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Issues of low activation brazing of SiC_f/SiC composites by using alloys without free silicon

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Abstract

The paper presents a novel low activation brazing technique for SiC_f/SiC composites. The brazing alloy does not contain free silicon and is based on the use of a Si–44Cr at.% eutectic and the intermetallic $CrSi_2$ (melting temperatures 1390 and 1490 °C, respectively). These are advantageous because the melting point is low enough to avoid degradation of the advanced fibres and of the interphases in the composite, and the Si–Cr intermetallics are chemically compatible with silicon carbide. Both the eutectic and the intermetallic were prepared before brazing operations by melting a Si–Cr mixture. The joining was performed under vacuum (about 10^{-4} Pa). Systematic investigations of the microstructure and of the nanochemistry (TEM, EELS, ELNES) of the Si–Cr joints reveal that direct chemical Si–Si, Cr–C and Si–Cr bonds across the interface are responsible for the adhesion: the interfaces were proved to be nearly atomically sharp and adhesive. Altogether, this brazing procedure enables joints with sufficient strength and with a microstructure comparable with that of the starting powders to be obtained.

1. Introduction

SiC_f/SiC composites are under development worldwide because of their attractive high temperature properties and increased reliability in comparison with un-reinforced SiC [1]. Due to low activation under irradiation, their use in future fusion reactors has been recognized as very promising provided that some critical issues such as radiation stability, insufficient thermal conductivity, lack of gas tightness and of suitable joining techniques are overcome [2]. In particular a robust joining technique is necessary in order to manufacture complex systems such fusion reactor blankets. The possibility of setting up a joining technique suitable for withstanding fusion reactor service loads is under investigation at ENEA.

Among several joining techniques under development [3–7], brazing is one of the most promising [8]. The requirements of a suitable brazing material for SiC_f/SiC composites are: chemical compatibility and wettability with SiC substrate, thermal expansion coefficient similar to that of the SiC substrate, high shear strength and a brazing temperature low enough to avoid the degradation of the fibres and the fibre-matrix interface.

Si–16Ti and Si–18Cr at.% eutectic alloys have been already studied in a previous activity [9,10] and they were found to satisfy the requirements of a fusion relevant brazing technique such as low neutron activation, suitable brazing temperature, good wettability and compatibility with the composite. Conversely, both the alloys have a pure Si phase and the neutron induced swelling of pure silicon, which is different from that of SiC [11], can in principle limit their use in a fusion

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reactor environment. The radiation stability of these alloys is currently going to be investigated.

This paper presents our recent activity on the development of a brazing technique based on the use of Si–Cr alloys, free of a pure silicon phase.

2. Experimental

Si–Cr phase diagram [12] show the presence of two compositions of interest not containing free Si: Si–44Cr at.% and Si–33.3Cr at.% with melting points of 1390 and 1490 °C respectively. The Si–44Cr is a eutectic composed of two intermetallics i.e., CrSi and $CrSi_2$; the second composition is the $CrSi_2$ intermetallic alone.

The joining cannot be performed simply by using Si and Cr powder mixtures because in this way it is not possible to get the above-mentioned eutectics 'in situ'. Therefore, the alloys had to be prepared previously, by means of a procedure consisting in a plasma torch and electron beam melting of Si–Cr mixtures [13]. Fig. 1 shows a SEM picture of the Si–44Cr alloy prior to brazing; evidencing a microstructure composed of big $CrSi_2$ isles surrounded by a fine CrSi–$CrSi_2$ eutectic. X-ray diffraction (XRD) confirmed that no phases other than CrSi and $CrSi_2$ were detected in the alloy. SEM examinations of the $CrSi_2$ intermetallic showed the presence of only one phase and XRD confirmed that no other phases than $CrSi_2$ were present.

After melting, the obtained ingots were reduced to powders (10–50 μm size) by crushing and milling and finally used for the brazing experiments. The joining was carried out by using a SiC_f/SiC composite produced by SNECMA (CERASEP® N3-1). The material consists of a pseudo tri-dimensional weave of Nicalon™ CG fibres, densified by chemical vapour infiltration (CVI) and finally SiC coated by chemical vapour deposition (CVD) up to a thickness of 100 μm. The typical properties of the composite used are reported elsewhere [14]. In all activities, the above composite has shown the necessary chemical stability at the brazing temperature used.

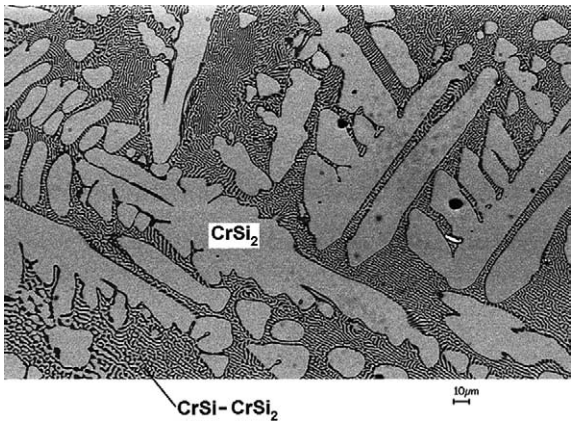

Fig. 1. Micrography of Si–44Cr alloy before the joining process: grey zones = Si; white zones = $CrSi_2$.

The samples to join were $12 \times 10 \times 3$ mm^3 plates that were polished in order to reach a surface roughness on the order of a few microns thus increasing the contact area. In this way the CVD coating was partially removed by surface preparation, thus some fibres remained uncoated and exposed to the brazing alloy.

After ultrasonic cleaning in acetone and the application of the brazing alloy between the two pieces to be joined, the samples were inserted in the oven and kept in contact during thermal cycle with a small load. The joining was carried out in a vacuum furnace (10^{-4} Pa) in order to suppress undesirable reactions with oxygen. The samples were heated up to a temperature 30–50 °C higher than the melting point with a heating rate of 10 °C/min; the hold time at melting temperature was about 10 min; cooling down to 600 °C was performed at 20 °C/min followed by natural cooling down to room temperature.

3. Microstructure and nanochemistry

At first, all the joints were examined to detect macroscopic defects or cracks. Afterwards cross-sections of monolithic SiC and SiC_f/SiC composite joints were examined by scanning electron microscopy (SEM). For both alloys, the joint thickness was in the range 10–50 μm and varies according with the profile of the joined sample and the amount of powder used. The duration of the brazing cycle allowed the infiltration of the brazing alloy in the composites to be sufficiently controlled. SEM micrographs (Figs. 2 and 3) showed a fully melted alloy but also some discontinuities in the brazing layer of Si–44Cr joints and small cracks in the $CrSi_2$ joints. Nevertheless, no macroscopic reaction layers were visible at the interface.

In order to study the interface microstructure and the nature of the bonds between the brazing alloys and the SiC_f/SiC composites, investigations were performed by transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) for chemical analysis (cf., e.g., [15,16]). The EELS method allowed an estimation of the kind and concentration of the chemical elements with a spatial resolution in the order of 1–2 nm. In particular, the analysis of the near-edge fine structures (ELNES) of the relevant ionisation edges allowed to characterise the chemical bonding state of individual elements to be characterised with the same resolution. As an example, the chemical analysis of the Si–44Cr alloy is detailed in Fig. 4. A set of EEL spectra Fig. 4(a) were obtained across individual interfaces Fig. 4(b). In Fig. 4(c) the chemical bond specific ELNES of the

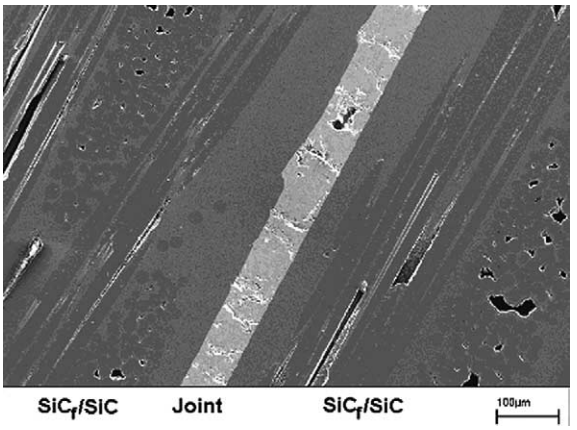

Fig. 2. SEM image of a Si–44Cr brazed joint.

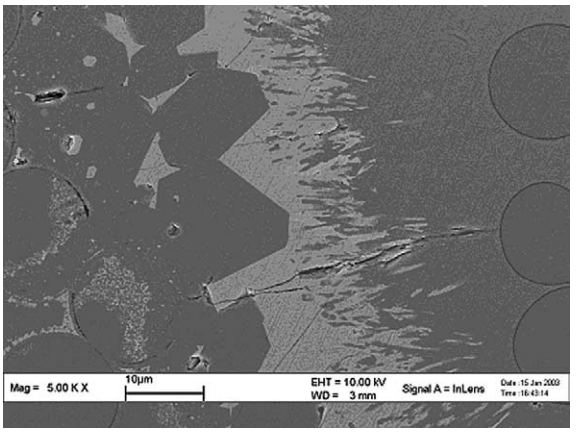

Fig. 3. SEM image of a $CrSi_2$ brazed joint.

Si–L_{23} edge of selected spectra are magnified with the background subtracted. It can be seen that the interface spectrum is almost the sum of SiC and SiCr standard spectra. From these findings it must be concluded that all the analysed interfaces between the substrate and the brazing alloy could be proved to be nearly atomically sharp and adhesive, i.e., there is no detectable interdiffusion or formation of new phases by chemical reaction. Thus, the high strength macroscopically measured in these joining systems must be attributed to direct chemical Si–Si, Cr–C and Si–Cr bonds across the interface.

TEM images showed that in the brazing alloys the joint layer consists of $CrSi_2$ grains of several micrometers in diameter while in SiC–44Cr sample grains of SiCr were also detected. Further on, as can be seen in Figs. 5 and 6, the interface of the joining part of both materials has a pronounced serrated or tongue-shaped appearance so that a strong interaction and high joining forces are expected. Therefore the appearance of cracks in the

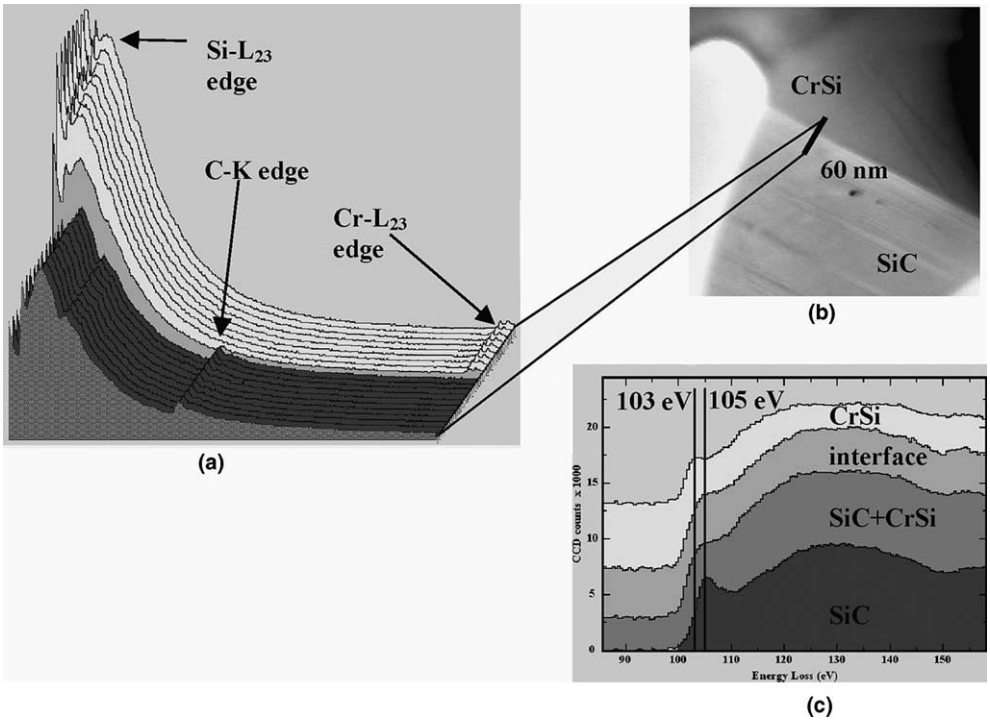

Fig. 4. Nanochemistry of the interface between SiC and SiCr, (a) series of EEL spectra (separation 2.5 nm), (b) TEM image, (c) Si–L_{23} ELNES of selected spectra.

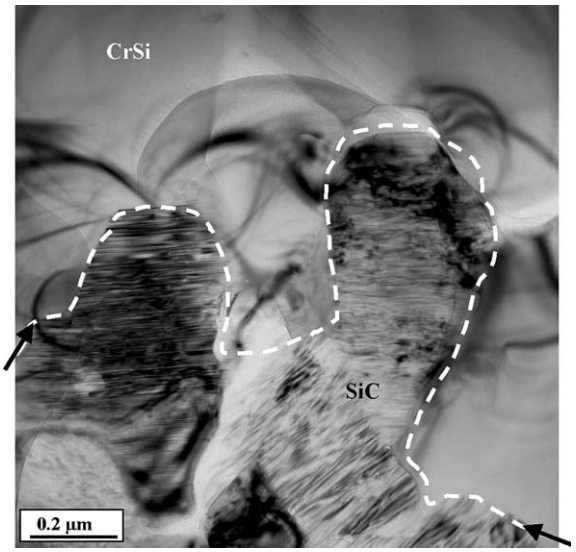

Fig. 5. TEM image, showing the microstructure of the interface between SiC brazed with Si–44Cr at.% eutectic.

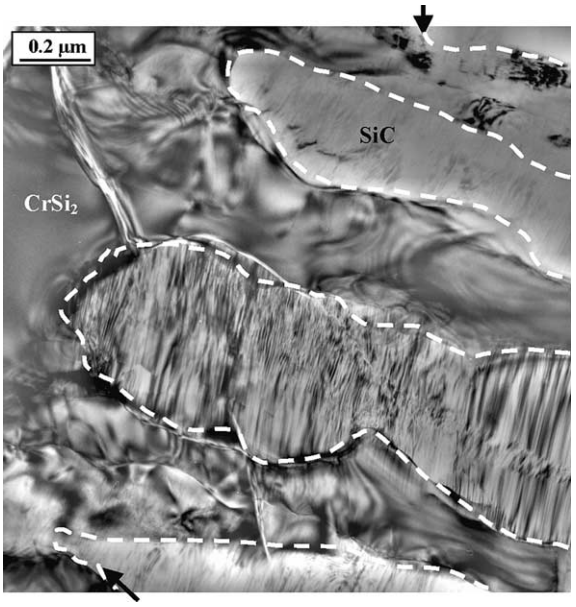

Fig. 6. TEM image, showing the microstructure of the interface between SiC brazed with $CrSi_2$ intermetallic.

joints should result from the thermal expansion mismatch between the SiC bodies tightly bonded with the brazing alloy.

4. Shear test

The shear strength is one of the most important properties to estimate the reliability of a joining technique. In this work, the shear tests were performed following a modification of the ASTM D905-98 test procedure already set up and used [17]. In particular, this method provides a simple procedure to obtain a rather good estimation of the shear strength and a good way for a comparative evaluation. The test have been performed at RT for all the joints realized. The crosshead speed was 0.6 mm/min.

Table 1
Comparison of the strength of joints obtained by using different brazing alloys

Joint	Si–16Ti	Si–18Cr	Si–44Cr	$CrSi_2$
Shear strength (MPa)	71 ± 10	80 ± 10	66 ± 20	64 ± 5

The results can be summarised as follows. The samples joined by using the Si-44Cr eutectic exhibited a shear strength of 66 ± 20 MPa. The samples joined by using $CrSi_2$ exhibited a shear strength of 64 ± 5 MPa. Table 1 shows a comparison of the shear strength of joints obtained in our previous activities [10], i.e., Si–16 Ti and Si–18Cr at.% joints, and the current ones.

The shear strength is similar to those obtained by high performance reaction forming technique but tested with a different method [18]. Moreover, all the tests, carried out at least on five specimens for each type of brazed joints, gave sufficiently reproducible results with a limited scattering. The joint strength was slightly affected by the residual roughness and open porosity of the composite substrate.

In the joining analyzed, failure sometimes occurred in the composites in Si–44Cr joints and always at the interface in $CrSi_2$ joints. The alloys described in this work have lower strength in comparison with our previous ones (obtained by means of Si–16Ti and Si–18Cr). As already noticed direct chemical bonds between the alloys and SiC_f/SiC are responsible for the adhesion and thus account for the shear strength performances. However, the joints presented here also showed some macroscopic defects due to the elevated thermal expansion mismatches between SiC and brazing alloy after cooling from melting temperature; moreover, the effects of these mismatches are not reduced by the deformation of the brazing layer which is composed of hard and brittle intermetallics.

5. Conclusions

A brazing technique for SiC_f/SiC composites has been presented and discussed. By using Si–44Cr and $CrSi_2$ alloys, joints with interesting shear strength have been obtained. The SEM analysis of the joints realised showed that the brazing alloy infiltration looked sufficiently controlled, the alloy microstructure was maintained after joining. Nevertheless, the occurrence of

cracks due to thermal expansion mismatch, mainly for $CrSi_2$, as well as discontinuities for eutectic Si–44Cr joints, was observed. Systematic investigations of the microstructure and of the nanochemistry (TEM, EELS, ELNES) of Si–Cr joints led to the conclusion that direct chemical bonds are responsible for the adhesion. Shear tests of the joints of SiC_f/SiC composites showed quite remarkable values of the bonding strength (about 60 MPa) although the above mentioned defects.

To assess the suitability of the alloy for fusion reactor application, joint irradiation performances shall be assessed in the near future.

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