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Low activation brazing materials and techniques for SiC_f/SiC composites

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Abstract

A low activation brazing technique for silicon carbide fiber reinforced silicon carbide matrix composites (SiC_f/SiC) is presented; this technique is based on the use of the 78Si–22Ti (wt%) eutectic alloy. The joints obtained take advantage of a melting point able to avoid composite fibre-interface degradation. All the joints showed absence of discontinuities and defects at the interface and a fine eutectic structure. Moreover, the joint layer appeared well adherent both to the matrix and the fibre interphase and the brazing alloy infiltration looked sufficiently controlled. The joints of SiC_f/SiC composites showed 71 ± 10 MPa almost pure shear strength at RT and up to 70 MPa at 600 °C.

1. Introduction

SiC_f/SiC ceramic matrix composites (CMCs) are an attractive material for fusion reactors because of their good mechanical properties at high temperature, low chemical sputtering, high oxygen gettering and very low activation at short and medium term [1,2]. Nevertheless, there are some technological issues connected to the long production time, their relatively high porosity and permeability, and the difficulty to accomplish complex geometries which still need to be solved. Moreover, since these materials can only be produced in limited shapes, in order to assemble a complete blanket system, a suitable method of joining SiC_f/SiC components is required. The possibility to set up a junction suitable to withstand service loads (estimated within several blanket design activities), has been under investigation at ENEA.

The basic requirements of a suitable joining technique are the chemical–physical compatibility with the SiC_f/SiC substrate (wettability, thermal expansion), high shear strength, applicability to the joining of large components with no contact pressure, joining temperature below 1400 °C in order to avoid fibre and fibre-interphase degradation, high operating temperature (800–1000 °C) and, for fusion environment, low activation composition, radiation stability and resistance, and good compatibility with breeders.

Several joining techniques are under development. They include: assembling by sewing at textile stage, sticking and co-infiltration during composite component's manufacturing, direct diffusion bonding, homogeneous joining by pre-ceramic polymers, joining by glass and glass ceramic, reaction forming, metallic brazing [3–9]. Among all these techniques, metallic brazing generally leads to high strength bonds and gives well reproducible results. Conversely, special attention has to be paid to the choice of the element in order to avoid the formation of brittle compounds or elevated residual strains.

In this paper, a silicon carbide brazing technique and its performance are illustrated and discussed. The alloy used is based on a eutectic composition of silicon and titanium. This low activation brazing alloy can, in principle, be used for coating SiC_f/SiC composites.

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2. Experimental

Pure silicon has a good chemical compatibility and wettability with silicon carbide (at 1480 °C the contact angle θ between liquid Si and solid SiC is 38° [10]) and has been used both to infiltrate and join SiC_f/SiC composites. Moreover, silicon has a thermal expansion coefficient α similar to that of silicon carbide ($\alpha_{Si}(RT) = 3.0 \times 10^{-6}$ 1/K and $\alpha_{SiC}(RT) = 4.0 \times 10^{-6}$ 1/K). Conversely, the high melting temperature of silicon ($T = 1410°$), the limited joint strength exhibited in a previous work [11] and the differences in neutron-induced swelling behaviour of pure silicon as compared to silicon carbide [12] make its use rather questionable in a fusion reactor environment. The basic idea for the development of a new alloy and brazing technique was the use of a 78Si–22Ti (wt%) eutectic alloy (melting temperature 1330 °C) in order to take advantage of the lower melting point, avoid the composite fibre-interface degradation and the presence of titanium which behaves as an active element in increasing the joint strength via the formation of intermetallic compounds and/or carbides at the interface with silicon carbide.

Several preliminary experiments were performed, trying to obtain 'in situ' the eutectic by melting Si–Ti powder mixtures, directly applied on SiC_f/SiC samples by heating them to a temperature higher than the Si melting point. The results were not satisfactory, because of incomplete melting of mixtures leading to heterogeneities and defects (Fig. 1). Moreover, molten Si has a very low viscosity, and this causes difficulties in the infiltration control both in vacuum and inert atmosphere.

For the above reasons, the eutectic alloy was prepared before the brazing operations, by means of an 'ad hoc' melting procedure able to produce a fine eutectic structure [13]. Powders were then prepared by milling the small ingots obtained, which were subsequently used for the brazing experiments. Firstly monolithic, and then SiC_f/SiC composites samples were brazed.

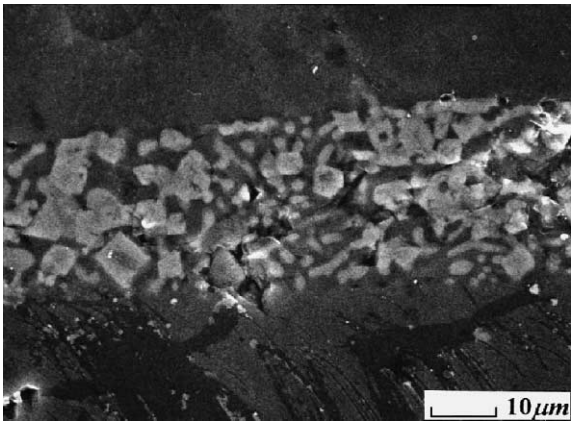

Fig. 1. Morphology of joints performed by direct melting of Si–Ti powders.

The experimental work was carried out by using monolithic polycrystalline SiC (Hexoloy-Carborundum) and a SiC_f/SiC composite produced by SNECMA (CERASEP N3-1), consisting of a pseudo-tri-dimensional weave of Nicalon™ CG fibers, densified by chemical vapor infiltration (CVI) and finally coated by chemical vapor deposition (CVD). The general properties of the composite substrate used can be found elsewhere [14].

The samples used were $12 \times 10 \times 3$ mm^3 plates of monolithic SiC and SiC_f/SiC composite. The surface morphology of the composites was rather complex (roughness $Ra \sim 15$–25 μm, average peak-to-valley height $Rz \sim 100$–150 μm). Direct joining of 'as-received' composite specimens is generally difficult to achieve, because the rough surfaces contain cavities that are hard to be filled. This results in discontinuities or defects in the joint layer. In order to improve the surface quality, the composite specimens were ground to reach a surface roughness in the order of a few microns. The mentioned CVD coating (>100 μm) was partially removed by surface preparation, thus some fibers remained uncoated and participated in the joint formation. For the composite specimens, the real area of contact can be estimated in the order of 80%. The samples were ultrasonically cleaned in acetone prior joining, then the brazing alloy was applied in form of powder or mixed with an organic colloidal compound to form a paste. After overlapping, the samples were loaded with a moderate axial load (1 N) only to the purpose of keeping them in place during the thermal cycle. The joining was performed in vacuum (10^{-4} Pa) or inert atmosphere (Ar + 3% H_2) furnaces. The samples were heated up to the eutectic temperature with a heating rate of 10 °C/min; the hold time at melting temperature was 5 min in vacuum and 30 min in Ar, followed by cooling down to 600 °C (at 20 °C/min) and a natural dwelling time.

3. Characterization of the joints

The joint quality was determined by microstructural examination by scanning electron microscopy (SEM). Fig. 2 shows a SEM picture of the structure of the alloy prior brazing; a fine structure composed of Si and $TiSi_2$ appears from the micrography, and the X-ray diffraction showed no other phase than Si and $TiSi_2$ (Fig. 3).

Cross-section of monolithic SiC and SiC_f/SiC composite joints were examined by SEM equipped with energy dispersive X-ray spectroscopy (EDX). The joint thickness of composite joints is in the range 20–30 μm, but a consistent variation in the thickness can be observed depending on surface conditions; the monolithic specimens' thickness reached values up to 100 μm

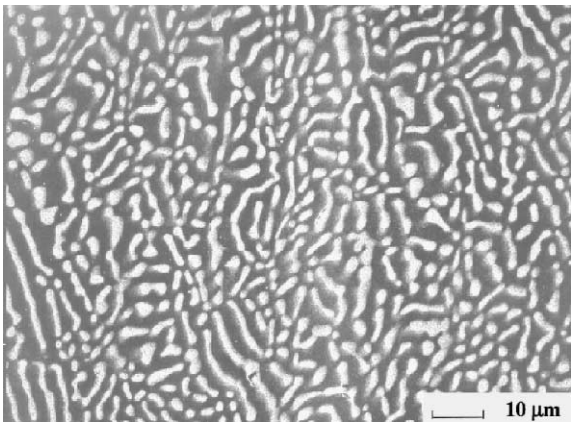

Fig. 2. 78Si–22Ti alloy micrograph before joining process: gray zones = Si; white zones = $TiSi_2$.

(absence of infiltration). In any case, the joint layer showed absence of discontinuities and defects at the interface as a result of a complete melting of powders and a fine eutectic structure, with a morphology comparable with that of the starting powder. In particular, the composite joint layer appear well adherent to the matrix and the fibre interphase (Fig. 4). The infiltration looks sufficiently controlled and is limited to no more of a couple of fabric layers close to the joints.

EDX maps (Fig. 5) showed no macroscopic diffusion of Ti into SiC possibly due to the short reaction time and the absence of free Ti in the brazing alloy. Moreover, no macroscopic reaction layers were visible at the interface

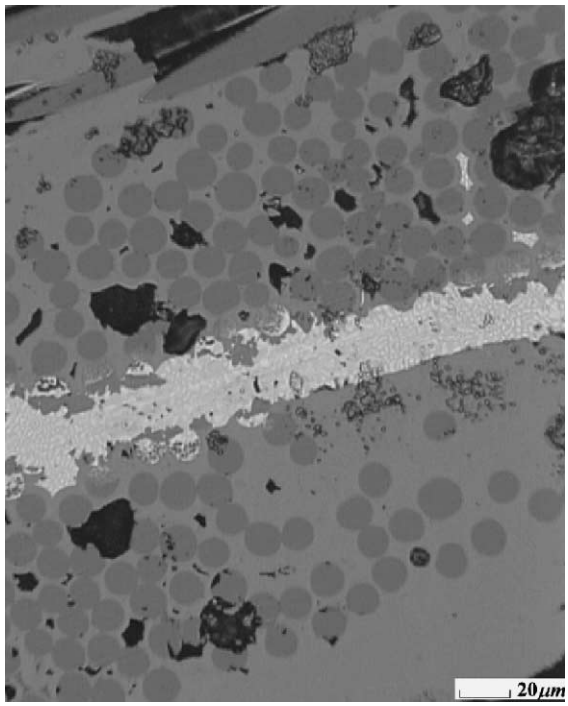

Fig. 4. SEM image of a joint performed between SiC_f/SiC composites.

SiC–Si and thus we believe that the limited interdiffusivity of the Si into SiC and a surface reaction between $TiSi_2$ and SiC are responsible for the strong adhesion of

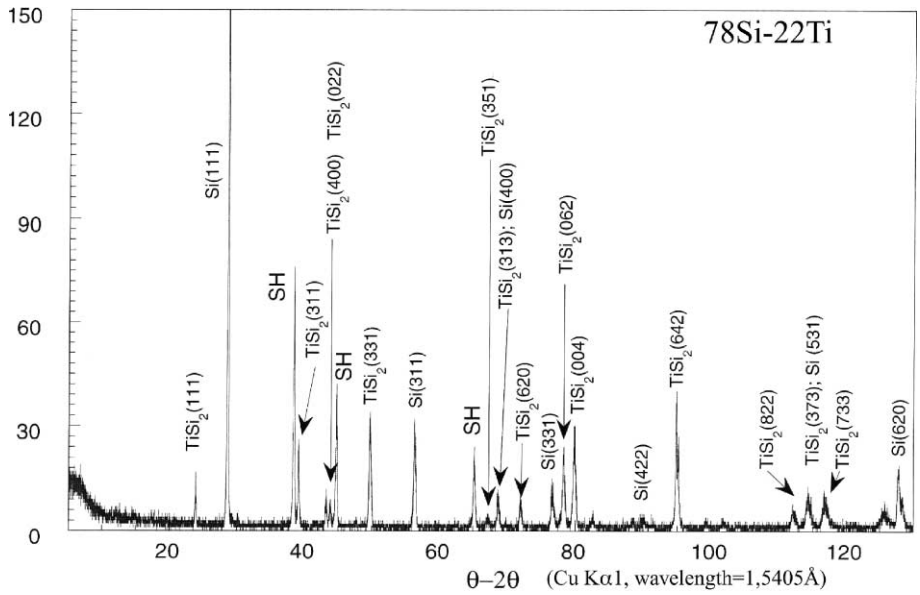

Fig. 3. XRD pattern of 78Si–22Ti alloy (SH = substrate holder in Al).

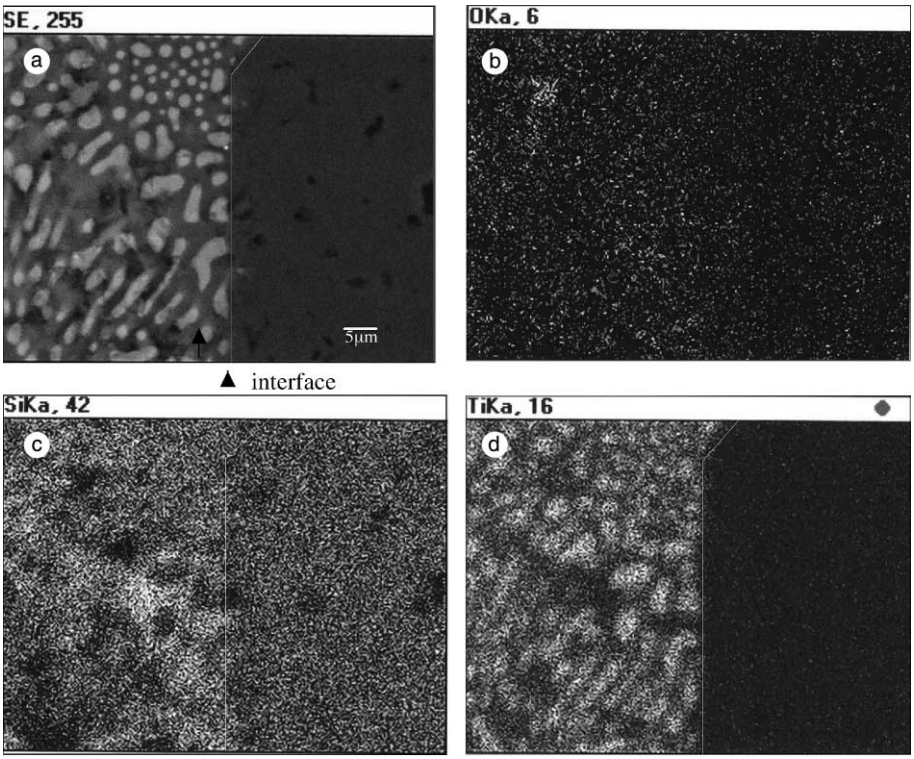

Fig. 5. Oxygen, silicon and titanium mapping at the interface between joint and bulk SiC (EDX): (a) SEM image, (b) oxygen mapping, (c) silicon mapping and (d) titanium mapping.

joints. This aspect will have to be investigated more in detail.

The joint performances were determined by means of shear tests, performed following an ad hoc modification of the ASTM D905-89 test procedure [7]. The crosshead speed was 0.6 mm/min. Even if the presence of a pure shear stress field was not assured by this procedure, it was however a suitable method to obtain a rather good estimation of shear strength and a good mean for a comparative evaluation of the performances of specimens obtained with different process parameters. The strength values were computed by estimating the joint area for each sample. Shear test performed at room temperature and 600 °C gave remarkable results: the samples manufactured with monolithic SiC cracked at 50 MPa at RT, while the composite samples exhibited 71 ± 10 MPa shear strength at RT and up to 70 MPa at 600 °C. Generally, the joints made in the vacuum furnace showed better performances because of their better control of thermal cycle. Observation of the fracture surfaces revealed that failure was always cohesive. In monolithic samples, the failure started sometime at the joint interface but propagated in the bulk SiC. In the composite samples, the failure always occurred in the composites (Fig. 6), leading to the conclusion that the limiting parameter was the shear strength of the

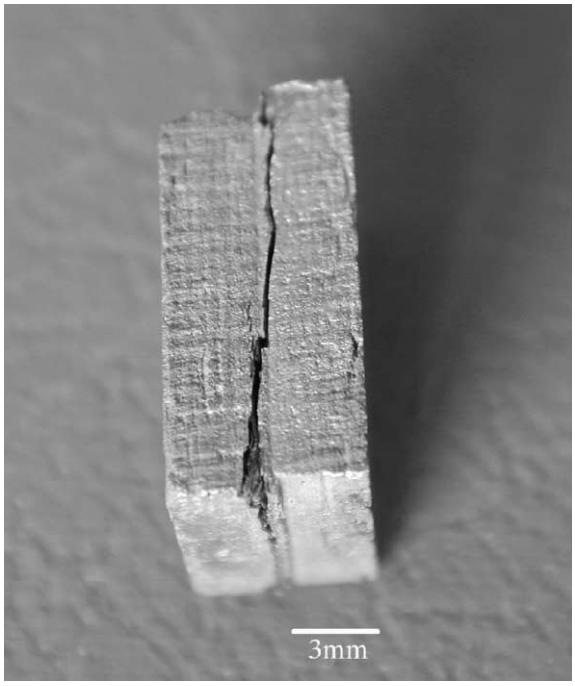

Fig. 6. Typical specimen failure image.

composite. From the results obtained, it appears that the joint strength depends on a few parameters (substrate roughness and porosity, thermal cycle) but the performance is sufficiently reproducible.

4. Conclusions

The proposed joining technique, which employs an eutectic Si–Ti alloy, seems suitable for joining large surfaces of SiC_f/SiC composite, such as those that will need to be fabricated for the breeding blanket of fusion reactors. In fact, in this way it is possible to obtain joints with reduced residual stresses and thermo-mechanical properties similar to those of the SiC_f/SiC composites with really low activation.

Nevertheless, the technique has some disadvantages, namely the need of grinding the surfaces to joint in order to get tight tolerances. The stability of the joints under irradiation is the most important item to be assessed, in order to demonstrate the suitability of the alloy for fusion application. The activity is continuing by investigating the performances of other eutectic alloys, such as for example Si–Cr.

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