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Ceramics International 34 (2008) 1297–1301
CERAMICS INTERNATIONAL
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Protective coatings for carbon bonded carbon fibre composites

F. Smeacetto [a], M. Ferraris [a], M. Salvo [a], S.D. Ellacott [b], A. Ahmed [c], R.D. Rawlings [c], A.R. Boccaccini [c,*]

[a] *Materials Science and Chemical Engineering Department, Politecnico di Torino, Torino, Italy*
[b] *Calcarb Ltd., Bellshill ML4 1EN, UK*
[c] *Department of Materials, Imperial College, London SW7 2BP, UK*

Received 12 October 2006; received in revised form 30 January 2007; accepted 14 March 2007
Available online 13 April 2007

Abstract

Carbon bonded carbon fibre composites (CBCF) were modified by direct reaction with molten silicon in order to obtain a silicon carbide layer on the composite surface. Subsequently, the Si-infiltrated CBCF material was coated with a silica-based glass containing yttria and alumina by means of a slurry-dipping technique. On heat treatment the glass yielded a glass-ceramic layer thus giving a multi-layered oxidation and erosion protection system. The microstructural characterisation of the coating was conducted by standard microscopy techniques and by X-ray diffraction. The controlled crystallization of the glass-produced cristobalite, yttrium silicate ($Y_2Si_2O_7$, keiviite, β-form) and mullite as main crystalline phases. These are excellent ceramic materials for oxidation and erosion protection of SiC-coated carbon-based composites since their coefficients of thermal expansion (CTE) closely match that of SiC. The possibility of healing (closure) of micro cracks by a thermal treatment at 1375 °C, thus exploiting the viscous flow of the residual glass in the glass-ceramic, was explored in order to extend the service life of the protection system.

Keywords: D. Glass ceramics; Carbon matrix composites; Oxidation protection; Slurry infiltration

1. Introduction

Carbon bonded carbon fibre (CBCF) composites are a special class of low density, highly porous carbon–carbon composites [1]. They are utilized as thermal insulation in vacuum and inert gas furnaces involving inert gas cooling, at temperatures up to 2800 °C. There are mainly two problems related to the use of CBCF: the erosion due to the particles carried by the cooling gas and the poor oxidation resistance typical of carbon-based composites.

Investigations into the microstructure [1,2] and mechanical properties [3,4] of these materials have been reported. CBCF composites consist of a carbon fibre network bonded together at the intersections of the fibres by discrete regions of carbon matrix; the vast majority of the volume (70–90%) consists of interconnected pores. A consequence of the vacuum moulding process used in the composite production is that the carbon fibres are oriented into layers to form a two-dimensional planar random structure which imparts anisotropy to the properties (Fig. 1a) [3–5].

Due to the poor oxidation and erosion resistance of CBCF composites, there has been strong interest in developing protective ceramic coatings for these materials [6,7]. The oxidation of these composites at temperature above 500 °C limits their use to inert atmospheres and vacuum. The inherent reactivity in oxidizing environments makes it necessary to design a complex system of inhibitors or sealants and coatings to provide reliable oxidation and erosion resistance at high temperatures.

This paper presents the results of a preliminary study on the modification of CBCF composites to provide erosion and oxidation protection by developing a multi-layered system involving a glass-ceramic coating.

2. Experimental

The CBCF composite used as the substrate was a standard commercial material (density 0.18 mg m^{-3}), manufactured by Calcarb Ltd. (UK). A schematic diagram showing the 2D-oriented structure of the material is presented in Fig. 1a, while a

* Corresponding author.
E-mail address: a.boccaccini@imperial.ac.uk (A.R. Boccaccini).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.03.012

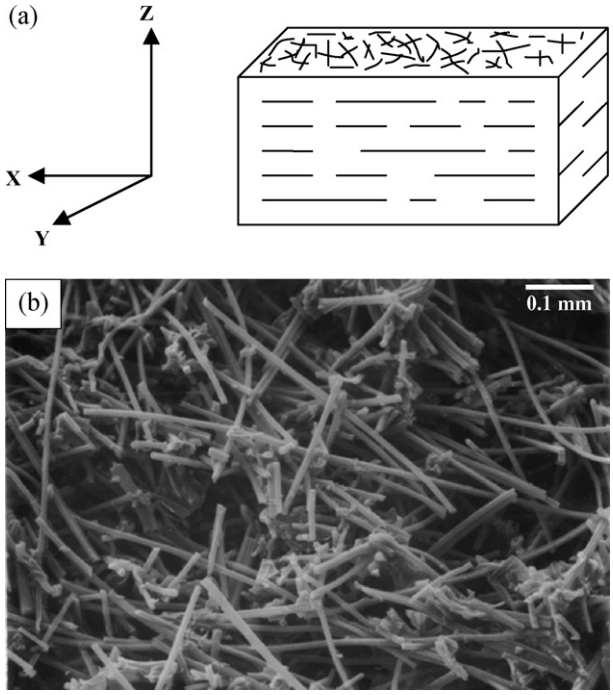

Fig. 1. (a) Schematic representation of CBCF composite [1]; (b) SEM micrograph of a CBCF sample (*xy* plane).

scanning electron microscopy (SEM) image of a sample in the plane of orientation of fibres (*xy* plane) is shown in Fig. 1b. This plane is perpendicular to the direction of minimum thermal conductivity and hence it is the exposed surface of the insulation in a furnace. Therefore the modification of the surface was performed on the *xy* plane of CBCF samples.

As reported in Ref [8], the wettability of glasses on carbon–carbon composites can be largely enhanced by the formation of a silicon carbide layer on the composite surface. Therefore a two-step coating process was followed in the present study, a first coating by SiC and a subsequent coating by the glass-ceramic layer.

The initial surface modification of the CBCF material was obtained using a tubular oven to produce SiC by direct chemical reaction between infiltrated silicon from a silicon slurry (Si dispersion in either, ethanol or polyvinyl alcohol, as discussed below) and the composite at a temperature (1450 °C) above the silicon melting point under a low argon flow. In order to examine the depth of penetration of silicon and the reacted product (silicon carbide) into the porous CBCF sample, SEM observations and energy-dispersive spectroscopy (EDS) measurements were performed on cross-sections of the modified CBCF material.

The glass chosen as the precursor for the glass-ceramic coating was based on SiO_2, Al_2O_3 and Y_2O_3 (designated SAY glass). The SAY composition was: SiO_2 54 wt.%, Al_2O_3 18.07 wt.%, Y_2O_3 27.93 wt.% (SiO_2 74.92 mol%, Al_2O_3 14.77 mol%, Y_2O_3 10.31 mol%). The thermal expansion coefficient of this glass, as calculated by SciGlass^{TM} software, is $3.4 \times 10^{-6}\,C^{-1}$. The glass was produced by melting the appropriate oxides. The starting oxides were purchased from Sigma Aldrich. The raw materials in powder form were mixed together in a platinum–rhodium crucible and heated for 5 h at 1700 °C in air. The melt was cast on a metal plate and the transparent glass was ground to a fine powder. Preliminary experiments were carried out on this powder to study the crystallization behaviour and the structure of the resulting glass-ceramic. Differential thermal analysis (DTA, Perkin Elmer DTA7) and hot stage microscopy experiments (Leitz GmbHAII) were used to obtain the crystallization temperature. The crystalline phases present in the glass-ceramic material after heat treatment were determined by X-ray diffraction (XRD) analysis.

A glass layer was subsequently deposited on the surface modified CBCF composites. The layer was deposited by slurry-dipping method. The slurry was made of a mixture of glass powder (mean size 50 μm) dispersed in ethanol (solid content 40 wt.%). The coated samples were heated in a tubular oven at 1375 °C for 20 min and at 1235 °C for 1 h under argon atmosphere at 40 mbar. After heat treatment selected samples were characterised by SEM, XRD and a simple qualitative pulling test was carried out for determination of the adhesion between coating and substrate.

3. Results and discussion

3.1. SiC layer

The first surface modification treatment of the CBCF material was carried out by direct reaction of a silicon ethanol-based slurry with the fibrous carbon substrate by heating the infiltrated CBCF material at 1450 °C for 20 min in argon atmosphere. Fig. 2 shows an optical micrograph of the formed layer; where silicon carbide crystals (β-SiC) can be observed embedded in a large amount of residual free silicon. This crystalline structure of the layer was confirmed by the XRD analysis conducted on the CBCF surface as shown in Fig. 3 (curve (a)).

In order to reduce the amount of free silicon, CBCF samples coated with silicon were subsequently heat treated at 1500 °C for 1 h in argon atmosphere. As can be observed from curve (b) in Fig. 3, the amount of residual silicon was drastically reduced.

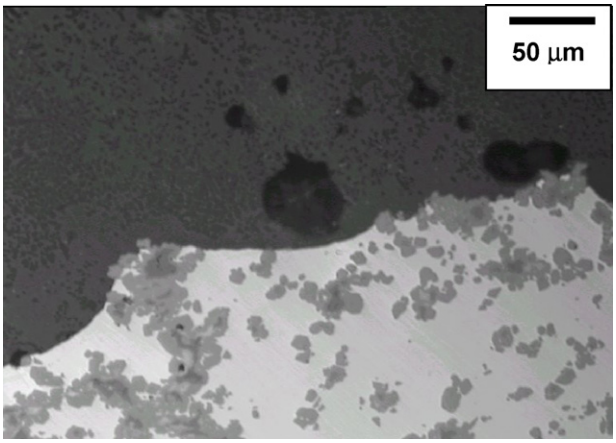

Fig. 2. Silicon carbide (β-SiC) crystals embedded in residual silicon on the surface modified CBCF material (slurry of Si in ethanol was used).

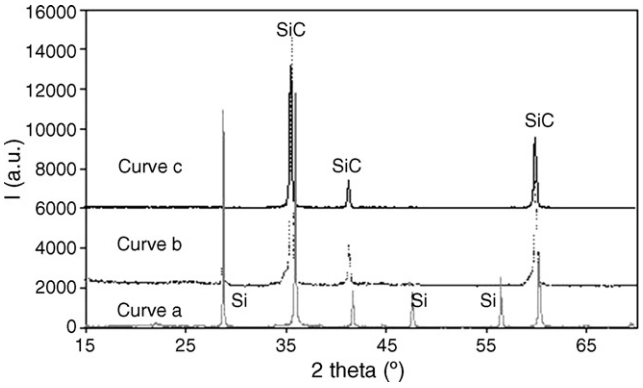

Fig. 3. XRD measurements on CBCF + Si obtained under different conditions: (a) 1450 °C, 20 min (ethanol slurry); (b) 1500 °C, 1 h (ethanol slurry); (c) 1500 °C, 2 h (polyvinyl alcohol slurry).

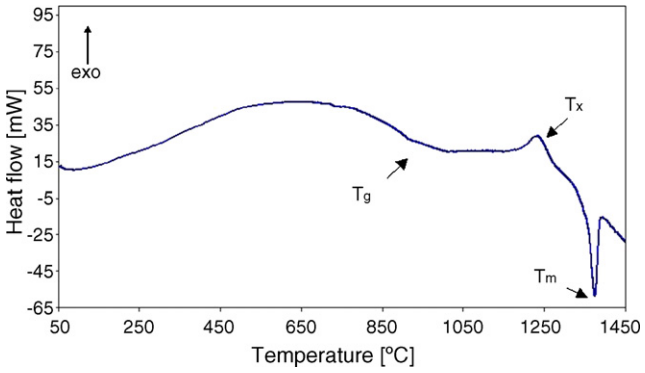

Fig. 4. DTA analysis of the SAY glass, showing T_g (910 °C), T_m (1375 °C) and T_x (1235 °C).

Since the CBCF material has a large porosity (about 80%), the ethanol used as dispersant for the silicon powder effectively infiltrated the CBCF substrates during deposition. This rapid infiltration has the disadvantage, however, of making difficult the control of the homogeneity and the thickness of the deposited silicon layer.

Polyvinyl alcohol was therefore used as a dispersant instead of ethanol; polyvinyl alcohol acts as a 'glue' which bonds together the silicon particles, enabling a slower and more homogeneous infiltration of the porous fibre network leading to better control of the process. CBCF samples coated with silicon using the polyvinyl alcohol slurry were heat treated at 1500 °C for 2 h in argon atmosphere. As can be observed from curve (c) in Fig. 3, no free silicon was detected by XRD analysis on the modified CBCF surface.

EDS measurements conducted on the cross-sections of CBCF samples infiltrated with silicon revealed a penetration depth of silicon carbide into the CBCF structure of about 500–600 μm which is unnecessarily thick; it should be possible to optimise the process using a polyvinyl alcohol slurry to obtain a suitable coating thickness. Further work is being carried out on optimisation as well as a preliminary investigation of the erosion protection properties of these SiC-based coatings.

3.2. Glass-ceramic coating of CBCF material

The time and temperature parameters required for the crystallization of the SAY glass deposit on the β-SiC-coated CBCF samples were deduced from the DTA measurements on as-produced SAY powders (heating rate 20 °C/min). Fig. 4 shows the DTA analysis on the SAY glass, revealing a glass transition temperature (T_g) at 910 °C, a crystallization temperature (T_x) at 1235 °C and the melting point (T_m) at 1375 °C.

Fig. 5 shows a SEM micrograph of the interface between the SAY glass-ceramic layer and the β-SiC-coated CBCF substrate. The image demonstrates the high density achieved for the glass-ceramic. The average thickness of the SAY coating was found to be about 300 μm, while the SiC layer can exceed 500 μm. The interfaces between the layers of this multi-layered glass-ceramic coated β-SiC-CBCF substrate system are shown in the SEM images of Fig. 6a and b. The SAY glass-ceramic exhibited a very good adhesion to the β-SiC-coated CBCF substrates as qualitatively assessed by the pull tests. From Fig. 6b it is apparent that the SAY coating partially infiltrated the SiC layer thus accounting for the good adherence of the glass-ceramic layer.

The XRD pattern of the SAY glass-ceramic coating, reported in Fig. 7, revealed the presence of cristobalite, yttrium silicate ($Y_2Si_2O_7$, keiviite, β form) and mullite, as expected from the silica–alumina–yttria phase diagram, shown in Fig. 8.

Yttrium-silicates are excellent candidates as coating material for high temperature applications because of their thermal expansion coefficient is low and similar to that of SiC. Moreover, they exhibit low evaporation rate and oxygen permeation constant [9–11]. Mullite is another candidate for the coating of SiC/SiC and carbon–carbon composites, because its coefficient of thermal expansion (CTE) matches very well that of SiC, and its corrosion and oxidation resistance is very high at elevated temperatures [12,13].

Fig. 9 is a SEM micrograph of the top view of the polished SAY glass-ceramic coating. No cracks are detected. As observed in the cross-sections (Figs. 5 and 6) it is noticeable that the coating is very dense without large (i.e. >50 μm) pores and with acceptable homogeneity. This indicates that at

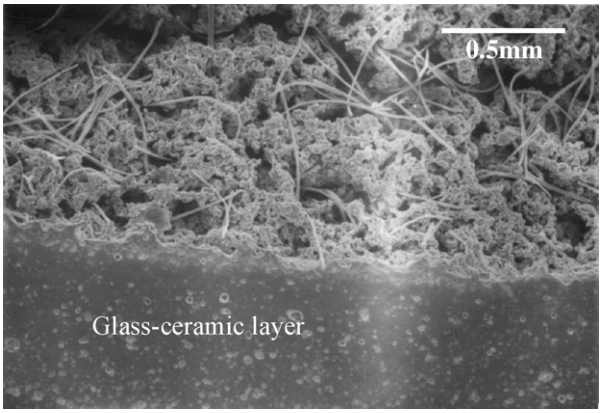

Fig. 5. Cross-section of SAY glass-ceramic coated β-SiC-CBCF substrate showing the high density of the SAY glass-ceramic layer.

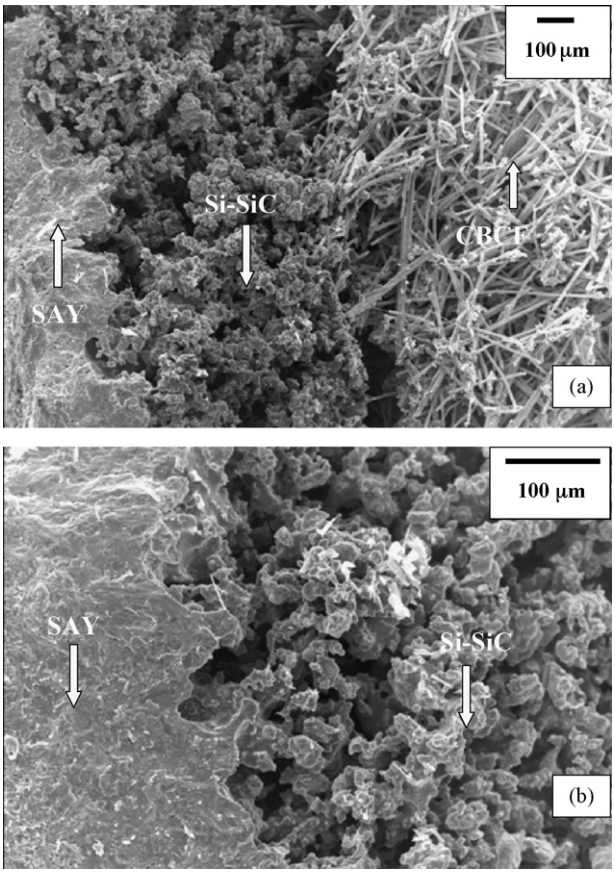

Fig. 6. SEM micrographs of the cross-section of a SAY glass-ceramic coated β-SiC-CBCF substrate showing the interfaces at (a) low and (b) high magnification.

1375 °C, the SAY glass coating had a sufficiently low viscosity for viscous flow sintering to have taken place.

Fig. 8 shows the phase diagram of the system $SiO_2-Al_2O_3-Y_2O_3$ [14]. The glass composition chosen for our investigation is located within the eutectic transformation region of the diagram; this fact leads to a maximum service temperature of the coating of about 1400 °C.

Based on the phase diagram, cristobalite, mullite and yttrium silicate ($Y_2Si_2O_7$, keiviite, β form) are confirmed to be the major devitrification products expected, and all these crystalline phases were detected by XRD (see Fig. 7). A similar glass composition was studied by Hyatt and Day [15]; a thermal

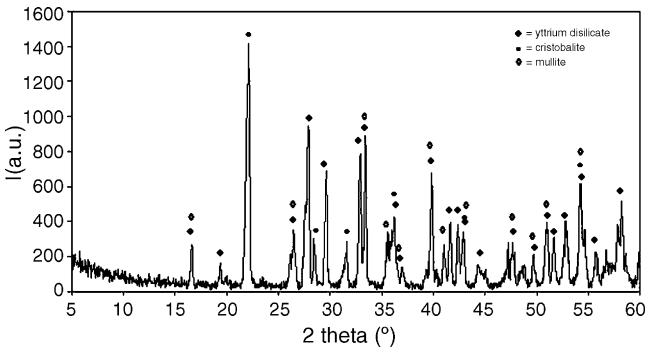

Fig. 7. XRD pattern of the SAY glass-ceramic coating.

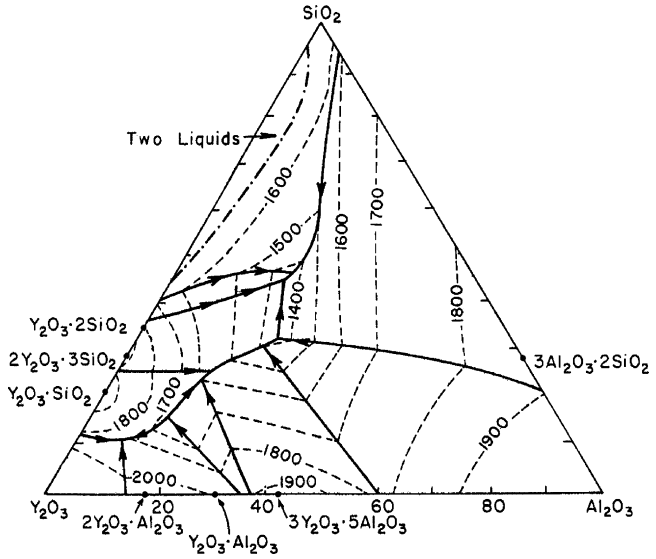

Fig. 8. SiO_2–Al_2O_3–Y_2O_3 phase diagram [14].

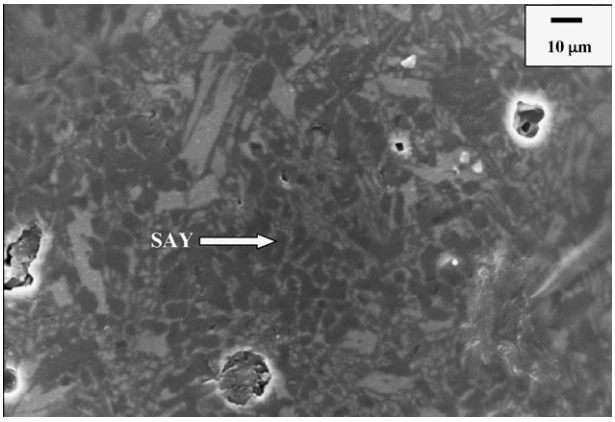

Fig. 9. SEM micrograph showing the surface of SAY glass-ceramic coating.

expansion coefficient of $3.1 \times 10^{-6}\,K^{-1}$ was assigned to this glass, very close to the calculated CTE value of SAY glass. The SAY glass crystallization heat treatment did not seem to affect this value, since no transversal cracks were observed in the glass-ceramic coating, demonstrating that the SAY coating and substrate have compatible thermal expansion coefficients.

Further investigations will focus on the quantification of the amount of residual glassy phase in the SAY glass-ceramic coating in order to investigate the possibility of healing (closure) of microcracks (which might develop for example under thermal cycling and oxidation conditions) by a viscous flow mechanism.

4. Conclusions

This work proposed a simple and low-cost slurry-dipping method to produce oxidation resistant multi-layer protection system consisting of SiC and a glass-ceramic for CBCF materials. The glass-ceramic layer, of suitable composition and properties, was easily applied as a pore free coating on the Si-

modified CBCF composites by a conventional firing technique at temperatures above the glass softening point. The refractoriness of the coating was enhanced by a controlled crystallization which resulted in a chemically and thermo-mechanically compatible glass-ceramic coating. The controlled crystallization produced cristobalite, yttrium silicate ($Y_2Si_2O_7$, keiviite, β-form) and mullite as main crystalline phases. These phases have excellent oxidation and erosion resistance.

Acknowledgement

Part of this research was funded by the EU Network of Excellence ''Knowledge-based Multicomponent Materials for Durable and Safe Performance'' (KMM-NoE, NMP3-CT-2004-502243).

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