PRESSURE-LESS JOINING OF CERAMIC MATRIX COMPOSITES

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Abstract

A critical issue for a wider use of Ceramic Matrix Composites (CMC) is the development of cheap, user-friendly joining methods to assemble large components into more complex structures, but also to repair damaged parts after mission. Some pressure-less joining techniques and joining materials for CMC will be described: results obtained by using glass ceramics, modification of a commercial adhesive and W/SiC based joining materials will be discussed.

Different kinds of joined samples have been manufactured to couple the reliability of a machined joint with bonding properties of the joining materials. The mechanical characterization of the joints will be also discussed.

The use of glass-ceramics as joining materials in a neutron environment has been demonstrated up to 820°C, 5 dpa: comparison of bending and shear strength for neutron irradiated and non-irradiated glass-ceramic joined SiC and SiC/SiC indicates that the mechanical strength is unaffected by irradiation at the used irradiation conditions.

1 Introduction

Ceramic Matrix Composites (CMC), i.e. SiC/SiC, C/SiC and C/C, are being considered the primary candidates for components and subsystems in the field of satellite (sun-near) missions, defence aerospace and aircraft missions (e.g. body flaps, nose cones, wings, leading edges, turbine components) and for terrestrial/industrial applications under extreme environmental conditions (e.g. valves, shaft sleeves for pump sliding bearings, etc.). Furthermore, search for new materials for hot structure elements in nuclear reactor technology has triggered development programs for SiC-fibre reinforced SiC materials.

A critical issue for a wider use of CMC is the development of cheap, user-friendly joining methods to assemble large components into more complex structures [1], but also to repair damaged parts.

There are many possible techniques for joining SiC-based materials to themselves and to dissimilar materials: diffusion bonding using various active fillers [2], transient eutectic phase methods such as nano-infiltration and transient eutectic-phase (NITE) [3-5], laser joining [6], selected area chemical vapour deposition [7], glass-ceramic joining [8-10], solid state displacement reactions [11], preceramic polymer routes [12], reaction forming [13], brazing

[14]. In the field of nuclear energy production (fusion and fission), requirements for SiC based joints are extremely severe: a joining material must be compatible with a neutron environment and the joining technique must comply with the fusion nuclear reactor design where SiC/SiC components several meters long and 5 mm thick must be joined in a reliable and feasible way [15]. The very few available solutions for SiC/SiC joining in the field of nuclear applications are reviewed in [16].
Glasses and glass-ceramics have been proposed as joining materials for SiC and SiC/SiC because of their unique properties such as tailorable characteristic temperatures, coefficient of thermal expansion (CTE) and wettability on SiC substrate; glasses and glass-ceramics can be designed to be low activation materials (LAM), transmutation free and stable under neutron irradiation; their thermo-mechanical stability at working temperature can be higher than 1000°C and they are not affected by oxidation; due to their tailorable viscosity vs temperature they allow pressure-less joining processes, hermeticity and can be self-sealant,.
The refractoriness of a glassy joining material could be enhanced by a controlled crystallization, the so-called *glass–ceramic method*, to obtain joining materials mechanically reliable up to the softening point of the residual amorphous phase, which can be minimized by suitable thermal treatments [4].

This paper focuses on the use of:

1) silica and non-silica based glass-ceramic sealants for nuclear applications
2) a tungsten/SiC based composite as joining material, prepared by aid of a SiC based pre-ceramic polymer for high temperature and nuclear applications
3) a carbon fibre reinforced commercial adhesive modified by a negative CTE glass–ceramic powder (GC) or SiC powders for a low temperature (300°C), pressure-less joining/repairing process in air, for ultra-stable structures and aerospace applications.

2 Materials and testing methods

2.1. Composite materials

The SiC-based materials used are: CVD-SiC (Rohm and Haas, USA) and SiC/SiC with a CVD-SiC coating (MT Aerospace AG, Germany). The composites used for this study are 2D SiC/SiC composites provided by MT Aerospace, Germany. The fibre is SiC Tyranno Type S, the matrix is crystalline CVI SiC with a pyrolitic carbon fibre/matrix interface (few micron thick pyrolitic carbon). The SiC/SiC composite has a 0°/90° plain weave fabric, which is parallel to the mechanical loads used to characterize the joined samples.
The C/C to be joined are sandwich panels composed of two C/C skins joined to a honeycomb C/C core. Honeycomb C/C cores are made of ex-PAN T300 fibres, fabric plain weave and lay-up 45°/−45°.

2.2. Joining materials and processes

2.2.1 Glass-ceramic sealants

The compositions (wt.%) of the parent glasses (one SiO_2–Al_2O_3–Y_2O_3 based glass, referred to as SAY and one CaO–Al_2O_3 based glass, referred to as CA) used as joining materials were designed prepared and characterized as described in [10]. Their composition was chosen according to the simulated neutron-induced radioactivity of the elements present in the glasses, by using the European Activation System EASY-2007 code package [17].
The SAY and CA glasses were synthesised by melting/quenching: the powdered raw products have been melted in a platinum–rhodium crucible in air at 1750°C for 5 h, and at 1750°C for 30 min, respectively, then each glass was poured on a brass plate and subsequently powdered and sieved. Composition, glass transition temperature (Tg) and CTE of the parent glass,

joining process temperature, time and atmosphere to obtain the glass-ceramic sealants, CTE, softening temperature (T soft) and crystalline phases of the glass-ceramic sealants are shown in Table 1.

2.2.2. Tungsten/SiC based composite joining material

Suspensions used for joining contained 70 to 87 wt. % of tungsten powder (mean particle size 1.3 μm) in pre-ceramic polymer allylhydrido polycarbosilane (SMP-10, Starfire Systems Inc., USA). The suspensions were homogenised at 60 °C (to lower viscosity) and applied between the two SiC/SiC or SiC samples. Slight uniaxial pressure was applied to align the two parts. Thermal treatment (1550°C, 1 hour) was carried out in Ar atmosphere, taking special care for low heating rate (2°C/min) up to 800 °C. The chemical and phase compositions of the resulting materials were analysed at the joint cross-section and at the bulk joint material samples prepared in parallel.

2.2.3. Modified carbon fibre reinforced commercial adhesive

The joining material is composed by a carbon fibre reinforced commercial adhesive (Graphibond 551RN produced by Aremco products, Inc., USA), referred to as CFA, in which silicon carbide particles were added as follows: β-SiC 400 mesh powder (< 38 μm, Sigma Aldrich, purity > 97.5%) 5, 10, 30, 40 or 50 wt. %; SiC nano powder (max particle size 0.05μm, Goodfellow) 5 and 10 wt.%.

The CFA was also modified by adding 25 vol.% (40 wt.%) of a negative CTE glass–ceramic powder (GC). The composition of GC is BaO 33.3 mol.%,B_2O_3 33.3 mol.% and Al_2O_3 33.3 mol.%. The GC was produced as a glass material by melt/quenching at 1500 °C for 1 h then heat treated (720 °C, dwelling time 24h+780°C, dwelling time 8 h) to obtain a glass–ceramic. GC has been added to CFA as follows: CFA+ 25 vol.% glass–ceramic powder (<105 or <44 μm).

The joining process, consisted in 2-4 hours ageing at room temperature, 0.1-0.6 °C sec^{-1} heating up to 130°C, followed by a final curing at 260°C (in air). A slight uniaxial pressure (<1kPa) was applied during the joining process to keep the two parts aligned.

Glass-ceramic sealant	**Composition (wt%)**	**Joining process (pressure-less)**	**Tg±5 (°C) (parent glass)**	**CTE (parent glass) (10^{-6}°C^{-1})**	**CTE (glass-ceramics) (10^{-6}°C^{-1})**	**Tsoft±10 (°C) (glass-ceramic)**	**Crystalline phases (glass-ceramic)**
SAY	54% SiO_2, 18.07% Al_2O_3, 27.93% Y_2O_3	1375°C, 20 min; 1235°C, 1h, Ar flow	910	3.8	5.5	975	Mullite, cristobalite, keivyite
CA	49.77% CaO, 50.23%Al_2O_3	1480°C 1h, Ar flow	850	9.4	5.2	1380	$3CaO·Al_2O_3$, $12CaO·7Al_2O_3$

Table 1. Composition, Tg and CTE of the parent glass, joining process temperature, time and atmosphere to obtain the glass-ceramic sealants, CTE, softening temperature (T soft) and crystalline phases of the glass-ceramic sealants [10].

2.3. Characterisation of the joined samples

The SAY and CA coefficient of thermal expansion (CTE) has been calculated by Sciglass 6.6 (ScienceServe GmbH, Germany) and/or experimentally measured by TMA (Perkin–Elmer TMA) and dilatometer (DIL 402 PC Netzsch); glass transition temperature (Tg) and crystallization temperatures have been measured by Differential Thermal Analysis (DTA 404 PC Netzsch, Selb, Germany). Wettability on CVD-SiC and softening temperature (Tsoft)

have been measured by hot stage microscopy (Leitz GmbH AII) up to 1450 °C in Ar flow, (HSM Expert System, Modena, Italy). Polished cross-sections of the joined samples were characterized by optical microscopy and scanning electron microscopy, SEM, equipped with EDS analyzer (Philips 525 M, SW9100 EDAX). The phase composition of the joining materials was determined by X-ray diffraction analysis (X'Pert Philips diffractometer) using the Bragg Brentano camera geometry and the Cu Kα incident radiation.

The flexural strength of joined SiC/SiC (adapted from ASTM C1341-00) was measured on 2.6 mm x 5.2 mm x 45 mm samples. Three different geometries of SiC/SiC were prepared by machining the composite faying surfaces before joining; samples were joined and tested by four-point bending test at room temperature, as described in [9] and in Figure 1. Type 2 is a modification of the Mortise and Tenon joint configuration and type 3 geometry is a half-lap joint. SAY joined SiC/SiC were tested by four point bending test before and after neutron irradiation. CA joined samples were tested at room temperature by using a new torsion test, adapted from ASTM F734-95 and F1362-97 and modified to obtain miniature samples [10] before and after neutron irradiation.

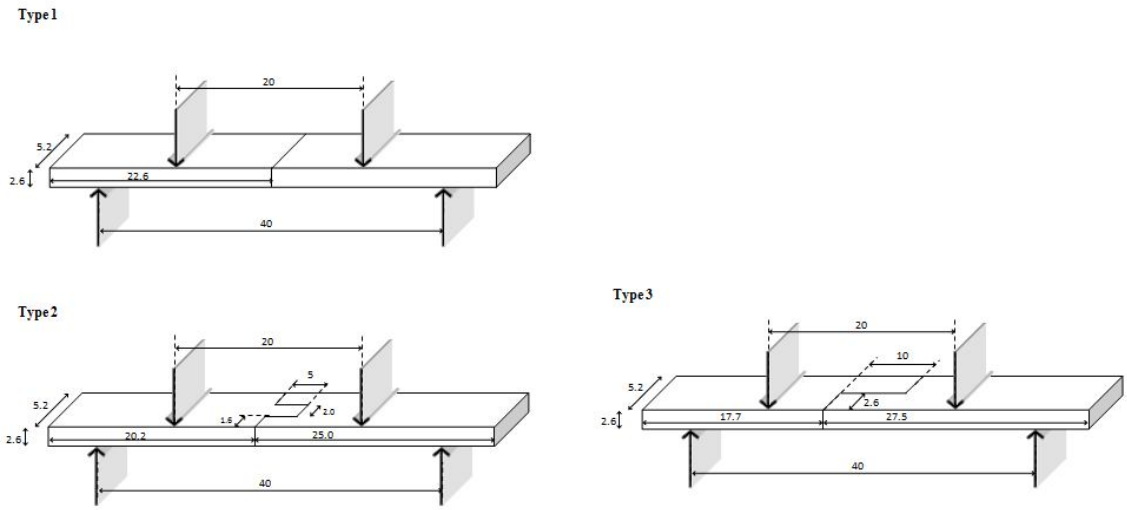

Figure 1. Three different joint configurations of joined SiC/SiC composites tested by four-point bending test. (SiC/SiC thickness = 2.6 mm, width = 5.2 mm, length = 45 mm).

3 Results and discussion

3.1 Glass-ceramics

SiC/SiC (CVD–SiC coated 2D composites) have been joined by SAY glass-ceramic (Figure 2). Three different kinds of joined samples have been manufactured to couple the reliability of a machined joint with the sealant properties of the glass–ceramic joining material. The bending strength results are very promising: higher shear strength than 120 MPa at room temperature were obtained with Type 2 (e.g. Mortise and Tenon like) configuration.

Neutron irradiation tests have been done at HFR-NRG, Petten, NL on the joined samples: the microstructure observed by SEM of SAY joined SiC/SiC before (a) and after (b) irradiation at 600 °C, $16.3 \cdot 10^{24}$ n/m^2 did not change in a detectable way.

The SAY joined SiC/SiC materials of this study remained intact and were apparently unaffected by irradiation up to 820°C, $31\text{-}32 \cdot 10^{24}$ n/m^2. When submitted to bend testing, Type 2 SAY joined SiC/SiC resulted in an encouraging 118 MPa comparable to 122 ± 10 MPa measured on the non-irradiated joined sample [18].

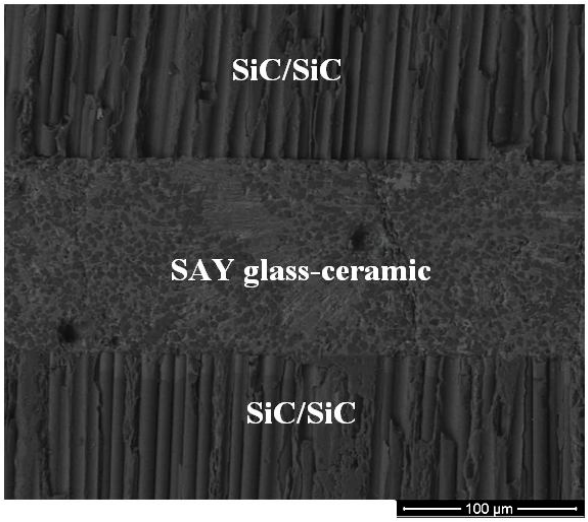

Figure 2. Back-scattered SEM micrograph of the cross-section of a SiC/SiC joined by SiO_2–Al_2O_3–Y_2O_3 (SAY) glass–ceramic.

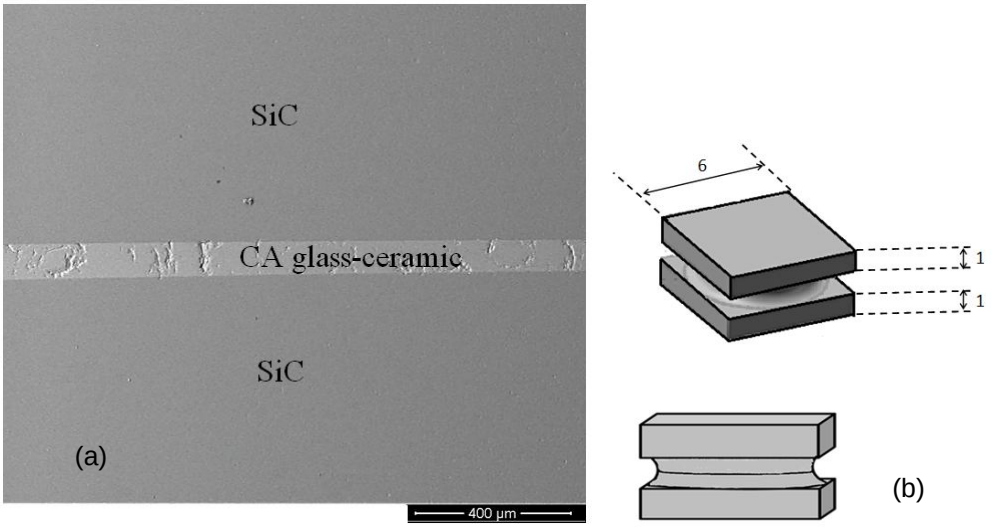

Figure 3. (a) SEM micrograph of the cross-section of a glass hour SiC joined by CaO–Al_2O_3 (CA) glass–ceramic; (c) Sketch of the joined glass hour sample for torsion test (dimensions in mm).

Figure 3 shows a SEM cross section of a CA glass-ceramic joined SiC sample. Figure 3 shows a SEM cross-section of CA joined hourglass, developed in cooperation with ORNL, USA and IAE-Kyoto Univ., Japan (10): the interfaces and CA are continuous and defect free, which is a promising result for a pressure-less joining process. Vertical cracks, due to CTE (coefficient of thermal expansion) mismatch were detected in some areas of joint, but they do not propagate through the CA/SiC interface. Pure shear strength of 104 ± 25 MPa have been measured by torsion tests of CA joined hourglass SiC.

2.2.2. Tungsten/SiC based composite joining material

Figures 4a and 4b illustrate the feasibility of a W-based composite joining material. The cross-section of the two SiC/SiC samples joined by W and preceramic polymer reveals that the wetting of the composites with the W-based material is very good, but large voids, most probably resulting from gas evolution in the early stage of the thermal treatment, are present. W-polymer suspension infiltrated the nearby voids in the SiC/SiC composite and may

contribute the joint strength, but could also have an advantageous effect on the thermal conductivity and strength of the composite.
Figure 4b reveals a homogeneous and relatively dense microstructure of the bulk joining material with closed porosity and small particle size. The XRD analyses of the samples revealed fully crystalline structure and presence of W, WC, W5Si3 and SiC, the composition being strongly dependent on W/polymer ratio. Further work will be therefore focused in avoiding the gas evolution-related voids and optimisation of the joint material properties.

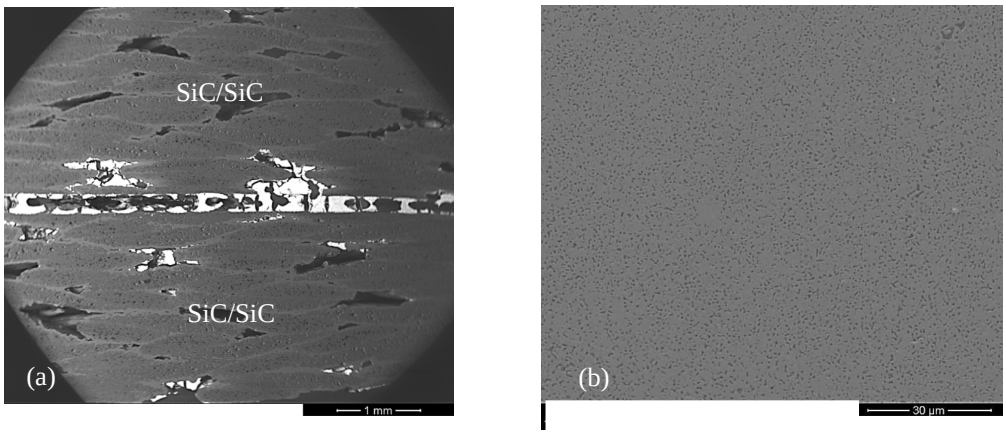

Figure 4. SEM micrograph of (a) the cross-sections of the W-based joint of SiC/SiC composites and (b) bulk W-based joining material

2.2.3. Modified carbon fibre reinforced commercial adhesive
Joining materials and innovative bonding technologies for ultra-stable joints of carbon/carbon composite (C/C) sandwich panels for the manufacturing of next generation space instruments have been studied [19]. The proposed solutions have low coefficient of thermal expansion (CTE) and coefficient of moisture expansion (CME), and a good mechanical strength, in order to guarantee the dimensional stability and mechanical reliability of the joined C/C panels.
The carbon fibre reinforced commercial adhesive (CFA) used to join C/C was chosen because of its carbon based composition after curing process, but the CTE is higher than the requirement established by end-user. In order to reduce the CTE, the commercial adhesive has been modified by adding a negative CTE glass-ceramic (GC) filler. This glass–ceramic was selected for its negative CTE of −1.2×10−6 ◦C−1 (100–300 ◦C); 25 vol.% GC glass–ceramic powder (<105 or <44 μm) has been added. The joined C/C resulted in higher mechanical strengths: 17±3MPa. The scalability of this bonding technology has been assessed on a quite large sandwich panel by ESA (European Space Agency) and Thales Alenia Space (France) [20].

The carbon fibre reinforced commercial adhesive was also reinforced by nano- and micro-SiC powders for a low temperature (300°C), pressure-less joining/repairing process in air for SiC/SiC. The introduction of the 5 wt% SiC particles caused an initial increase in strength on as joined samples, and the use of SiC or nano SiC gave comparable results; further SiC particle addition resulted in a lower shear strength. The microstructure of these joints is shown in Figure 5: the SiC particles homogenously filled CFA pores, reducing joint porosity and then assuring good mechanical strength.
Mechanical characterisation of joined SiC/SiC was performed before and after heat treatment at 1100°C for 1 hour in Ar atmosphere, the maximum working temperature for the SiC/SiC used in this work. The advantage of nano SiC was negligible; furthermore, concentration higher than 10 wt% of nano SiC and of 40 % of SiC resulted in a too viscous joining material.

The bending strength results with the joint Type 2 and 3 are very promising: flexural strength higher than 200 MPa and 90 MPa were obtained before and after heat treatment on machined SiC/SiC at the composites working conditions (1100°C, 1 hour, Ar), respectively.
In particular, the flexural strength of half-lap SiC/SiC joined by CFA+40 wt% SiC, after heat treatment at 1100°C,1 hour under Ar flow, was found 7.4 times higher than for butt-joined SiC/SiC (13±2 MPa) [21]. Research activity is currently on-going in order to increase the effect of machining on flexural strength of joined composites and to exploit the risk-reduction of joints obtained by coupling joining by screws and chemical joining.

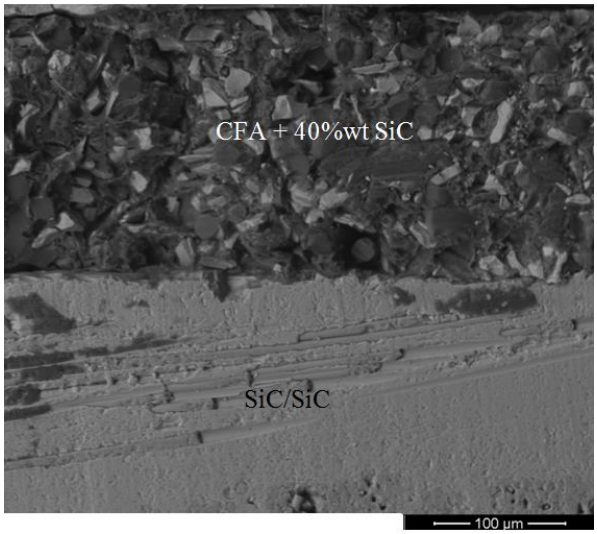

Figure 5. Back-scattered SEM micrograph of the cross-section of SiC/SiC joined by CFA+ 40 wt% SiC (<38 mm) heat treated at 1100°C 1 h in Ar.

4 Conclusions

The feasibility of pressure-less joining techniques for CMC and SiC obtained by using glass ceramics, modification of a commercial adhesive and W/SiC based joining materials has been discussed. Furthermore, the use of glass-ceramics as joining materials in a neutron environment has been demonstrated.
Preliminary study of W-based joining material, prepared by aid of pre-ceramic polymer reveals good wetting of the SiC/SiC and fairly dense microstructure.

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