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Al–O–N and Al–O–B–N thin films applied on Si–O–C fibers

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ABSTRACT

Protective coatings (Al–O–N and Al–O–B–N) on Si–O–C fibers (Tyranno ZMI) were applied in order to enhance oxidation resistance under severe thermo-mechanical conditions in the 400–600 °C temperature range. The coating process consisted in three steps: (i) the transformation of the Si–O–C fiber surface into microporous carbon; (ii) the impregnation of these carbon microporous layers by an aluminium trichloride ($AlCl_3$) solution and then, (iii) a final heat treatment under ammonia. Processing parameters were studied in order to select the best conditions. Using these conditions, obtained results have shown that coatings were present around each fiber, with a controlled thickness, and that the mechanical properties of the fibers were preserved. Although, these coatings did not entirely stop the oxygen ingress, it has been shown that they strongly reduced the oxidation of the fiber.

1. Introduction

New environmental rules as well as economical competition have constrained the aeronautic industry to develop new products with low structural weight and ceramized engines in order to reduce NO_x and CO_2 emissions. This is the result of a better combustion and enables also a reduction of aircraft noise.

In order to reach these objectives ceramic–matrix composites (CMC) have been selected since they display excellent thermo-mechanical properties as well as low densities [1].

The aim of the present study was focused on developing low cost raw materials and processes in order to be competitive on the civil aeronautic market. Low cost ceramic fibers such as Tyranno ZMI fibers were therefore selected [2]. When used in an oxidizing environment at elevated temperature, it has been shown that the use of a self healing matrix usually provides an accurate protection of the CMCs against oxidation [3]. However, when moderate temperatures are considered, self healing matrices have proved to be not so efficient. Hence, when CMCs exhibit matrix cracks, these cracks are not entirely healed because of the low rate of formation of the oxide. Further oxygen diffuses into the fibers, leading therefore to a catastrophic failure of the CMC [4]. In order to prevent any propagation of the oxygen up to the fibers, and therefore to enhance the lifetime of these materials, it has been decided to set up a protective oxidation barrier on the surface of the Si–O–C fibers. This layer should posses all the following distinct features: to provide an individual and uniform coating around the fibers, while avoiding bonding between them; to prevent any oxygen diffusion to the fibers; to be stable during the processing of the matrix and of the interphase; to present a good adhesion with both the fibers and the interphase; and to preserve the mechanical properties of the fibers.

Different materials may be considered regarding these expected properties: refractory oxides such as ZrO_2 or Al_2O_3 [5,6]; silicon based ceramics such as Si–B–C–N, Si–C–N [7,8] or Si–Al–C–N [9–11], monazite [12–15], BN [16–21] and $LaAlO_x$ [22–26].

Two new materials were selected for the present work: Al–O–N and Al–O–B–N [27–30]. As a matter of fact, the aluminium as an element exhibits a low density as well as a stable oxide (Al_2O_3). Besides, most nitrides have attractive refractory properties. Boron was also selected as an adequate element because of an important property of all boron containing species which is to form fluid oxide phases (B_2O_3) over a broad temperature range (600–1200 °C) in an oxidizing atmosphere. The Al–O–N–B material could thus be used to design self-healing composites with improved lifetimes. It bases on the in situ formation of the fluid oxide, which fills the matrix cracks and slows down the in-depth diffusion of oxygen [3,31].

2. Experimental procedure

2.1. Thin coatings deposition

As already mentioned, Tyranno ZMI Si–O–C fibers (from UBE Industry, Japan), were used for this study. The microstructure of this first generation of Si–O–C fibers is composed of β-SiC crystallites (2 nm), free carbon and a Si–O–C phase resulting from the precursor reticulation step [32]. The chemical composition of these fibers (Si 37.7 at.%, C 53.4 at.%, O 8.8 at.% and Zr 0.1 at.%) has been determined using an electron probe microanalyser (SX 100 from CAMECA). The average fiber diameter is 13 μm.

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In order to promote an adequate adhesion between the Al–O–N or Al–O–N–B thin coatings and the fiber surface, microporous carbon layers with a controlled thickness were first produced, using a thermochemical treatment around 600 °C with chlorine gas [33]. This specific treatment leads to an extraction of Si from SiC by chlorine at the fiber surface, according to the following reaction 1 [34]: $SiC_{(s)} + 2\ Cl_{2(g)} = SiCl_{4(g)} + C_{(s)}$. The microporous carbon thus obtained was found to possess a specific surface area, calculated using the Brunauer–Emmet–Teller equation, of 994 m^2/g. Most of the pores size (>91%) are smaller than 2 nm and the pore volume measures 0.45 cm^3/g (these values were calculated using the semi-empirical Horvath and Kawazoe approach). After this heat treatment, fibers were impregnated with an anhydrous aluminium trichloride ($AlCl_3$) solution.

Only one impregnation was performed during 15 min, at ambient temperature, using a batch process. The samples were then heated up to about 120 °C in order to evaporate the solvent, and a thermal treatment in an ammonia atmosphere during 60 min, at a constant flow rate of 20 sccm and at various temperatures (900, 950 and 1000 °C), was finally performed.

In the case of the Al–O–B–N thin coatings, the fiber preforms were impregnated with boron acid prior to the impregnation with an aluminium trichloride solution. A heat treatment at 1150 °C during one hour was then performed under an ammonia flow.

Three different types of composite materials were produced and tested: composites C1 only made with a pyrocarbon interface and a SiC matrix, considered as the reference material; composites C2 made with Al–O–N thin coatings and a SiC matrix; and composites C3 made with a pyrocarbon interface, an Al–O–N thin coating and a SiC matrix.

2.2. Thin coatings characterization

Both structural, chemical and mechanical characterizations were performed for each kind of coating.

The cross-section morphology was investigated with the aid of a high resolution Scanning Electron Microscopy (SEM, Hitachi S4500). Coating thicknesses as well as the quality of their adhesion to the fibers were studied by the observation of the fracture surfaces. Microstructural characterizations of the various coatings were performed with a Philips CM30ST (LaB_6, 300 kV) Transmission Electron Microscope (TEM). The chemical composition and thicknesses of the coatings were evaluated using an Auger Electron Spectroscopy (VG Microlab 310 F) coupled with an argon sputter device. The analysis of the atomic content of each element was determined in the depth profile mode.

Room temperature fiber strength was determined by tensile tests performed on single fibers according to a procedure describe in [35]. These tests were performed on twenty fibers for each sample, with a gauge length of twenty-five millimetres. Each fiber extracted from a tow was fixed on paper frame holders using a hard acrylic resin. Ultimate tensile strength (σ_r, in GPa), strain to rupture (ε_r, in%) and Young's modulus (E, in GPa) of the Si–O–C fibers were derived from these tests. Mechanical tests on single ply (2D fiber weaves) with a SiC matrix were also performed.

Static oxidation tests were performed at 600 °C in air during 7000 h. Silica thicknesses developed at the surface of the fibers were determined by SEM after a few weeks.

3. Results and discussion

Various processing parameters related to the impregnation and the nitridation have been studied.

3.1. The impregnation process

As mentioned before, aluminium compounds were deposited at the fiber surface through the impregnation by an aluminium trichloride solution ($AlCl_3$) of microporous carbon first created at the ZMI fiber surface by chlorination [27,28,36,37]. In this respect, in two fluids were tried to solve the $AlCl_3$ powder, namely water and ether.

Although water proved to be a good solvent for hydrated $AlCl_3$ powder, this solution yet caused an important introduction of oxygen into the coating. Conversely, ether also proved to be a good solvent when using anhydrous $AlCl_3$ powder, and consequently forms a coating with a lower oxygen content. Ether was therefore preferred to impregnate the aluminium trichloride solution.

In a first attempt to impregnate a maximum of aluminium compounds into the microporous carbon, a saturated aluminium trichloride solution was realised. Yet, the high viscosity of this solution did not easily allow the impregnation of the fiber preforms by the aluminium compounds, as illustrated by the high resolution SEM image exhibited in Fig. 1. This which shows that thin coatings at the fiber surface were not homogeneous, with an excess of matter deposited at the fiber surface. It was therefore then decided to use only thin coatings requiring a lower concentration of aluminium trichloride solution. As expected, a homogeneous microstructure could thus be obtained (Fig. 2a) in which no bridge between Si–O–C fibers could be evidenced (Fig. 2b). These amorphous coatings, which formed an individual and uniform coverage around each fiber, could thus be expected to efficiently protect the fiber surfaces.

3.2. The nitridation process

Nitridations were performed on samples previously impregnated with $AlCl_3$ solutions at 900 °C following the method described by Chen et al. [27,36,37], and then extended at 950 °C and 1000 °C.

The samples thus obtained were also analysed by Auger Electron Spectroscopy. Results, shown in Fig. 3, confirm that the impregnation of the aluminium compounds into the microporous carbon network was quite successful. However, the chemical compositions presented in Tables 1 and 2 reveal that although all silicon compounds should have been consumed (after reaction (1)), it was yet possible to observe the presence of this element but in low amounts (Fig. 3).

Variations in the concentration of the chemical elements (Al, N, O, B and C) present in the coatings were observed according to the

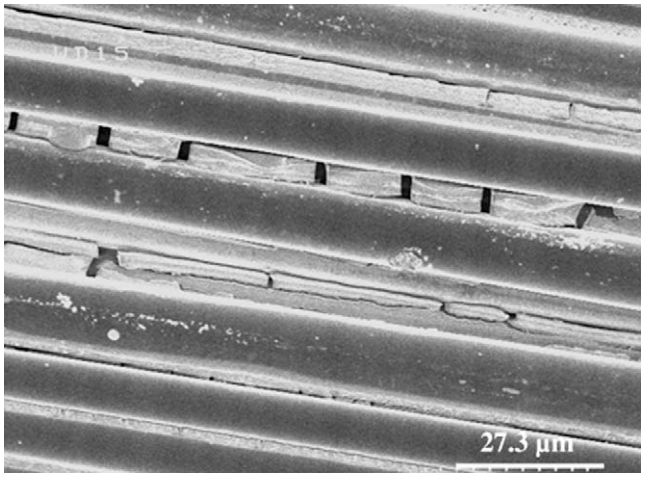

Fig. 1. High resolution SEM image of thin coatings at the fiber surface with a saturation concentration of aluminium trichloride solution (4.3 M).