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Cordierite–mullite coating for SiC_f/SiC composites

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Abstract

A glass of suitable composition for coating of SiCf/SiC composites has been developed. The resulting coating is a crystalline cordierite-mullite material. The SiCf/SiC composites were coated by a simple and low cost slurry technique: a slurry made of glass powder and ethanol was put on the as-received SiCf/SiC composite and heat treated at 1180 °C for 1 h in order to obtain a uniform, pore-free and crystalline coating through the ''glass–ceramic method''. The thermal analysis could not reveal any residual glass transition in the obtained coating material and the melting point of the crystalline phases formed in the coating during the coating process (cordierite, $2MgO–2Al_2O_3–5SiO_2$ and mullite, $3Al_2O_3–2SiO_2$ rate of 3:1 wt. %) was measured at about 1430 °C.

Keywords: Coatings; Composites; Cordierite; Glasses; Mullite; SiC/SiC

1. Introduction

Silicon carbide fibre reinforced silicon carbide matrix composites are candidate structural materials for applications in high temperature environments, such as aerospace, gas turbine and thermo-nuclear fusion structural materials, etc.

Nevertheless, these composites are porous, permeable to fluids, and they can be subjected to cracks in the SiC matrix under operative conditions and, therefore, to the oxidation of the fibre/matrix carbon interface. This problem can be solved by applying a sealant and high temperature oxidation resistant coating, especially designed for these composites.

Mullite and cordierite are prime candidates for the coating of SiC and SiC/SiC composites: their coefficient of thermal expansion (CTE) match very well those of SiC and SiC/SiC composites, they are corrosion and oxidation resistant.[1,2]

There are several proposed methods to coat SiC and SiC/SiC composites, [i.e. chemical vapour deposition (CVD) and plasma spray methods (PS)]; CVD is very effective to obtain pure and crystalline coatings, e.g. SiC_f/SiC composites are currently coated by a SiC CVD coating in order to reduce their porosity and to enhance their oxidation resistance, but the presence of some cracks in the CVD coating make it not fully satisfactory for this purpose. Moreover, the CVD deposition rate is very low. Plasma sprayed coatings have higher deposition rates, but they also have intrinsical porosity and microcracks. Furthermore, CVD and PS are both expensive techniques.[1,2]

Glasses of suitable composition and properties can be easily applied as pore free and crack free coatings on the as received SiC_f/SiC composites by a low cost firing technique at temperatures above their softening point[3–5] and below 1200 °C, which is the upper limit temperature for the SiC fibres used in these composites.

It must be underlined that, if necessary, the refractoriness of the glassy coatings could be enhanced by a controlled crystallization (''glass–ceramic method''), in order to obtain a chemically and thermo-mechanically compatible ceramic or glass–ceramic coating. The residual glassy phase of the coating can be reduced to values comparable with those of the residual glassy phase of several commercial SiC_f/SiC or completely eliminated by the choice of a suitable glass composition.

In this work a $SiO_2–Al_2O_3–MgO$ based glass is proposed to obtain a high temperature resistant mullite–cordierite coating on SiC_f/SiC composites through the glass-ceramic method. It is a simple coating process which does not need high temperature processing, which is detrimental for the composite itself: in fact, the degradation of the Nicalon–SiC fibres of most SiC_f/SiC

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composites begins to be relevant at 1200 °C and this glass can be applied and crystallized at 1180 °C. Moreover, the proposed glass wets very well the as-received SiC_f/SiC composites at this temperature, fills pores and forms a strong bond. The SiC_f/SiC composites do not need any surface pre-treatment before the coating process, as reported in Ref. 1 where a commercial cordierite glass–ceramic powder is used to coat SiC. Furthermore, the use of a commercial cordierite glass–ceramic powder needs a processing temperature of about 1550 °C, unacceptable for the SiC_f/SiC composites, which dramatically degrades their thermo-mechanical properties after 1200 °C.

The SiO_2–Al_2O_3–MgO based glass coating proposed in this work can be crystallized in glass–ceramic directly during the coating process, giving a ceramic coating thermo-mechanically compatible with the SiC_f/SiC composites and of higher refractoriness (up to 1430 °C).

2. Experimental

The silicon carbide fibre (Nicalon, Nippon Carbon, Japan) reinforced silicon carbide matrix composites used for this study were produced by liquid infiltration and pyrolysis of a ceramic precursor polymer (SICFILL® FN-ENEA, Italy). The coefficient of thermal expansion (CTE) for the SiC_f/SiC is about 4×10^{-6} °C^{-1}, and the XRD on its surface showed the presence of amorphous SiC, together with some α- and β-SiC crystalline phases.

The composition of the glass (referred to as SAMg), chosen as coating material is based on SiO_2, Al_2O_3 and MgO. Powders of oxides and carbonates were mixed together in a platinum crucible and heated for 1.5 h at 1700 °C in air. After cooling in air, the transparent glass was extracted by drilling and ground for X-ray diffraction (XRD) analysis, differential scanning calorimetry (DSC, Perkin Elmer DSC7, Thermal Analysis Controller TAS 7/DX), differential thermal analysis (DTA, Netzsch 4045) and hot-stage microscopy (Leitz GmbH AII).

The glass was powdered, sieved and mixed with ethanol to obtain a slurry, then applied on the as-received SiC_f/SiC surface and heated in a tubular oven at 1180 °C (3000 °C/h during the heating and 6 °C/h during the cooling) for different time, under argon flow, resulting in a white ceramic coating on the SiC_f/SiC. Polished cross-sections of the coated samples were characterized by scanning electron microscopy (SEM, Philips 525M, EDS, SW9100 EDAX). Some Vickers indentations were performed near the coating zone to determine qualitatively the presence of residual stresses in the coating or in the composite.

The phase composition of the coating layer was determined by X-ray diffraction analysis. SEM analysis was performed on HF (1% in H_2O) etched coatings to investigate their phases. Some thermal properties of the coating were measured by DTA and a dynamic mechanical analyzer (DMA7, Perkin-Elmer).

3. Results and discussion

The glass composition was selected in order to obtain a glass material with the following properties:

- CTE very close to the SiCf/SiC one (about 4×10^{-6} °C^{-1}),
- cordierite and mullite as principal crystalline phases,
- characteristic temperatures which allow the coating process below 1200 °C, the technological limit for the Nicalon fibres present in the composites.

In fact, for this glass composition, a CTE value of 3.1×10^{-6} C^{-1} and a softening point of 975 °C was reported.[6] As expected from the phase diagram, a crystallization treatment on this glass gave rise to a cordierite–mullite based ceramic coating, enhancing the working temperature of the coating up to 1430 °C, as measured by DTA on the coating.

The high viscosity of the glass at the preparation temperature (1700 °C) did not allow its pouring, but a drilling was necessary. The obtained material was transparent and completely amorphous, as it is evident from the X-ray diffraction pattern in Fig. 1, curve a.

The characteristic temperatures of SAMg, detected by thermal analysis (the DTA plot is shown in Fig. 2a) and heating stage microscopy, are listed in Table 1. From these data, the coating process temperature was chosen at 1180 °C, a temperature between the softening and melting points, so as to reach an adequate viscosity for a homogeneous glass deposition on the composite, without overcoming the limit for the Nicalon fibre decomposition. Furthermore, at a temperature above the SAMg softening point, a contact angle near to zero was measured by the hot-stage microscope between the glass and the as-received SiC_f/SiC. This result avoided the time consuming pre-deposition processes described in Ref. 1.

Table 1
Characteristic temperatures of SAMg glass

Glass transition (°C)	Softening point (°C)	Crystallization temperatures (°C)	Melting point (onset; °C)	CTE (10^{-6} C^{-1})[5]
867±5	985±10	1053±5 1151±5	1240±5	3.1

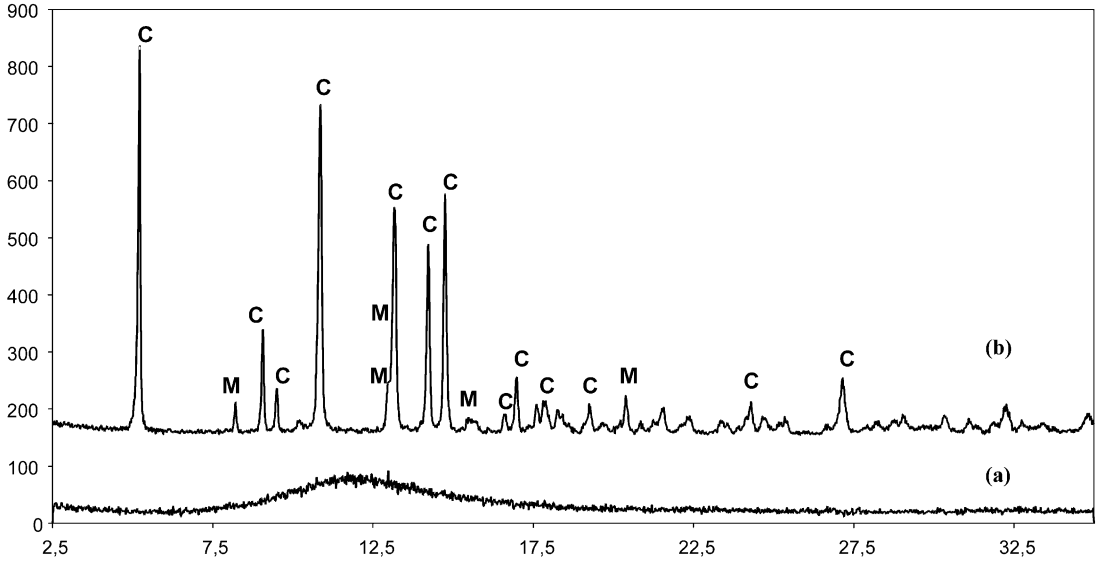

Fig. 1. X-ray diffraction powder patterns of (a) SAMg glass as obtained by melting of its components and (b) crystallized SAMg after heat treatment at 1180 °C for 1 h (C = cordierite; M = mullite).

The dwell time for the isothermal treatment at 1180 °C was varied in a range between 15 min to 1 h to reduce the porosity of the coating layer. From the comparison among the cross-sections of the SAMg coatings deposited for different times, it is evident that the coating porosity is inverse related to the time of the isothermal step. This is related to the relatively high viscosity of the glass at 1180 °C which does not allow an efficient air bubble removal. Otherwise, enhancing the treatment temperature, to decrease the glass viscosity, could be detrimental for the composite mechanical properties and increase the coating porosity as a result of the fibre decomposition that generates gaseous products (e. g. $SiO_xC_y \rightarrow SiC + C + CO\uparrow$).

Fig. 3 shows a cross-section of a SAMg coated SiC_f/SiC composite fabricated at 1180 °C for 1 h with cooling rate of about 6–7 °C/min. The coating is homogeneous, crack-free and the SAMg/composite interface is continuous: this result confirms the good wetting of the coating material on the as-received composite surface and the compatibility of their CTEs.

At higher magnification (Fig. 4), no porosity at the interface is observed, so that reactions giving gaseous products can be excluded between SAMg and SiC_f/SiC, at least up to the process temperature.

At the end of the coating process, the SAMg appeared white and crystalline. The X-ray diffraction scan on the powdered coating (Fig. 1, curve b) showed the formation of cordierite and mullite, while no residual amorphous phase could be detected by this analysis. The cordierite to mullite ratio concentration was determined by comparison of integrated peak intensities of the (100) cordierite and (110) mullite peaks. These peaks were chosen because they were non-overlapping reflections. The calculation was done taking into account the intensity scale factor (ISF), observed intensity, I_{obs}, divided by the PDF intensity, I_{PDF}, and the Reference Intensity Ratio (RIR, I/I_{cor}) reported on PDFs (I/I_{cor}: 2.12 for α-cordierite and 0.75 for mullite). The ISF calculated for the (100) peak of cordierite and the (110) peak of mullite was 100 and 12, respectively. The weight ratio of cordierite to mullite, calculated dividing each ISF for the corresponding RIR, was 3:1.[7]

The DTA on the SAMg coating after treatment at 1180 °C for 1 h is shown in Fig. 2, curve b. As for the XRD scan, the thermal analysis did not reveal any amorphous phase, i.e. any glass transition was detected. These XRD and DTA results clearly indicate that a crystallization of the starting glass coating was obtained during the coating process at 1180 °C. Furthermore, a melting temperature of about 1430 °C was found by DTA for the cordierite–mullite coating material: it is about 200 °C above the melting temperature of the starting glass. That means that the coating material refractoriness, i.e. its working temperature, was successfully enhanced by the glass–ceramic method, and that the chosen glass can give a ceramic coating at a temperature below 1200 °C, preserving the mechanical properties of the composite substrate.

Some Vickers indentations were performed with a load of 4.9 N in the coating layer and near the coating/composite interface. The indentation in the SAMg layer (Fig. 5) showed that the cracks propagated parallel to the composite surface, while minor or any perpendicular crack propagation can be observed. This preferred propagation of the induced cracks indicates a compression residual stress in the ceramic coating, which is the most suitable condition for a mechanical resistant coating. Moreover, the crack propagation indicates that also after the crystallization of the glass coating occurred during the coating process, the

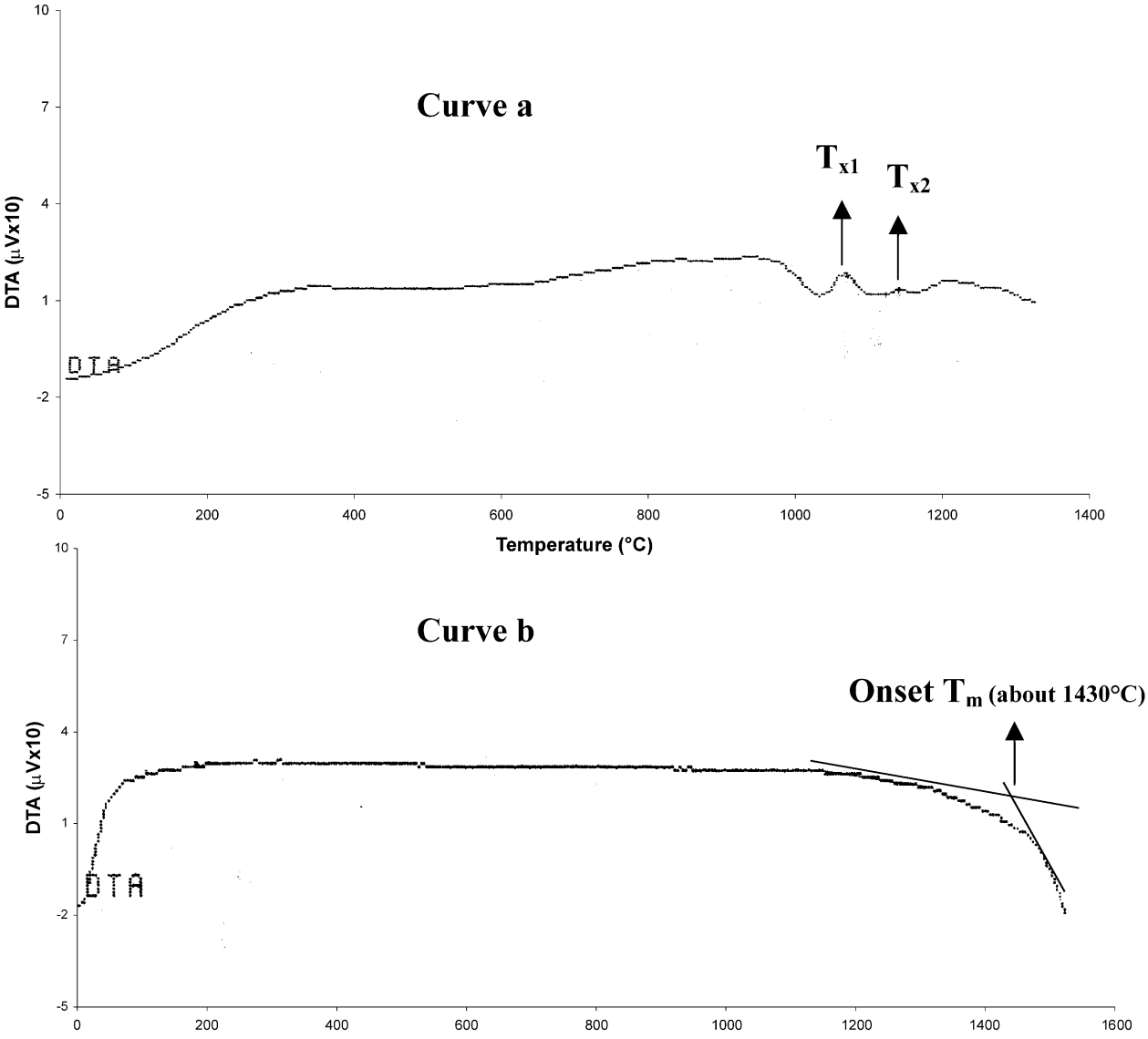

Fig. 2. Differential thermal analysis patterns of curve (a) SAMg glass and curve (b) SAMg after heat treatment at 1180 °C for 1 h.

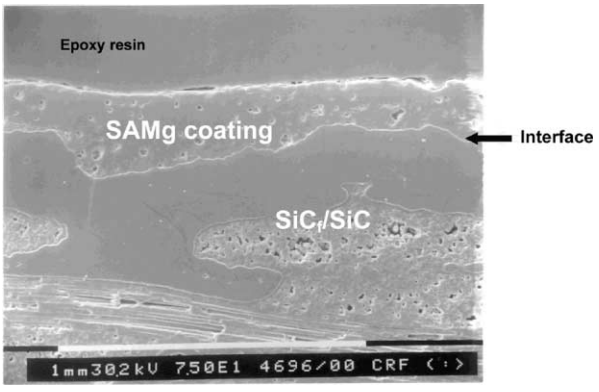

Fig. 3. Cross-section of a SAMg coated SiC_f/SiC composite prepared at 1180 °C for 1 h.

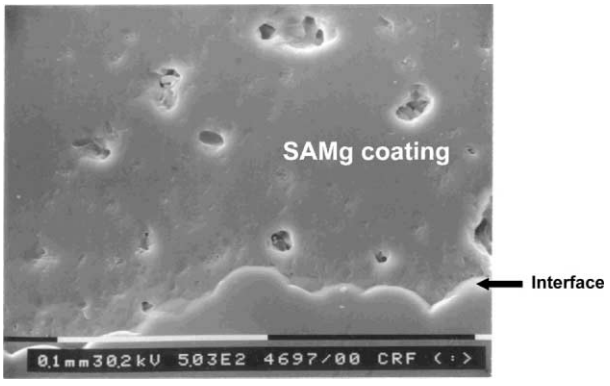

Fig. 4. Cross-section of a SAMg coated SiC_f/SiC composite prepared at 1180 °C for 1 h. Magnification of the interface zone.

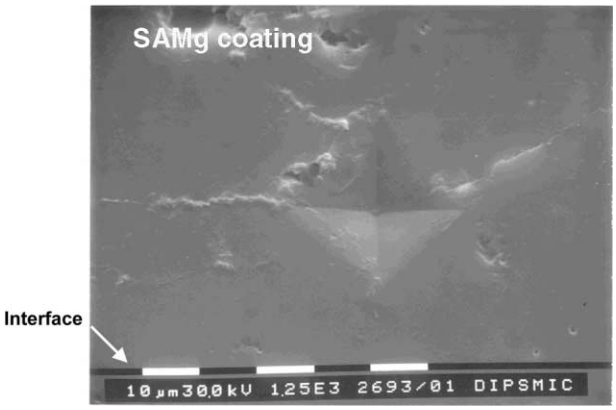

Fig. 5. Cross-section of a SAMg coated SiCf/SiC: magnification of the coating zone near the interface. Vickers micro-indentation on the SAMg coating layer: the crack propagation is evident only in the direction parallel to the interface.

ceramic coating CTE is still suitable for these SiC/SiC composites: e.g. the crack propagation through the interface composite/coating was never observed.[7–9]

The coating CTE is expected to be lower than that of the composite, because of the compression stress found in the coating. In fact, the CTE of the SAMg after the heating treatment at 1180 °C for 1 h was measured by DMA and resulted to be 3×10^{-6} K^{-1} (200–600 °C). If the coating is in compression it will not crack at low temperature, during the cooling process or under thermal cycling.[10] In the case of SAMg coating on SiC_f/SiC, the achieved compression state in the SAMg layer is sufficient to ensure a crack-free coating, but it is not too high to cause the well-known spallation phenomena.

The formation of residual stresses is also confirmed by the crack deflection observed in the SAMg coating near the interface with the SiC_f/SiC (Fig. 6). Instead of being parallel to the composite/coating interface the cracks deflect toward the SAMg coating layer indicating a tension state near the interface.

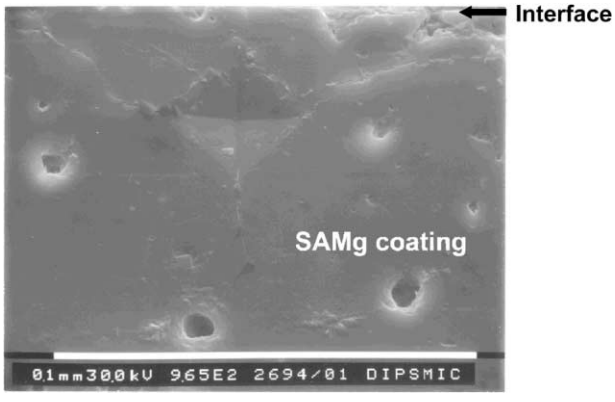

Fig. 6. Cross-section of a SAMg coated SiCf/SiC: magnification of the coating zone near the interface. Vickers micro-indentation in the SAMg coating, very closed to the interface with SiC_f/SiC: the cracks are deflected toward the SAMg coating layer.

Finally, the composition of this coating allows its use also for thermo-nuclear fusion applications.[11]

4. Conclusions

The magnesium alumino-silicate glass (SAMg) resulted in being effective in the development of a ceramic coating for SiC_f/SiC composites. The obtained coating is a crystalline cordierite–mullite based material. The coating technique is a simple and low cost slurry technique and it is effective to give uniform, pore-free and crystalline coating through the ''glass–ceramic method''.

The foreseen thermal resistance of this coating was measured at about 1430 °C.

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