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Development of wound $SiC_{BNx/SiNx}$/SiC with near stoichiometric SiC matrix via LSI process

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ABSTRACT

In order to develop SiC/SiC ceramic matrix composites with a low porosity, liquid silicon infiltration (LSI) was chosen as a technique, characterized by short processing times. To create the matrix, a tailored phenolic resin containing ß-naphthol units was synthesized and infiltrated in wound fiber preforms, thermally cured, pyrolysed and siliconized. The aim is to obtain a high carbon yield during pyrolysis and to create a dense carbon foam between the SiC fibers. Instead of a classic liquid silicon infiltration via capillary forces through a carbon block-like microstructure, this foam promotes a softer infiltration with less fiber degradation and a maximized carbon conversion to near stoichiometric SiC. To protect the SiC fibers from an attack of the liquid silicon and to simultaneously provide a weak fiber matrix bonding, a BN_x/SiN_x fiber coating was chosen. The coating was applied by means of low-pressure chemical vapor deposition (LPCVD) using gaseous chlorine free precursors.

1. Introduction

To obtain SiC/SiC composites, liquid silicon infiltration process [1,2] has been chosen. It is a three-stage process, beginning with the infiltration of a SiC fiber-preform with a resin (Fig. 1, step I). Resin transfer molding (RTM) was used as a production technique, allowing a homogeneous infiltration of resins and controlling temperature and pressure during the curing process, which results in a dense SiC fiber-reinforced polymer (SiCFRP). An additional pyrolysis step transforms the polymer matrix to carbon with a porous structure, creating a SiC fiber-reinforced carbon (SiC/C) (Fig. 1, step II). The final step of the process is the infiltration of liquid silicon into the pores. This is achieved by capillary forces and results in the conversion of the carbon matrix to a SiC matrix in an exothermic reaction (SiC/SiC).

Previous research has shown that a single coating layer of SiN_x on SiC fibers is resistant against liquid silicon but did not provide damage tolerant crack behavior. The phenolic resin utilized was also unsuitable, as it shrinks to form dense carbon blocks during pyrolysis and long hollow channels along the fibers [3–5]. These channels were filled with large amounts of silicon, which was found to be fairly aggressive to the coating. The carbon blocks were not infiltrated with liquid silicon to form SiC. Thus, C and Si remain in the composite which might be disadvantageous at application conditions. In order to improve the carbon conversion and to decrease the amount of free silicon, a novel resin was developed (Fig. 1, step 0″) that has shown to create a carbon-foam in composites with uncoated SiC fibers during processing, rather than carbon blocks. Furthermore, to create composites with damage tolerant crack behavior, a novel double coating technique was utilized. The inner layer consisted of BN_x and the outer layer is comprised of SiN_x (Fig. 1, step 0′). The SiN_x layer serves as a protective coating against liquid silicon [6], while the inner BN_x layer creates a weak interface, which is needed in SiC/SiC composites to provide energy dissipating effects like crack deflection, crack bridging and fiber pull-out to create a pseudo-ductile and therefore damage tolerant composite [7].

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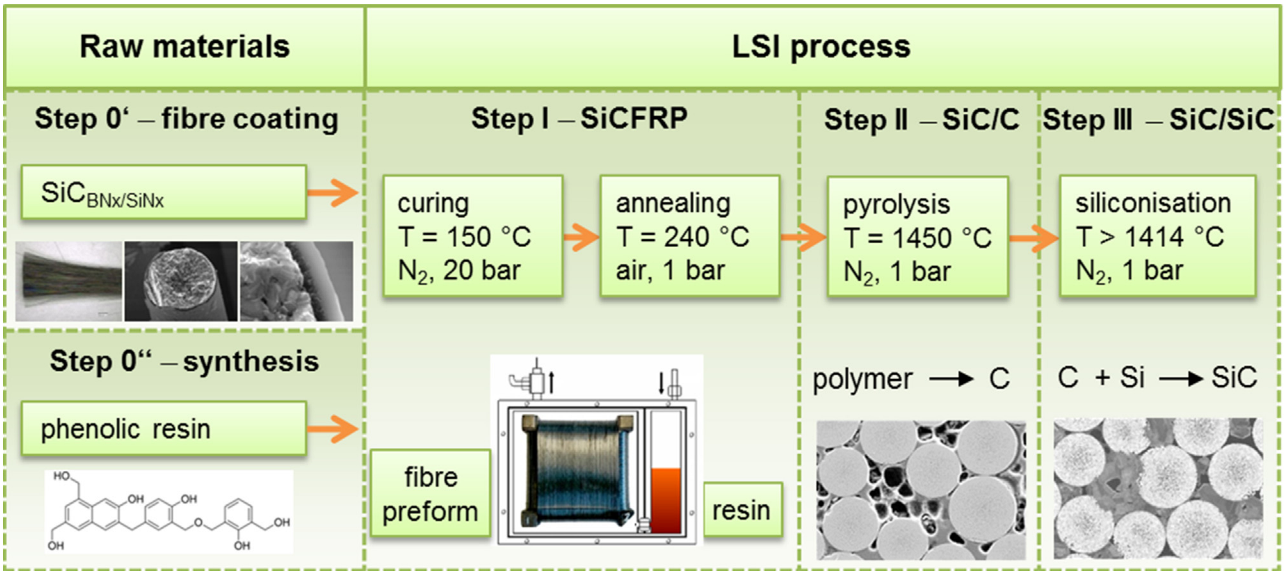

Fig. 1. Scheme of the LSI process.

2. Experimental procedure

2.1. Development of BN$_x$/SiN$_x$ fiber coating (Step 0′)

The commercial SiC fiber Tyranno SA3 from UBE Industries was used for coating experiments. The yarn consists of 1600 single filaments with a diameter of 7.5 µm [8]. The coating was applied by means of low-pressure chemical vapor deposition (LPCVD). The process was carried out discontinuously in a horizontal tubular hot-wall reactor of the laboratory system TCVD 100 LAB from FHR Anlagenbau. For the coating process the CVD system was evacuated. The reactor was heated until the processing temperature was achieved. Simultaneously, the gas supply system and the reactor were purged with nitrogen. During this step, the fibers were desized in-situ. The BN$_x$ coating took place at a temperature of 975°C. The gaseous precursors diborane (B_2H_6) diluted in 95 vol% hydrogen (H_2) and ammonia (NH_3) were introduced to the reactor with a constant flow rate of 100 and 150 sccm. The mixing ratio of NH_3/B_2H_6 was 30:1. The pressure was set to 3 mbar using a butterfly valve. The coating time was 60 min. For the SiN$_x$ coating a temperature of 800 °C was used. Furthermore, the flow rate for the deposition was set to 12.5 sccm silane (SiH_4) and 125 sccm ammonia (NH_3) and a pressure of 1 mbar was also adjusted. All in all the SiN$_x$ coating took 30 min. After the coating process the gas supply system and the reactor were purged with nitrogen again and the reactor cooled down.

The coated fibers were subjected to a high-temperature heat treatment in order to examine the stability of the films under the processing conditions of the LSI process. The fibers were treated in a furnace (Ing.Büro Vakuumtechnik, Anl.Nr. 9055) at a temperature of 1450 °C in nitrogen for 30 min.

2.2. Synthesis of the R2 phenolic resin (Step 0″)

The phenol-β-naphthol-formaldehyde resol R2 was synthesized according to the procedure as described in the literature [3]. For the synthesis, 100.0 g (1.06 mol) phenol, 76.6 g (0.53 mol) β-naphthol, 237 ml formalin (37 wt%; 3.18 mol) and a 3 M aqueous sodium hydroxide solution (8.9 g; 0.22 mol) as catalyst were used. The obtained phenol-β-naphthol-formaldehyde resol R2 (263.2 g) is a red liquid at room temperature (RT). It reaches its minimum viscosity of 0.31 Pa·s at 102 °C and the self-curing begins at approximately 110 °C, which was determined with differential scanning calorimetry and rheology measurement [3]. For a better understanding of the mechanisms during the different steps of the LSI process within the fiber-reinforced composites, pure specimens of the R2 resin were investigated under the processing conditions.

2.3. CMC manufacturing with coated fibers and R2 phenolic resin (Step I–III)

A flat graphite mandrel was manufactured to provide a fiber preform. A total of eight cross-ply layers with an orientation of 0/90° of uncoated Tyranno SA3 fibers were wound on the mandrel (Fig. 2). Between the fourth and fifth layers a BN$_x$/SiN$_x$-coated SA3 roving was manually integrated. After being wound, the mandrel was infiltrated with the R2 resin at the temperature of minimum viscosity by means of resin transfer molding. After being fully infiltrated, the curing process was realized at a temperature of 150 °C and a pressure of 20 bar in a nitrogen atmosphere. The infiltrated preform was cut, leading to two long fiber-reinforced plates with the size of $60 \times 60 \times 2\,mm^3$ and a fiber volume content of 47%. Afterwards, the plates were annealed in an ambient atmosphere at 240 °C, resulting in the creation of a silicon carbide fiber reinforced polymer (SiCFRP).

The SiCFRP was pyrolysed at 1450 °C in a nitrogen atmosphere and a pressure of 1 bar to convert the polymer matrix to a carbon matrix. This was followed by a silicon infiltration at a temperature just above the melting point of silicon at 1415 °C and the same pressure and atmospheric conditions. The silicon was infiltrated in the plates from above by means of gravity. The same furnace (Ing.Büro Vakuumtechnik, Anl.Nr. 9055) was used for the pyrolysis and for the infiltration.

2.4. Characterization methods

2.4.1. NMR

The carbon nuclear magnetic resonance spectroscopy measurement (liquid ^{13}C NMR) was performed with a Bruker Avance 250 MHz spectrometer. Deuterated acetone-d$_6$ (C_3D_6O) was used as a solvent for the uncured R2. The samples were referred to the solvent (C_3D_6O $\delta = 2.05$ ppm).

For the solid state carbon cross polarization magic angle spinning measurement (^{13}C CPMAS) of cured R2 a Bruker