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Spray winding, a novel one-step spray-technology to perform CMCs from preceramic polymers

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Abstract

A novel spray-technology to perform CMC tubes has been developed in order to establish an one-step process which enables shorter process times along with the saving of costs. The manufacturing route combines the textile fibre technique with both matrix polymer spraying and IR heated curing/pyrolysis which transfers the preceramic polymers into an inorganic amorphous Si–O–C matrix.

The applied metalorganic polymer as a commercial polysiloxane precursors which can be easily handled in air. The use of an organic solvent and WC-filler particles enables a low viscous suspension. Carbon fibres were wound onto a rotating tapered mandrel and simultaneously spray-coated with the polymer suspension, i.e. fibre winding and matrix spraying occurred at the same time to build up the CMC tube layer by layer. A heatable two flux nozzle is positioned perpendicular over the rotating mandrel and coats the surface continuously. An ellipsoid IR-mirror furnace which cures and pyrolyses the matrix (up to about 900 °C) was in 180° orientation displaced, focusing its radiation onto the surface. Rotation and traverse speed of the mandrel were computer controlled to facilitate a variability in fibre architecture. In a circular ring-test small winding angles leads to a maximum strength of 45 MPa. Because the shrinkage of the matrix polymer occur at a free surface only very limited strain hindrance arises.

Keywords: Spray winding; One-step process; CMC

1. Introduction

CMC materials are commonly processed by very elaborated but time-consuming techniques. Especially high potential composites derived from various silicon-based preceramic polymers are already in demand but their manufacturing processes are costly.

The manufacturing routes for producing CMC components may be classified as follows:[1,2]

- The first category is to use common powder techniques (powder + fibres, shaping, sintering or hot pressing) in combination with fibres. Because of sintering back stresses hindered densification; the microstructures and the resulting properties were not really satisfactory. Additionally the process cost is comparably high.
- Infiltration with liquid phases such as molten silicon have been used to produce ceramic matrices. Typical reactions are silicon carbide formation (Si + phenolic resins) or silicon nitride formation. The process technology is comparably easy and the materials can be made at a reasonable cost.
- Chemical vapour infiltration: As an advantage, the very volatile movable precursor can penetrate very small diameter porosity. The major problem of this process is a risk of oxidation, an outstandingly complicated technology, strict safety regulations (explosive and burnable gases) and very long infiltration cycles. This technology was only used for military application.
- In the last years, polymer precursor processes have been developed in which the matrix is produced from a preceramic polymer-based silicon in the main chain. Typical precursors are polysiloxanes, polysilazanes, polycarbosilazanes or even polyborocarbosilazanes. The problem with this route is the shrinkage of the polymer during pyrolysis

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which leads to stresses and the formation of cracks and pores.

All these methods are starting from a fibre fabric which is already shaped in a dimension close to that of the final product. The changes in the dimensions of the fibre network throughout the whole process are commonly less than half a percent. In contrast, the shrinkage of the matrix polymer is in the order of 10% and more. Consequently, all shrinkage of the matrix occurs in a strain hindered situation within a stable fibre environment which leads to stress formation, cracks and pore opening. Many of these infiltration processes had to be repeated several times in order to reach high density and strength.

In the manufacturing of polymer-based reinforced materials as well as metal matrix composites a coaxial fibre coating (dip coating, PVD, etc.) was used [3]. The fibres carry the matrix and can be further processed. This was tested for CMC as well but the strain hindrance again caused back stresses and crack/pore formation.

1.1. Previous work

The idea for this work based on experiments which have been gained from previous work done on spray coating of siloxane or silazane derived coatings (Si-O–C, Si–C–N).[4,5] The system used a ceramic precursors which were dissolved in an organic solvent. The target was to reach a viscosity sufficiently low enough for spray processes. A typical nozzle exhibits a one millimetre central guide for the feedstock which is surrounded by a half millimetre slit outlet for an atomisation gas. Either air or nitrogen at a pressure of two bars were used. Under these conditions spray droplets of a primary size varying from 2 to 10 μm could be produced which stayed in the liquid state until about 30 cm of diameter of distance from the nozzle. Similar to the formulation of a varnish two solvents with a different evaporation temperatures have been used, i.e. a part of the solvent evaporates during spraying. For longer distances the droplet lost more solvent and is solidified. Thus a working distance of approximately 25 cm enabled semi-dried droplets which then formed a continuous layer on a target. A good wetting behaviour between the solution and the surface was necessary. This required both the absence of moisture but also a certain polarity of the surface. This system was taken to temperatures of 800 °C and an entire pyrolysis occurred in which the side groups of the polymer chains were removed and a three dimensional network was formed (curing + pyrolysis).

2. Experimental

In this process, components showing a rotational symmetry were processed using continuous carbon fibres (M40B, 12000-50B, Toray Ind., Inc.) with a diameter of about 8 μm wound on a rotating ceramic mandrel (30 mm diameter). The reinforcement patterns varied between 0/90° and ±45° (fibre orientation) to obtain different mechanical and physical properties. A commercial methylphenylvinylhydrogen–polysiloxane (H62C, Wacker Chemie GmbH, Burghausen, Germany) in combination with cyclohexane and acetone as organic solvents performed a solution with a very low viscosity (about 1 mPa s). An optional pre-infiltration prior to winding enabled a better wetting behaviour. Hence, WC powder particles (PD24; VC, Cr_3C_2-doped; d_{50} = 1.2 μm; OMG Inc.) as ceramic fillers were added to the precursor solution in order to enable less shrinkage and a faster matrix formation [6]. The weight ratio of the precursor and filler was varied from 1:1 to 3:1. The solvent content in the suspension was between 40 and 60 wt.%. Ultrasonic treatment helped to disperse the powder within the precursor solution to achieve a suitable solution for the spraying process. This process was performed by a specially developed device using a twin fluid nozzle with compressed air. The position of the nozzle was perpendicular above the rotating mandrel (Fig. 1).

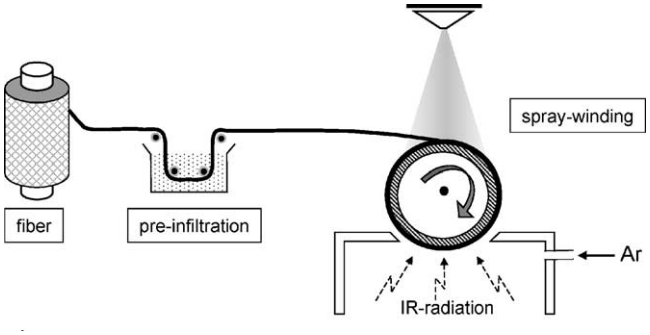

Fig. 1. Processing scheme of the spray-winding process to produce CMC tubes.

The thermal treatment/pyrolysis of the as sprayed precursor solution was performed with an IR-radiation oven (ellipsoidal polished aluminium mirror/halogen lamp with 1000 W; T_{max} = 1100 °C), flushed with Ar flowing gas. This heat stream was directed towards the arising composite (from bottom-up), reaching temperatures between 400 and 900 °C. An in situ matrix formation with the ceramic conversion of the precursor (or even partly) took place, reaching CMC tubes with a wall thickness up to 6 mm. Depending on the applied parameters during the winding process a further thermal treatment in a tube furnace (up to 1000 °C, Ar) could be necessary to run or even finish the pyrolysis.

The automation of the whole spray-fibre-winding process, using the LabVIEW-software (National Instruments Germany GmbH), gives the opportunity to control almost every parameter (mass flow, linear and rotating motion, temperature) [7]. The polysiloxane precursor, heat treated with the IR-radiation, was analysed by FTIR (ATR-technique, Equinox 55 spectrometer, Bruker Optik GmbH, Germany). The mass loss in consequence of gas evolution during the pyrolysis was monitored by TGA (STA 429, Netzsch GmbH, Germany). The final CMC tubes were cut in ring sections (1.5–3 cm

length), fractured in a spindle test machine (Z 005, Zwick GmbH, Germany). SEM characterisation was performed during the spray/infiltration process and after deflection during ring-test on fractured samples.

3. Results and discussion

3.1. Weight loss and shrinkage

The weight loss during pyrolysis of the matrix polymer is a major problem for CMC processing because of the resulting shrinkage.[4,6] Thus, a straight forward concept is to use additional fillers which are not prone to shape change.

The TGA curves in Fig. 2 show the diverse decomposition behaviour during pyrolysis of the silicon-oxycarbide matrix with various amounts of filler particles. The weight loss of the unloaded polymer precursor (28 wt.%) was reduced considerably (to 12 wt.%) by a maximum filler content of 50 wt.% in the suspension. In contrast to a conventional tube furnace heat treatment the pyrolysis took place via direct IR-radiation heating.

3.2. Pyrolysis

Fig. 3 shows the FTIR spectra of the polysiloxane precursor heat treated at different temperatures. Dominant vibrational modes of the Si–O–Si chain in the molecular configuration of the pure precursor can be observed at around 1090 cm^{-1}. Si–CH_3 bonds at 1260 and 766 cm^{-1}, aromatic phenyl groups with corresponding bonds at 1595, 1433 and 699 cm^{-1}, and several other typical binding oscillations of the side chains disappear at temperatures above 500 °C. After the pyrolysis only a broad asymmetric peak remained, which represents Si–O and alongside a second maximum due to Si–C vibrations (about 800 cm^{-1}). No significant differences to conventional heating could be observed.[4]

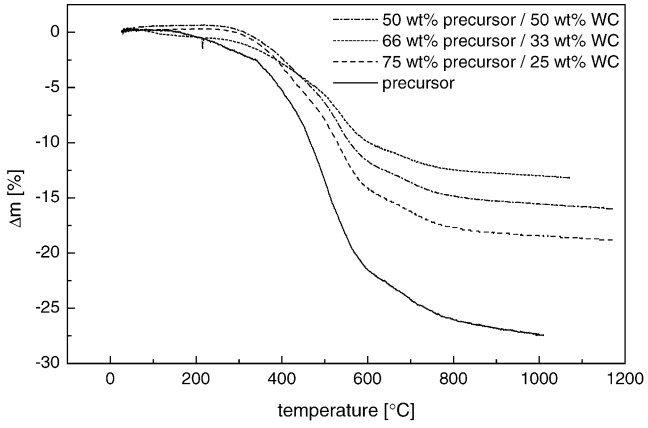

Fig. 2. Thermo-gravimetric analysis of matrix-materials with different filler content.

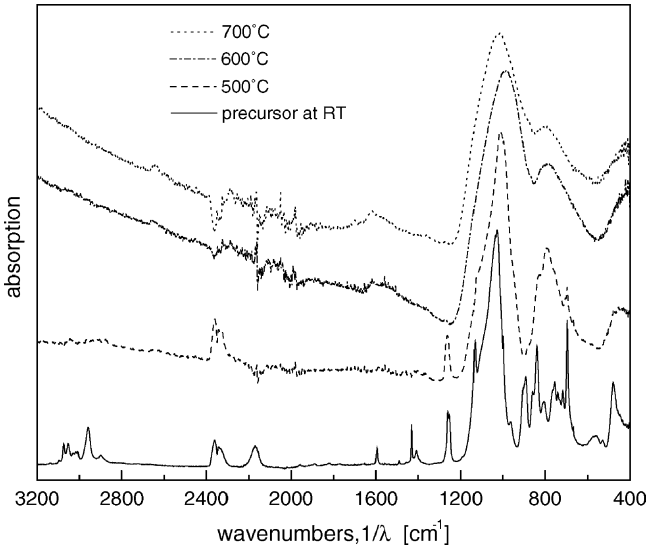

Fig. 3. ATR-infrared spectra of the heat-treated siloxane precursor using IR-mirror furnace.

3.3. Microstructural aspects

Various CMC tubes were performed by the spray-fibre-winding technique. From given requirements several parameters like roving width, winding angle, rotation and traverse speed of the mandrel and wall thickness had to be taken into account. Three tubes with different fibre architecture are depicted in Fig. 4.

Fig. 5 shows the polymer infiltrated multifilament fibre and the adjacent microstructure. As a basis step in this process, one has to consider the contact of a filler containing droplet with the surface of a multifilament fibre. The droplet will have lost a part of its solvent when contacting the surface. Provided the wetting angle of droplet to surface is sufficiently low, the droplet will adhere to that surface. Due to the fine interfilament porosity a capillary force is sucking the polymer solution into the fibre. The remaining filler-suspension will increase its content of solid which again reduces weight loss and shrinkage.

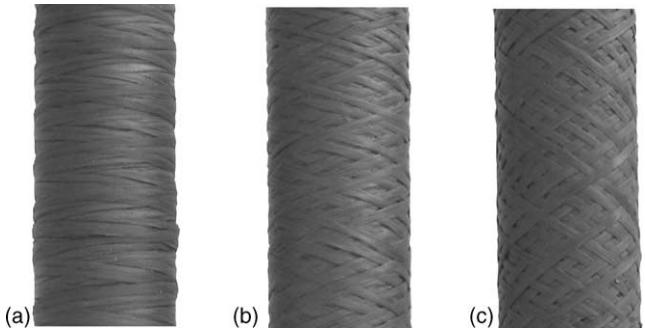

Fig. 4. CMC tubes with different patterns.

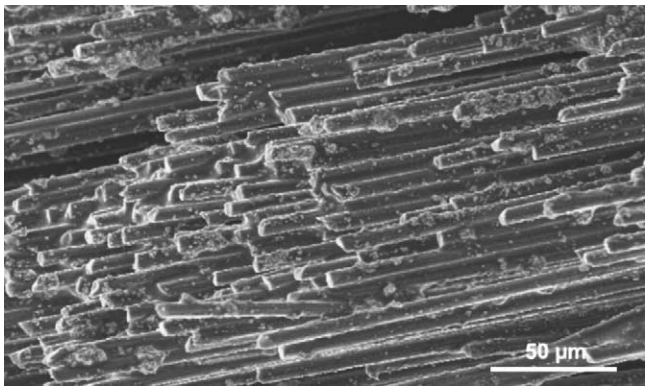

Fig. 5. Polymer infiltrated (plus WC filler particles) multifilament fibre.

3.4. Mechanical properties

For simple fracture strength tests the circular ring-test of tube sections which are loaded in plate-plate compression was used [8]. Due to the ring geometry, maximum tensile stresses occur at two locations, on the inner surface (at the load line) and on the outer surface (maximum distance from load line). The plotted load–displacement diagram (Fig. 6) shows the testing of carbon fibre reinforced CMC tubes with WC powder particles in a Si–O–C matrix. Three tubes with different fibre architectures (Fig. 4) were tested at room temperature. By changing the reinforcement pattern from an almost parallel fibre orientation to a 45° winding angle, the calculated strength of about 45 MPa as tensile toughness decreases to half the value.

The mechanical behaviour of the wound CMC tubes during the ring-test is mainly related to the damage state of the as-processed matrix material. The almost parallel fibre geometry (Fig. 4a) performed best in this test. However, for other load directions (tension parallel to the length axis of the rod) or even for multi-axial loading conditions quite different results may be expected.

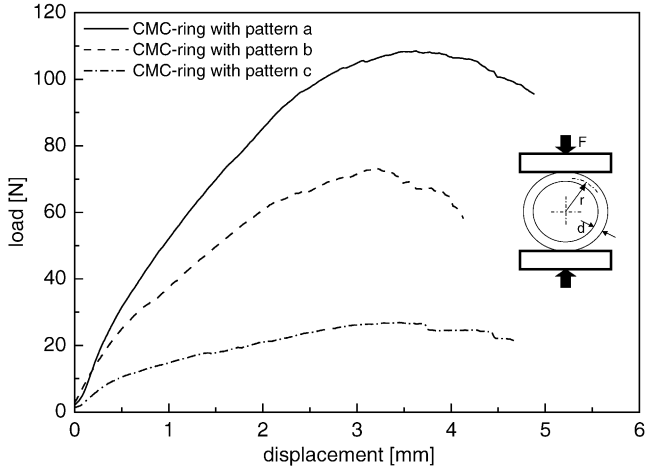

Fig. 6. Load–displacement diagram of the circular ring-test.

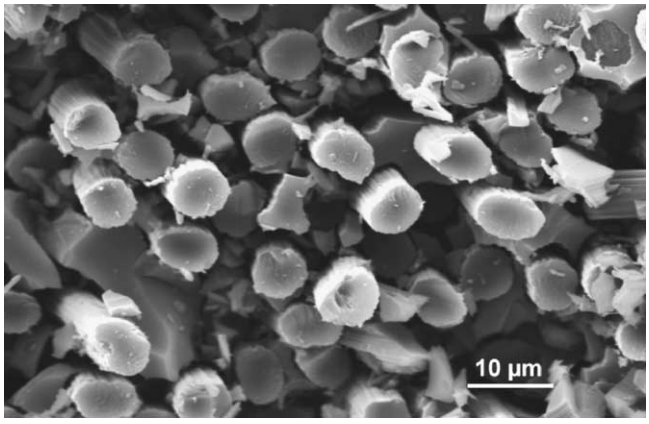

Fig. 7. Microstructure of CMC ring section after ring-test.

A fractured sample (cross section) after the ring-test with a rough surface is shown in Fig. 7. For these mechanical testing no further treatment of the fibre surface or a controlled bonding between fibre and matrix was applied. Nevertheless a certain amount of fibre pull out was observed. For the future, detailed studies including defined fibre matrix interfaces are needed.

4. Conclusions

This manufacturing concept to integrate fibre winding, matrix polymer spraying and curing pyrolysis by IR heating was basically successful. The great advantage of the process is the integration of three processing steps.

Critical points in this process are interlinking of various process parameters. Thus, the setting of the winding velocity is not independent from the heating during pyrolysis, etc. Hence, a lower rotation and/or traverse speed enable a longer exposure time at operating temperature but it also change the ratio from fibre to matrix.

The interaction between these major process parameters will be investigated.

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