

Long fibre reinforced ceramics with active fillers and a modified intra-matrix bond based on the LPI process

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Abstract

Silicon-based preceramic polymers are attractive candidates for the manufacture of high temperature and corrosion resistant ceramics, particularly in regard to the formation of a ceramic matrix in long fibre reinforced ceramic matrix composites (CMCs). The manufacture of CMCs constitutes of the infiltration of fibre preforms followed by a subsequent crosslinking and pyrolysis of the Si-precursor, yielding an amorphous ceramic matrix. However, due to the inherent shrinkage of ceramic precursors, a high number of polymer impregnation and pyrolysis (PIP) cycles is required to obtain dense composites. Nevertheless, their microstructure is characterized by large interbundle pores which show a negative impact on the mechanical properties.

In order to improve the performance of the long fibre reinforced CMCs as well as to accelerate the manufacturing process, a novel approach was investigated. Thereby, micro-sized powders of Al and Ti are used as active fillers. The powders were strewn between the fabric plies and infiltrated by the resin transfer moulding (RTM) technique. Since reactions with the polymer matrix are associated with a volume increase during pyrolysis, a more dense ceramic matrix is obtained.

The processing of the CMCs employs the commercial polysilazanes CERASET SN and VL20 as preceramic precursors. The reinforcement constitutes of Tyranno SA fibres. To densify the composites, up to five PIP cycles were performed. CMC samples were aged in air to evaluate the impact of oxidation on microstructure and mechanical properties. Microstructural characterization was conducted using both optical and electron microscopy. The conversion of the filler particles was analysed by means of EDX and XRD.

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1. Introduction

Ceramic matrix composites (CMCs) are candidate materials for structural applications in various industries, including automotive, aerospace and utilities, primarily because of their tribological properties, high temperature and shock resistance, and improved damage tolerance combined with a relatively low weight. Several processes, including chemical vapour infiltration (CVI), the liquid silicon infiltration process (LSI), solid and liquid infiltration followed by hot pressing (HP), or hot isostatic pressing (HIP) have been used for the manufacture of CMCs.¹ Another relatively novel processing route is the liquid polymer infiltration (LPI) based on organometallic preceramic precursors such as polysilazanes. Upon pyrolysis the ceramic precursors are converted into a

ceramic material yielding amorphous SiCN as well as crystalline SiC and Si₃N₄ phases.²

In this work the commercially available polysilazanes CERASET SN and VL20 (Kion Inc.) were employed as preceramic precursors. Despite the high ceramic yield of both polymers (63% for Ceraset SN, 64% for VL20) the pyrolysis product (SiCN) contains a network of microcracks and porosity due to the considerable shrinkage of the matrix (more than 50%) that occurs during pyrolysis. Consequently, multiple polymer impregnation and pyrolysis (PIP) steps are necessary to develop a relatively dense matrix by the PIP process. In order to reduce the shrinkage upon pyrolysis, suitable filler materials can be incorporated into the polymer precursors. Loading the polymer matrix with active filler particles, which undergo a volume expansion upon reaction with the decomposition products (CH₄, C₂H₄, NH₃) of the polymer matrix or the pyrolysis atmosphere (N₂) at elevated temperatures,

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is a viable solution of the problem as studied by Greil.^{3–4} Furthermore, the addition of such fillers has the advantage of producing a more dense ceramic matrix leading to enhanced mechanical properties of the CMC. Suitable active fillers are elements or compounds forming carbides, nitrides or oxides in combination with a high volume increase upon reaction, such as Al, B, Si, Ti, CrSi₂, MoSi₂, etc. In this work Al and Ti have been studied as active fillers. The maximum theoretical volume changes after formation of nitrides, carbides or oxides are shown in Table 1.

Considering the densification of the matrix of the CMCs via the addition of new pyrolysed polymer by every distinct PIP cycle, it is expected that the boundary in-between matrices from different PIP cycles is a weak point in the CMC microstructure. To further increase the mechanical properties of the CMC, a new attempt is made to increase the intra-matrix bond by treating the CMC with titanium(IV)-diisopropylate after every PIP cycle.

2. Experimental

For the manufacture of the CMCs, two types of fibres were used: carbon fibre (HTA, Tenax) and silicon carbide (Tyranno SA, UBE Ind.), respectively. A removal of the fibre sizing was abandoned since results from earlier experiments showed better interlaminar shear strength (ILSS) values in combination with Ceraset SN. The chosen fibre volume content was 50%. After fibre reinforced plastic composites (CFRP) were manufactured by means of RTM, they were submitted to pyrolysis at 1000 °C with an average heating ramp of 1 K/min. For matrix formation, the CMCs underwent up to four subsequent reinfiltration and pyrolysis steps. Contrary to the manufacture of CMCs without active fillers where RTM processing was performed with the Ceraset SN polymer, the CMCs containing fillers were manufactured with VL20 polymer as preceramic precursor. The manufactured CMC plates had final dimensions of 300 mm × 100 mm × 3.2 mm. The powders employed for CMC manufacture were aluminium powder (Eckard-Werke) and titanium powder (Chemetall). Both powders had average particle diameters below 10 μm. The dispersion of the fillers between the single plies was achieved by strewing and subsequent brushing for a more uniform distribution. The dry plies were then stacked and placed into a RTM mould for infiltration. Based on former studies, the amount of active filler was set to 2.5 vol.% relative to the matrix.

To study the mechanical properties of the CMCs, the ILSS was measured in a 3-pt. short beam test (span width/thickness

= 5), flexural strength (span width/thickness = 20) was measured in 3-pt. long beam bend test and finally tensile strengths were measured. The specimen number varied between 4 and 8. Additionally, samples were investigated by means of light microscopy (LM), SEM and TEM. Density and open porosity were determined by the Archimedes method. The analysis of the phase composition was performed by XRD on a D8 Advance diffractometer (Bruker AXS) using Cu Kα radiation.

2.1. CMC with increased intra-matrix bond

To increase bonding in-between distinct matrices formed in the reinfiltration steps, the CMC plates were immersed in a solution of titanium(IV)-diisopropylate in propanole using an ultrasonic bath for 30 min and subsequently dried at 80 °C before every reinfiltration. After reinfiltration of the CMC Ti bridges are preferably formed between remaining surface groups (hydroxyl or amino) on the pyrolysed matrix and the newly added polymer. Suggested reactions with the precursors from reinfiltration during pyrolysis are given in Fig. 1.

3. Results and discussion

3.1. CMC with Al and Ti filler

Based on earlier observations of the microstructure of CMC manufactured by the LPI method,⁵ it became clear that the high shrinkage of the matrix rich regions in-between plies (gussets) is linked to the formation of large intra-bundle voids. These gussets show a highly detrimental influence on the mechanical behaviour of the composite, as the maximum shear strength is decreased due to lowering the in-plane surface of the composite. The gussets also provide an increased notch sensitivity.

After attempts in former experiments failed to fill the voids by reinfiltration and pyrolysis even after the fifth PIP cycle,⁶ a different approach was pursued. In order to overcome the problems caused by the high shrinkage of the matrix, experiments aimed to modify the microstructure locally. This was

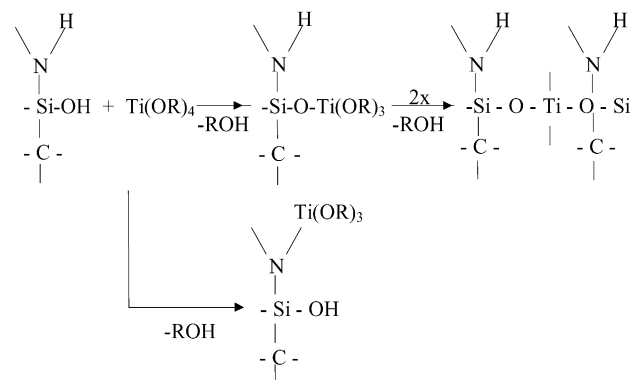


Fig. 1. Supposed reactions after pyrolysis at 1000 °C of SiCN matrix with titanium(IV)-diisopropylate.

Table 1
Molar volume changes of Al and Ti fillers upon reaction

Reactant	C(s)	C(g)	N ₂ (s)	O ₂ (g)
Al	9	53	26	28
Ti	-24	14	8	78

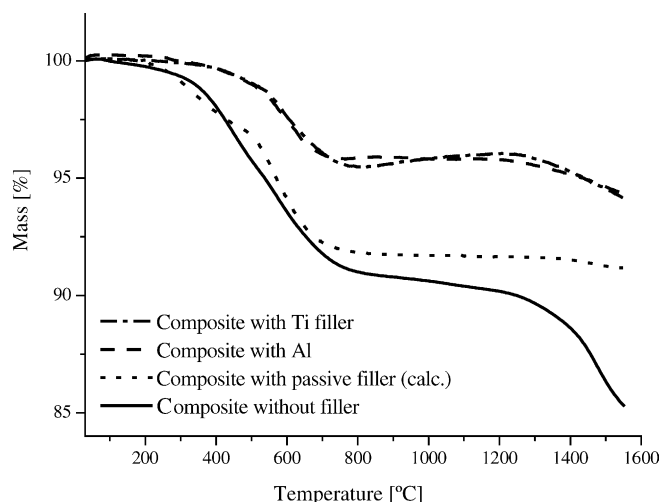


Fig. 2. TG analysis of CMC in nitrogen with and without fillers.

accomplished by incorporating filler particles into the matrix of the gussets. The placement of the filler particles mainly in the gussets was implemented due to the brushing of the plies after strewing.

The reactions of Al and Ti fillers embedded in Ceraset SN in N_2 atmosphere at different temperatures have been discussed earlier.⁷ Contrary to the expected nitrides and carbides, XRD analysis of the phase composition has shown only nitrides formation after annealing at 1550 °C for 4 h in N_2 atmosphere. In Fig. 2 the mass change of the polymer composites with and without filler loading are compared to each other. The mass loss of the composite with fillers could be diminished by more than 5% points at 1000 °C. The decrease in mass loss gets particularly pronounced at elevated temperatures (>1300 °C) when the matrix starts to decompose into SiC and Si_3N_4 and N_2 . The impact of lower mass loss decreases the shrinkage of the matrix, thus resulting in lower porosity and consequently fewer cracks. Unfortunately, the positive effect of active fillers on porosity was decreased by the bad RTM behaviour of the VL20 compared to Ceraset SN. After RTM processing, the plastic composites manufactured with VL20 showed higher open porosity, resulting in a higher porosity after the fifth PIP cycle (5.9 compared to 7.6, 10.0 and 10.9, Table 2).

Calculations based on TG analysis have shown that for the Al powder used, a 35% conversion to AlN was achieved at

Table 2
Mechanical properties of CMCs based on different fibres, after five PIP cycles

Fibre type	C-HTA	C-HTA	Tyranno SA	Tyranno SA (treated)
Filler	–	Ti	Ti	Ti
Porosity (%)	5.9	7.6	10.0	10.9
ILSS (MPa)	11.9	12.8	18.8	21.1
Flexural strength (MPa)	114	164	277	332
Tensile strength (MPa)	131	98.0	246	205
Young's modulus (MPa)	62600	72400	86500	89300

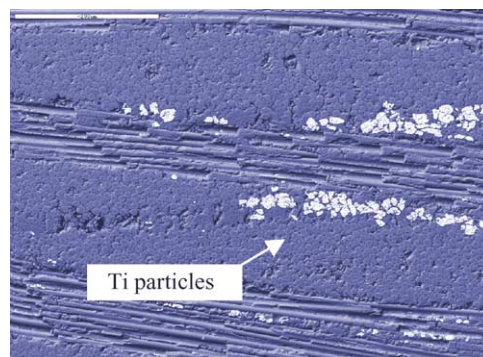


Fig. 3. SEM micrograph of overall microstructure of a CMC with Ti filler after five PIP cycles.

1000 °C. The conversion to TiN was calculated to 62%, respectively. However, even upon pyrolysis at 1550 °C a complete level of conversion could not be measured. This may be partially related to the fact that the active filler particles are covered with Ceraset SN or VL20, and therefore the nitridation reaction is more sluggish. The presence of gas species other than nitrogen, such as CH_4 , C_2H_4 and NH_3 in the reaction atmosphere, may also have a negative influence on the conversion of the active fillers to the expected amount of nitrides.

Fig. 3 shows an overview of the microstructure of a CMC with Ti filler. The Ti particles are well-embedded in the SiCN matrix, decreasing the overall porosity of the matrix. The gussets between the plies have been closed enabling a better load transfer. As observed in earlier manufactured CMCs with carbon fibres,⁵ the matrix in the fibre bundles is of a good shape, showing a relatively low porosity (Fig. 4). Small pores developed only in-between fibres. A possible explanation is bad wetting of the fibres during RTM. However, it is also possible that the matrix has just shrunk away from these regions. Also important is that matrices from distinct process cycles are distinguishable by intensity, which leads to the assumption of some interface between them. The existence of an interface was confirmed by TEM observations. As shown in Fig. 5 a crack propagates from the SiC fibre into the SiCN matrix along the boundary of distinct matrices, as-

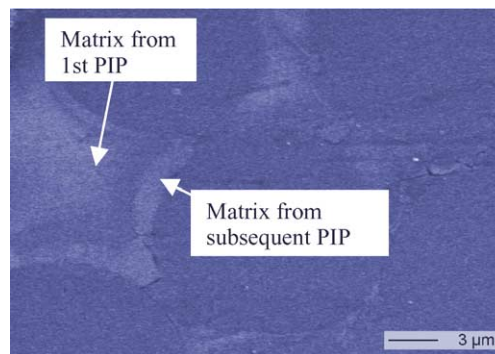


Fig. 4. SEM micrograph of a CMC with Ti filler after five PIP cycles showing different matrix regions between C fibres (dark).



Fig. 5. TEM micrograph showing two matrix regions in a CMC with Ti filler after five PIP cycles.

suming a weaker interface bonding between the two matrix regions.

3.2. Mechanical properties of CMCs

In short beam testing the samples failed in shear mode. In general the filler loaded CMCs show higher ILSS values even at higher porosity levels. ILSS of CMC with Ti filler stayed initially at the same level as the corresponding values of the CMC without filler, but the densification of the

CMC was more pronounced, even compared to the Al filled CMC. Due to the lower mismatch in coefficients of thermal expansion of SiC fibres and SiCN matrix, the CMC showed considerably higher mechanical properties (Table 2) comparable to CMC with carbon fibres, especially pronounced with regard to the flexural and tensile strength. The CMC immersed in titanium(IV)-diisopropylate solution encountered significantly higher mechanical values with respect to ILSS (+12%), flexural strength (+20%) and Young's modulus (+3%). A change in failure mode was also evident, from shear failure mode to delamination.

3.3. CMC after ageing in air

Finally, the CMCs were aged in air at 1100, 1200 and 1300 °C for 4 h, respectively. Thereafter, a formation of TiO₂ associated with a high increase in volume became apparent (Fig. 6a). The corresponding EDX-mappings (Fig. 6b–d) show the Si, Ti and O distribution after ageing. The TiO₂ formation is mainly due to the oxidation of unconverted Ti particles, but it could be also justified by oxidation of TiN.

To show the development in mechanical properties after oxidation under equal testing conditions, the flexural strength was calculated as a reference from the results of the short beam bend test. The calculated flexural strengths are of course considerably lower than the strengths measured with a span with/thickness ratio of 20. After ageing the failure mode changed from shear to tensile. As a consequence a smooth fracture surface was observed. The flexural strength, showed a decrease of nearly 50% in the cases of samples aged at 1100 and 1200 °C. After annealing at 1300 °C the strength level dropped to 34% (Fig. 7). The CMC, treated for bet-

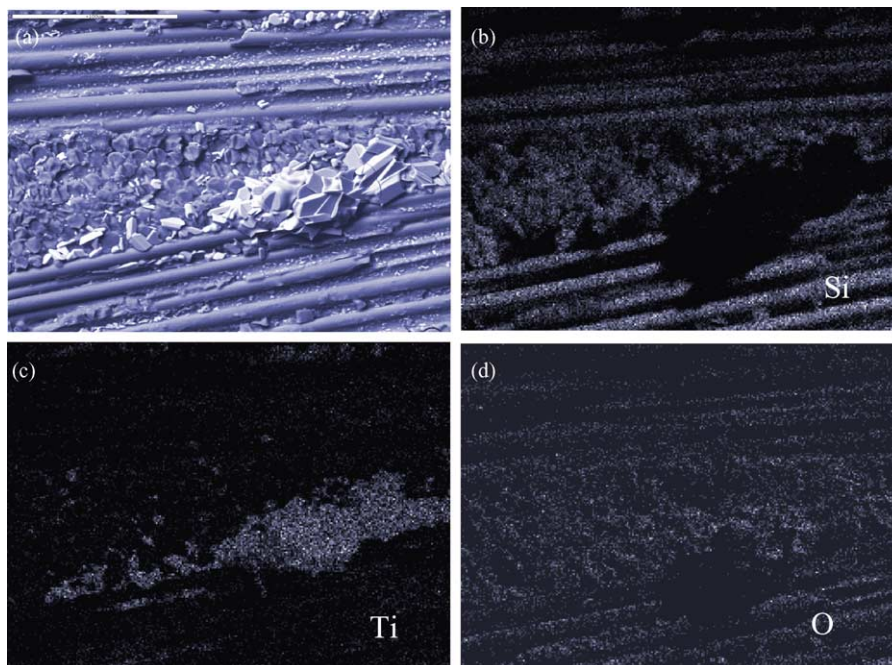


Fig. 6. SEM micrograph of CMC after ageing in air at 1300 °C with corresponding EDX maps.

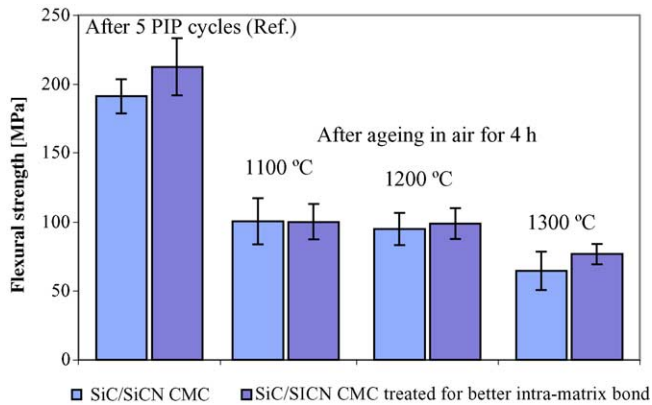


Fig. 7. Flexural strength of CMCs with Ti filler before and after oxidation (short beam test).

ter intra-matrix bonding, showed a constant flexural strength level after ageing at 1100 and 1200 °C. The flexural strength at 1300 °C was with 77 MPa considerably higher. The deterioration of flexural strength is caused mainly by the formation of an oxide layer in-between fibres and SiCN matrix leading to a strong fibre–matrix bonding with lower ability of crack deflection. Another reason is certainly the decrease of the fibre strength due to surface SiO₂ formation.

4. Summary

In order to improve the performance of CMCs processed via PIP, Al and Ti particles were studied as active fillers. As a result they were successfully incorporated in CMCs of different fibre type. Although the filler particles formed different types of nitrides, a complete conversion could not be

achieved. Due to the manufacturing process the filler particles were mainly located in the gussets of the CMC, thus leading to a more compact matrix. Based on the modified microstructure a considerable increase in mechanical properties could be observed. To strengthen the intra-matrix bond, CMCs were treated with titanium(IV)-diisopropylate before each reinfiltration step. As a result a considerable increase in ILSS and flexural strength was measured. Finally flexural strength values of CMCs aged in air at 1100, 1200 and 1300 °C were determined, respectively. The titanium(IV)-diisopropylate treated CMC showed a somewhat higher strength level.

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