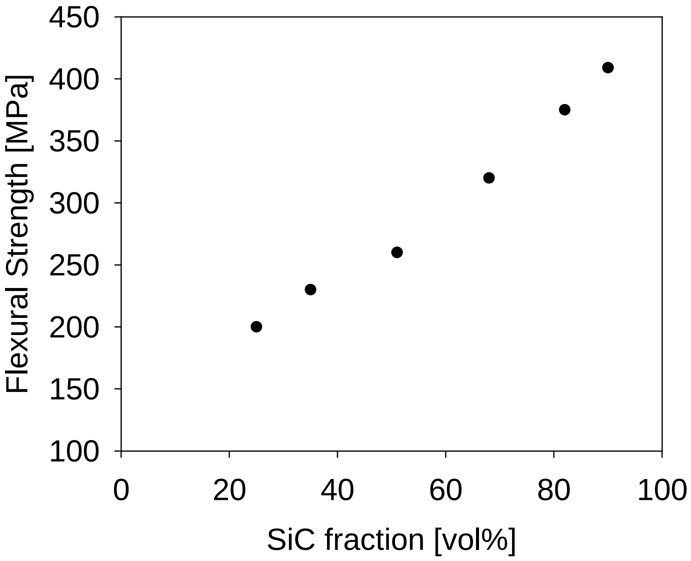

Figure 6: Flexural strength vs. SiC content

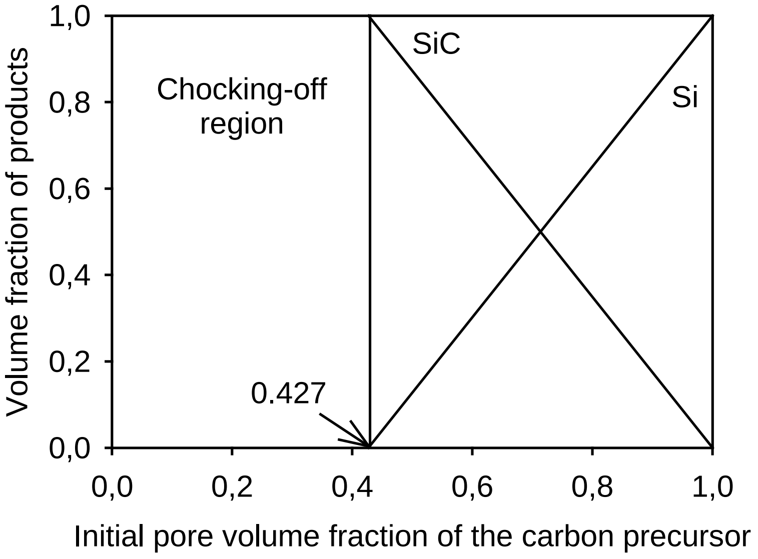

Figure 7: Influence of preform porosity on the phase composition.

Conclusions

SiSiC composites with a laminar structure were fabricated by Laminated Object Manufacturing. Carbon sheets made from pitch fibers were coated with an adhesive consisting of phenolic resin and butyl nitrile rubber and processed in a LOM-device, subsequently pyrolysed and finally infiltrated with silicon melt. Due to the extremely low dimensional changes, LOM of carbon sheets followed by post infiltration processing can be considered as a near net shape manufacturing process. Reduction of residual Si and unreacted carbon is expected to give rise for improving the mechanical properties of the LOM SiSiC composite materials,

Aknowledgements

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