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Microstructure and mechanical properties of low-activation glass-ceramic joining and coating for SiC/SiC composites

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Abstract

Calcia-alumina (CA) glass-ceramic was studied as a candidate low-activation joining and sealing material for SiC/SiC components for fusion blanket and diverter structures, in terms of microstructural stability and mechanical properties. The CA glass-ceramic joining and seal coating were applied to the Hi-Nicalon™ SiC fiber-reinforced SiC matrix composites in which the matrix had been formed through chemical vapor infiltration and polymer impregnation and pyrolysis methods. Microstructural characterization was carried out for the joined and coated materials by optical and scanning electron microscopy (SEM). The mechanical property of the joint was evaluated through a shear test on sandwich joints. The average shear strength of the joined structures was 28 MPa at room temperature. Fractography revealed that the fracture occurred in the glass phase and the shear strength may be improved by reduction of the glass fraction.

1. Introduction

Silicon carbide continuous fiber-reinforced silicon carbide matrix composites (SiC/SiC composites) are attractive potential materials for fusion in-reactor components [1]. In addition to their well-known superior high-temperature characteristics, non-catastrophic fracture mode and the inherent low-activation characteristic, recent advancement [2] in material performance and the prospect for drastic cost reduction by industrial development make SiC/SiC composites even more attractive. For practical use of the SiC/SiC composites for fusion, however, beside the critical issues related to the nuclear environment, technological issues including the joining methodology and hermetic sealing must be addressed [1,3,4].

Among the proposed joining and coating methodologies for SiC/SiC composites, glass-ceramics have unique characteristics, such as softening at high temperatures and tailorable properties (i.e., wettability, thermal expansion coefficient, softening and glass transition temperatures) [5–8]. Moreover, glass-ceramics are not affected by oxidation, and can be self-sealant at temperatures above the glass softening point [9]. If a single glass or glass-ceramic coating material cannot satisfy all the working conditions (i.e., thermal expansion coefficient, wettability, working temperature, sealing temperature, etc.), then the design of a double layer coating could be necessary. In this case, the first (internal) layer could consist of a homogeneous, crack free, glass-ceramic coating with high-characteristic temperatures and thermal expansion coefficient compatible with the composite; the second (external) layer could be amorphous and show self-sealing properties at the required temperature [10].

The calcia-alumina (CA) glass-ceramic has additional advantages such as low-activation composition, low after-heat, low-cost pressure-less processing and a demonstrated chemical compatibility with the ceramic breeder Li_4SiO_4 [11,12]. In this work, further characterization of CA glass-ceramic joining and coating was

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performed, mainly by microstructural examination, microchemical analysis and mechanical testing.

Alumina is considered to be one of the most radiation-resistant ceramic and calcium oxide is expected to exhibit similar radiation resistance. Therefore, CA glass-ceramic could be considered one of the most promising low-activation joining and coating for fusion applications: the residual amorphous phase of CA glass-ceramic can be lowered by appropriate heat treatments to a level lower than the amorphous phase present in SiC/SiC. In this case, the detrimental effects of irradiation on CA glass-ceramic should be avoided.

The irradiation behavior of CA glass-ceramic will be the subject of a further study. Neutron irradiation experiments on SiC/SiC composites joined with several different techniques, including CA glass-ceramic joining, are planned in Japan Materials Testing Reactor, Oarai, Japan (JMTR) and also proposed as one of the important tasks in Monbusho (Ministry of Education, Science, Sports and Culture, Japan) – Department of Energy, US (DOE) collaborative project for fusion materials research.

2. Experimental

The SiC/SiC composites used in this work had been prepared by matrix densification by chemical vapor infiltration (CVI) on 0/90 or 0/30/60 stacks of the Hi-Nicalon™ plain weave 2-D fabric (Nippon Carbon, Tokyo, Japan), following the pyrolytic carbon interphase deposition [13]. The surface of the materials was mostly matrix, consisting of fully crystalline β-SiC.

The chemical composition (mass percent) of the CA glass-ceramic was 49.77 CaO and 50.23 Al_2O_3 [11]. Powders of aluminium oxide and calcium carbonate were mixed together in a platinum crucible and heated in air at 1650°C for 1 h. After cooling, the glass-ceramic was ground for X-ray diffraction (XRD) analysis and thermal characterization. The results of these characterization have been reported previously [11].

Offset-sandwich joint samples were prepared by depositing a slurry of glass-ceramic powder and ethanol between two composite samples. Likewise, coated samples were prepared by deposition on the composite surface. These samples were then heated in a tubular oven at 1500°C for 1 h under a slight Ar flow, with no external pressure being applied. Morphological analysis of the joints and the coatings was made by optical microscopy and scanning electron microscopy (SEM). Further microstructural characterization and microchemical analyses were performed by cross-sectional SEM, energy dispersive X-ray spectrometry (EDS) and transmission electron microscopy (TEM). Mechanical shear tests were performed at room temperature on the as-joined sample. The fracture surfaces of the shear-tested specimens were then examined by SEM. The self-healing property of the coating was investigated by inducing cracks in it and subsequently observing the repair after heating to 1200°C.

3. Results and discussion

Figs. 1(a) and (b) show the optical micrographs of the surface and the cross-cut of the CA glass-ceramic-coated CVI-SiC/SiC composite. The glossy surface shown in Fig. 1(a) shows that the surface of the coating is covered with the glass layer. The glass phase and the ceramic phase could easily be distinguished by means of Nomarski differential interferometric microscopy, due to the optical property differences. The volume fraction of

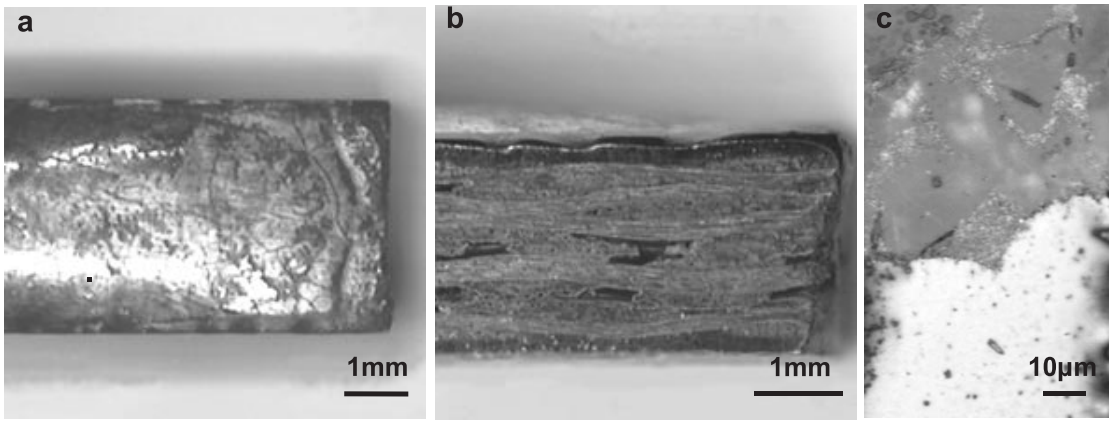

Fig. 1. Low-magnification optical micrographs of the surface (a) and cross-section (b) and Nomarski differential interferometric micrographs (c) of CA glass-ceramic-coated CVI-SiC/SiC composites. Cracks in the coating are indicated by arrows. In the interferometric image, the blocky gray particles correspond to the crystallites and the glossy matrix is the amorphous phase.

the crystalline phase determined by the cross-sectional area fraction was approximately 60%. The XRD analysis revealed that the crystalline ceramic in the CA consists of two phases, namely $3CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$. These two phases could not be distinguished in the optical microscope or SEM. The cracking shown in Fig. 1(a) corresponds to that in the CA glass-ceramic layer, presumably introduced during the cooling due to the coefficient of thermal expansion (CTE) difference from that of the composite's β-SiC matrix. The CTE of CA glass-ceramic used in this study is significantly higher than that of β-SiC [11], it can further be reduced by increasing the ceramic fraction. The cracking was not open but covered with the glass phase, therefore, it may not cause immediate loss of hermeticity. However, according to the preliminary unirradiated hermeticity study on the CA coating, it was not effective as a self-healing coating up to 1200°C; the cracks induced in the coating were not completely repaired after heating to 1200°C. It is necessary to perform further tests at higher temperatures to characterize the self-healing property of this coating. For improved hermeticity below 1200°C, a double coating structure with additional glass layer is being developed [14].

An optical micrograph of the cross-cut joint is provided in Fig. 1(c). The joint was typically 100 μm thick. The thickness was actually determined by the surface roughness of the original SiC/SiC bars and can largely be reduced even by the pressureless process employed in this work. No pores were observed by optical microscopy within the joint and on the CA–SiC boundaries. The matrix microcracks and the matrix pores (a few to 50 μm in diameter) in the joined composites close to the joint were filled with CA. These observations demonstrate the very good wettability of CA with β-SiC. This observation implies the potential applicability of CA glass-ceramic as the post-fabrication matrix filler for SiC/SiC composites. Cracking was also observed within the CA joint. Most of the cracks were observed across the joint, which also suggests that the CTE difference caused the cracking. The cracks were not deflected at the glass-ceramic boundaries but tended to traverse the crystalline grains. Suppressing the pre-existing crack density by reducing the CTE should improve the mechanical strength of the CA joint ($\tau_{average} = 28$ MPa [11]).

A representative SEM micrograph around the CA–SiC boundary and the elemental mapping by EDS in the corresponding region are shown in Fig. 2. In the CA joint on the left in the micrograph, islands of the crystalline phases are distributed in the glass matrix. The SEM examination at higher magnifications revealed that the glass phase was always facing the CA–SiC boundaries. The crystal islands were generally elongated round-shaped with a minor radius of a few to 5 μm. The elongated direction was locally equiaxed, presumably along the crystallization direction. According to the EDS analysis, crystal phases contained larger amounts of calcium and aluminum and a smaller amount of oxygen than the glass phase. A small amount of diffused silicon was detected only in the glass matrix close to the CA–SiC boundaries. No indication of impurities was detected through the EDS analysis.

The fracture surfaces of the shear-tested joints were observed by SEM. The micrograph in Fig. 3 shows the

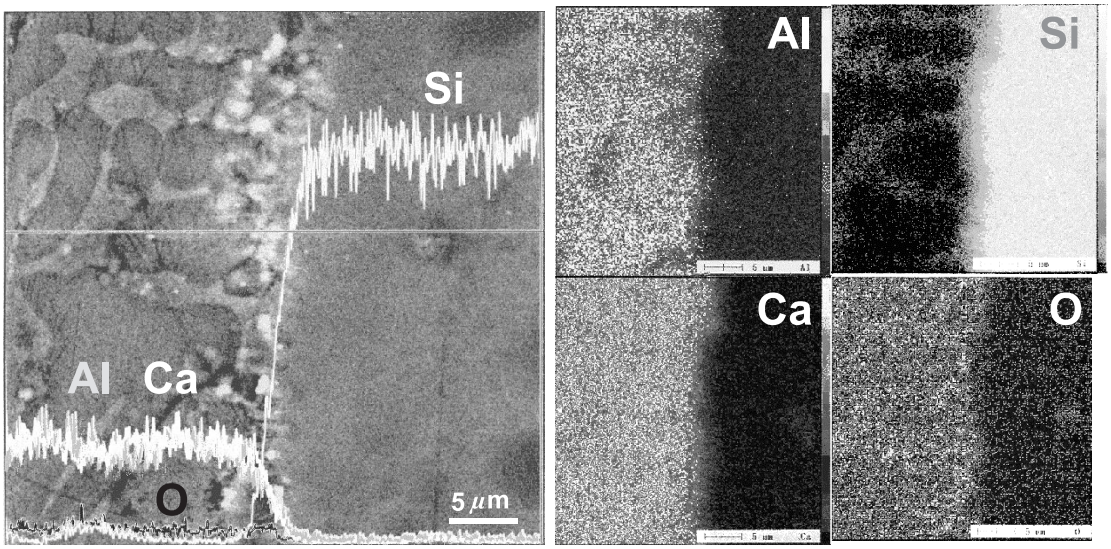

Fig. 2. SEM micrograph around the CA–SiC boundary and the elemental mapping by EDS in the corresponding region. In the EDS maps, images are adjusted to show the elemental differences between crystallites and amorphous matrix in CA and the brighter image corresponds to the richer content.

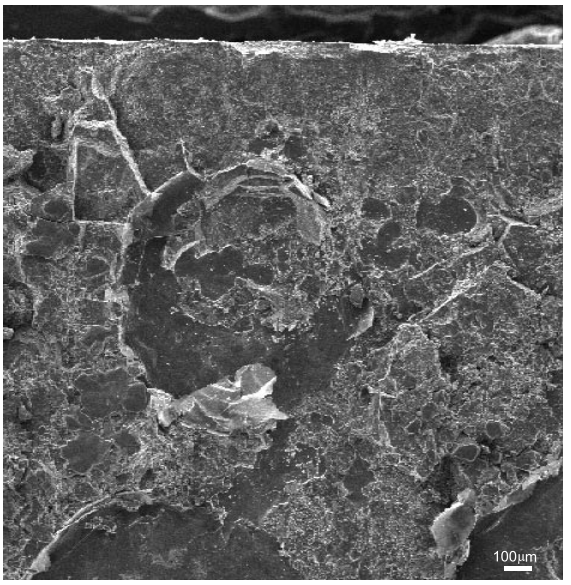

Fig. 3. An example of SEM fractograph of the joined sample after the shear test.

very uneven fracture surface with some crater-like features. It should be emphasized that the fracture did not propagate on the joint–composite interface, but ran through the joint. It confirms the excellent wetting between the CA and the composite and fairly strong interface. Furthermore, the fracture surface runs in a multi-planar way, as observed by the appearance of several crystallites in the CA glass-ceramic. Fig. 4 compares the EDS spectrum obtained by the broad

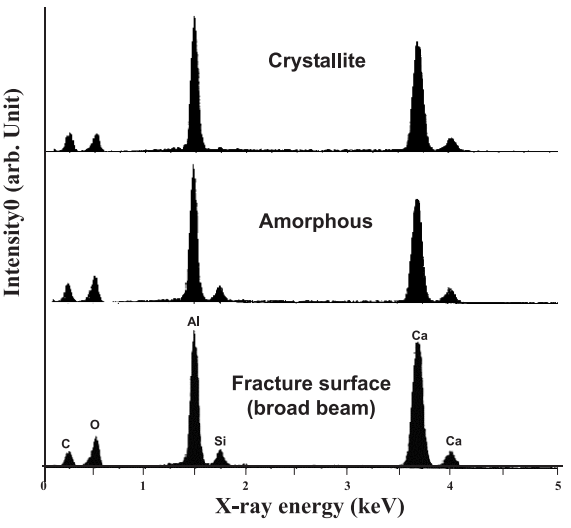

Fig. 4. EDS spectra obtained from the crystallite (top), amorphous phase (centre) and shear fracture surface by broad beam (bottom).

electron beam probe on the fracture surface with those from the crystallite and the glass phase on a polished surface. As clearly seen, the EDS spectrum averaged over the fracture surface is very close to that of the glass phase, in terms of oxygen and silicon contents. This result leads to the conclusion that the fracture occurred within the glass phase. Therefore, the presence of crystallites on the fracture surfaces improves the mechanical strength of the joint. The amount of residual amorphous phase in the CA glass-ceramic was not enough to give a smooth, brittle-type fracture surface.

It is likely that the increased fraction of crystalline phase improves the mechanical properties of the joint through a reduced CTE mismatch, an increased fracture surface area and an increased shear friction. Further work is in progress to maximize the crystalline phases and to reducing the amorphous one by thermal treatment at the crystallization temperature of CA and to study the influence of the thermal treatment on the mechanical properties of the joined composites.

4. Conclusions

Microstructural analysis and mechanical property evaluation were performed on SiC/SiC composites joined and/or coated by CA glass-ceramic. The sandwich joint exhibited good shear strength. The coating showed integrity in optical and SEM investigations, but the unsatisfactory self-sealing property will require an additional glass layer. The excellent wettability of CA with β-SiC was demonstrated. Therefore, a CA coating might be effective as the first layer of a double layer hermetic seal coating for SiC/SiC composites.

A significant amount of cracking, introduced during the cooling period after joining, was observed within the CA joint and is likely to reduce the shear strength of the joint. The mechanical properties of CA joints may be improved through reducing the crack density by lowering the thermal expansion coefficient.

Fractography after the shear test revealed that the fracture occurred within the glass phase leaving rough surfaces. Decreased glass phase fraction should further improve the joint strength.

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References

[1] P. Fenici, A.J. Frias Rebelo, R.H. Jones, A. Kohyama, L.L. Snead, J. Nucl. Mater. 258–263 (1998) 215.
[2] A. Kohyama, Y. Katoh, T. Hinoki, W. Zhang, M. Kotani, in: Proceedings of the Eighth European Conference on Composite Materials, vol. 4, 1998, p. 15.
[3] B. Riccardi, P. Fenici, A. Frias Rebelo, L. Giancarli, G. Le Marois, E. Philippe, Status of the European R&D Activities on SiC_f/SiC Composites for Fusion Reactors, Presented at the Fifth International Symposium on Fusion Nuclear Technologies, Rome, September, 1999.
[4] G. Aiello, L. Giancarli, Y. Poitevin, J.F. Salavya, J. Szczepanskib, SiC_f/SiC Composites for Structural Applications in Fusion Power Reactors: The Tauro Blanket, Presented at the 12th International Conference on Composite Materials, Paris, July, 1999.
[5] P. Lemoine, M. Salvo, M. Ferraris, M. Montorsi, J. Am. Ceram. Soc. 78 (6) (1995) 1691.
[6] P. Lemoine, M. Ferraris, M. Salvo, M. Appendino Montorsi, J. Eur. Ceram. Soc. 16 (11) (1996) 1231.
[7] D.N. Coon, Report N. NTIS DE90-01295. Composite Materials Research Group, Department Of Mechanical Engineering, University of Wyoming. 1989.
[8] C. Isola, P. Appendino, F. Bosco, M. Ferraris, M. Salvo, Carbon 36 (7–8) (1998) 1213.
[9] M. Ferraris, M. Salvo, C. Isola, M. Montorsi, Proceedings of IEA-International Workshop on SiC/SiC Ceramic Composites for Fusion Structural Applications, Ispra (Va), 28–29 October 1996, p. 113.
[10] M. Ferraris, M. Appendino Montorsi, M. Salvo, C. Isola, A. Kohyama, Proceedings of IEA-International Workshop on SiC/SiC Ceramic Composites for Fusion Structural Applications, Sendai, Japan, October 1997, p. 125.
[11] M. Ferraris, M. Salvo, C. Isola, M. Appendino Montorsi, A. Kohyama, J. Nucl. Mater. 258–263 (1998) 1546.
[12] P.L. Higby, R.J. Ginther, I.D. Aggarwal, E.J. Friebele, J. Non-Cryst. Solids 125 (1990) 209.
[13] H. Araki, W. Yang, Y. Shi, S. Sato, T. Noda, A. Kohyama, Ceram. Eng. Sci. Proc. 20 (4) (1999) 371.
[14] M. Ferraris, M. Salvo, C. Isola, M. Appendino Montorsi, Proceedings of the Eighth European Conference on Composite Materials, vol. 4, 1998, p. 299.