

Brazing of SiC and SiC_f/SiC composites performed with 84Si-16Ti eutectic alloy: microstructure and strength

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The microstructure and strength of brazed joints for monolithic SiC and SiC_f/SiC composites are presented and discussed; the brazing technique is based on the use of the 84Si-16Ti (at%) eutectic alloy. The rather low melting point of the used alloy allows to avoid a degradation of the fibre/matrix-interfaces in the composite materials. All the joints did not show any discontinuities and defects at the interface and revealed a fine eutectic structure. Moreover, in the case of composites, the joint layer appeared well adherent both to the matrix and the fibre interphase, and the brazing alloy infiltration looked sufficiently controlled. High resolving electron microscopic investigations of the microstructure and of the nanochemistry (HREM, EELS, esp. ELNES) revealed atomically sharp interfaces without interdiffusion or phase formation at the interlayer leading to the conclusion that direct chemical bonds are responsible for the adhesion. The joints of SiC_f/SiC composites showed 71 ± 10 MPa shear strength at RT and nearly the same values at 600°C.

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1. Introduction

SiC ceramics and SiC fibre reinforced ceramic matrix composites (SiC_f/SiC CMCs) are considered one of the most promising class of structural materials for some aerospace and energy conversion applications, because of their good mechanical properties and chemical stability at high temperature [1, 2]. Nevertheless, there are some technological issues connected to the materials properties, such as the brittleness of monolithic shapes and the relatively high porosity and permeability of CMCs, and to the production processes such as the difficulty to manufacture large components and complex geometries which still need to be solved. Therefore, in order to assemble complex components, a suitable method of joining SiC_f/SiC components is required.

The basic requirements of a suitable joining technique are the chemical and physical compatibility with the SiC substrate (wettability, thermal expansion), high shear strength, applicability to the joining of large components possibly with no contact pressure, joining temperature that must be below 1400°C in order to avoid

fibre and fibre-interphase degradation in the composites, and high operating temperature.

Several joining techniques are under consideration: Mechanical interlocking is capable to give high strength joints in a wide range of temperature but it doesn't guarantee hermetic sealing of the joined components [3]. Diffusion bonding of bulk silicon carbide has been attempted by using metals and SiC itself [4, 5] but this technique has the disadvantage to require pressure and joining temperatures which are too high for the SiC_f/SiC composites. Joining by glass or glass ceramic [6] is a quite simple technique able to provide joints with tailorable properties but of poor strength. Joining by preceramic polymers [7–9] is a promising technique which consists in applying the polymer in form of liquids or slurries to be converted into material similar to SiC even at temperature as low as 1200°C, but so far these joints exhibit low strength. Reaction bonding provides joints starting from silicon-carbon mixtures (sometime with addition of silicon carbide or sintering aids) which are forced to react at elevated temperatures to form silicon carbide: this technique shows

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high performances but needs high temperatures and sometime it exhibits elevated porosity [10]. Finally, the metallic brazing generally leads to high strength bonds and gives well reproducible results [11, 12]. Nevertheless, special attention has to be paid to the choice of the brazing filler, in order to avoid the formation of brittle compounds or elevated residual stresses.

Brazing of ceramics involves the use of a material which forms a liquid phase during the joining process; the brazing alloy must be chemically compatible with the ceramics to be joined and must have in principle good wettability; if this is the case, the braze material forms strong bonds. On the other hand, self diffusion rate in non oxide ceramics is low and thus bonding due to brazing is mainly due to chemical bonds formed by braze and ceramic and eventually to the braze diffusion into the ceramic. Two types of alloys are generally used [13]: noble metal braze (Ag, Pt, Cu, Ni etc) and reactive metal braze (Ti, Al, etc). Brazing with reactive metals requires the process to be strictly controlled to prevent undesirable reactions between the ceramic and the alloy. The possibility to use silicon as braze for silicon carbide has been investigated in previous works [14] without active metal filler. In effect, pure silicon has a good chemical compatibility and wettability with silicon carbide (at 1480°C the contact angle between liquid Si and solid SiC is 38° [15]) and has been also used to infiltrate SiC_f/SiC composites. Moreover, silicon has a thermal expansion coefficient α similar to that of silicon carbide: $\alpha_{\text{Si}}(\text{RT}) = 3.0 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{\text{SiC}}(\text{RT}) = 4.0 \times 10^{-6} \text{ K}^{-1}$. Conversely, the limited resulting joint strength makes its use rather questionable. Moreover, the silicon high melting point ($T = 1410^\circ\text{C}$) may degrade the fibres or fibre-matrix interfaces.

In this paper, a novel silicon carbide brazing technique is illustrated and discussed. The alloy used is based on an eutectic composition of silicon and titanium.

2. Experimental

The basic idea for the development of a new brazing alloy technique was the use of the Si-Ti eutectic alloy (melting temperature 1330°C) in order to take advantage of the rather low melting point, and the presence of titanium which behaves as an active element. The Si-Ti phase diagram [16] shows the presence of two eutectics of interest (84Si-16Ti at% and 13.5Si-86.5Ti at%) both with a melting point of 1330°C. The 84Si-16Ti eutectic is composed of free silicon and TiSi₂, while the 13.5Si-86.5Ti is composed of free Ti and Ti₅Si₃. The second eutectic was discarded because of the reactivity of free Ti with SiC ($\Delta G_{\text{TiC}} < \Delta G_{\text{SiC}}$ at all temperatures). The effects of this potential displacement reaction were verified by melting in vacuum (10^{-6} mbar) a small quantity of this eutectic on a SiC tile which was converted for a depth of about 500 μm with complete detachment of the reaction product.

Concerning 84Si-16Ti, preliminary joining experiments were carried out by melting Si-Ti powder mixtures applied on SiC and SiC_f/SiC samples and trying to obtain directly the eutectic structure during the brazing cycle performed at a temperature slightly higher than the Si melting point. However, these trials were not able to produce the eutectic structure, and thus the brazing layer showed an incomplete melting of the mixtures and, consequently, inhomogeneities and defects (Fig. 1) as well as a lack of infiltration control both in vacuum and inert atmosphere.

For these reasons, the eutectic alloy was previously prepared, by means of a melting procedure, able to produce a fine eutectic structure (Fig. 2) [17]. Small ingots were obtained by plasma melting of Si-Ti mixtures which were then re-melted several times by electron beam melting. Powders to be used for the brazing experiments were then prepared by crushing and milling the small ingots.

The experimental work was carried out by using monolithic polycrystalline β -SiC (Hexoloy-SA

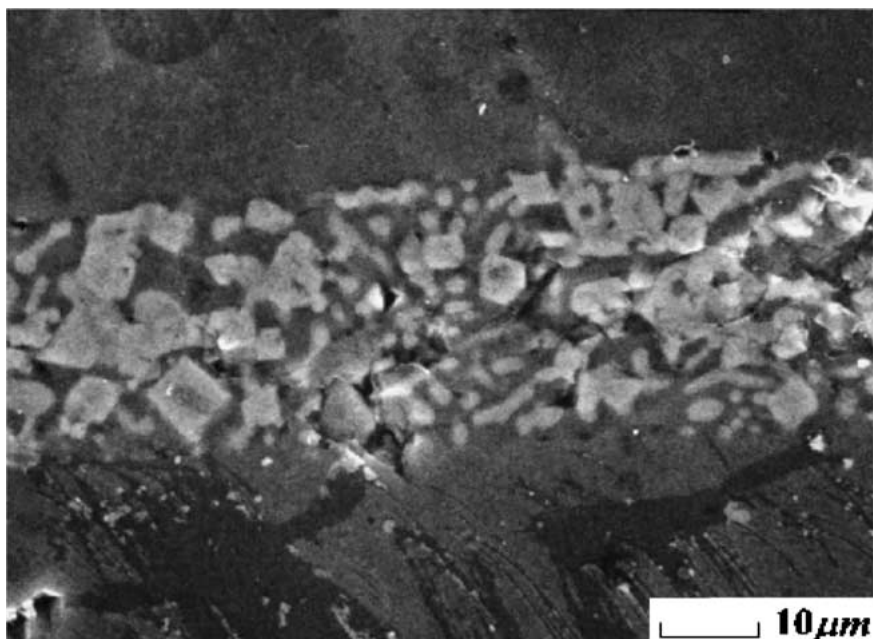


Figure 1 Morphology of joints performed by direct melting of Si-Ti powders.

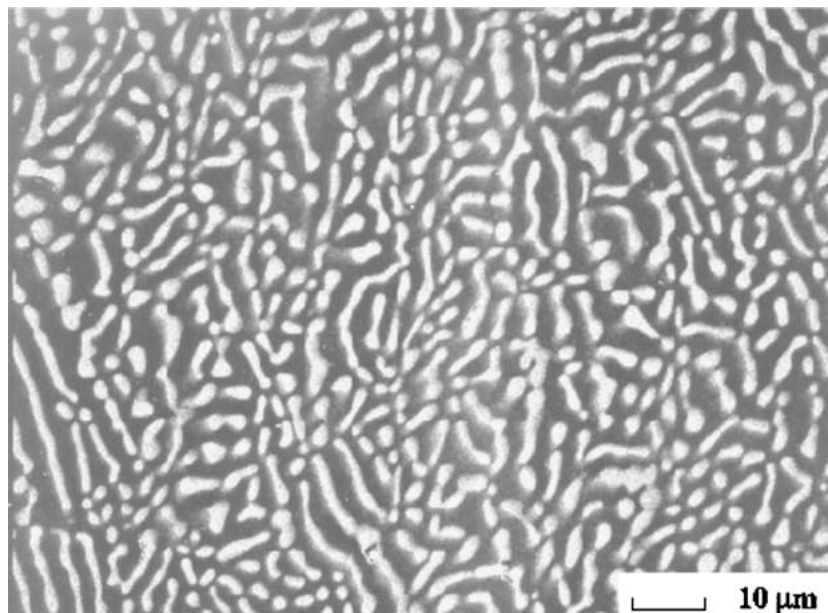


Figure 2 84Si-16Ti alloy micrography before joining process: grey zones = Si; white zones = TiSi₂.

TABLE I Main properties of Hexoloy-SA[®] Carborundum

Property	Temperature (°C)	
Density	20	3.07 g/cm ³
Apparent porosity	20	0%
Young's modulus	20	350 GPa
Thermal expansion coefficient	20–1000	4.02 × 10 ⁻⁶ 1/K
Modulus of rupture (MOR)	20–1600	380–410 MPa

TABLE II Main properties of SNECMA-CERASEP[®] N3-1 composite

Property	Temperature	
	20°C	1000°C
Density	2.4–2.5 g/cm ³	—
Thermal expansion coefficient	4.0 × 10 ⁻⁶ 1/K	—
Tensile strength (in plane)	300 MPa	—
Tensile strain (in plane)	≥0.6%	0.3–0.4%
Trans laminar shear strength	(200–20) MPa	—
Inter-laminar shear strength	40 MPa	30 MPa
4 points bending strength	600 MPa	—

[®] Carborundum) and a SiC_f/SiC composite produced by SNECMA (CERASEP[®] N3-1), consisting 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). The typical properties of the monolithic and composite substrates used are reported in Tables I and II [18, 19].

The samples used were 12 × 10 × 3 mm³ plates both of monolithic SiC and SiC_f/SiC composite. The R_a roughness of Hexoloy was in the order of 1 μm. The surface morphology of the composites was rather complex (roughness R_a ~ 15–25 μm, average peak-to-valley height R_z ~ 100–150 μm). 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 fibres remained uncoated and were in contact with the brazing

alloy. For the composite specimens, the real area of contact could be estimated to be about 80%.

All the samples were ultrasonically cleaned in acetone prior to joining, then the brazing alloy was applied in form of powder or mixed with an organic colloidal compound able to form a paste. After overlapping, the samples were loaded with a moderate axial load (0.1 Kg) with the only purpose of keeping them in place during the thermal cycle. The joining was performed in vacuum (10⁻⁶ mbar) or inert atmosphere (Ar + 3% H₂) 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 about 10 min in vacuum and 30 min in Ar; cooling down to 600°C was performed at 20°C/min followed by natural cooling down to room temperature.

3. Microstructure and nanochemistry

The joint quality was firstly determined by microstructural examination by using scanning electron microscopy (SEM). Fig. 2 shows a SEM picture of the alloy prior to brazing; evidencing a fine and homogeneous microstructure composed of Si and TiSi₂. By X-ray diffraction no other phases than Si and TiSi₂ were detected (Fig. 3).

Cross-sections 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 composites was in the range 20–30 μm, but a consistent variation in the thickness could be observed depending on the surface conditions; the joint thickness of monolithic specimens was generally higher due to the absence of infiltration in the impervious SiC; the values ranged from few tenth of microns up to 100 μm depending on the amount of braze deposited between the pieces to be jointed. In any case, the joint layer showed absence of discontinuities and defects at the interface as a result of a complete melting of the powders, and a fine eutectic structure, with a morphology comparable with that of the starting powder (Fig. 4a). In particular,

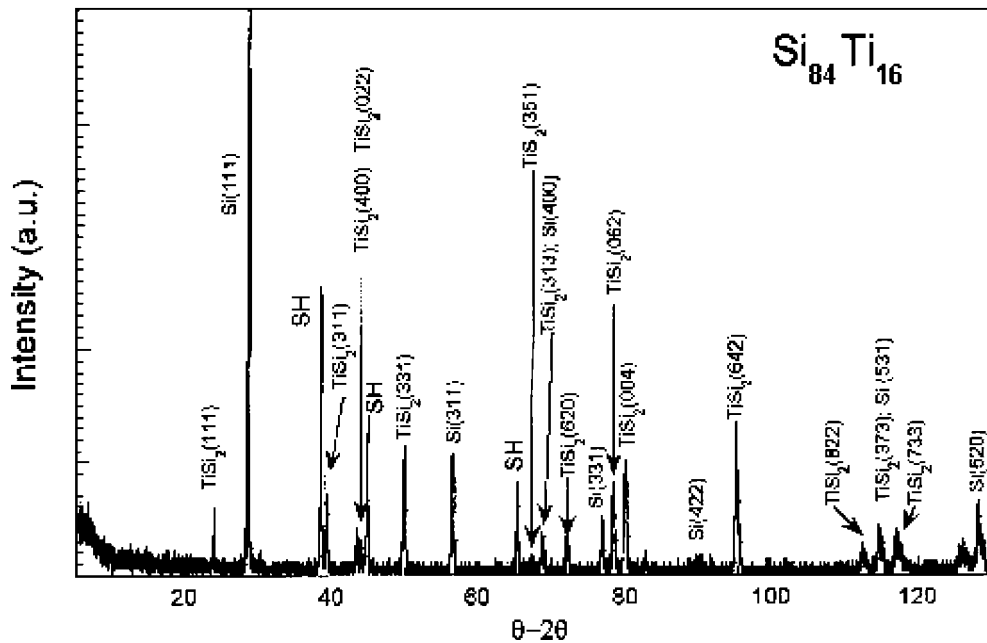


Figure 3 XRD pattern of 84Si-16Ti alloy.

in the joints of composites the infiltration looked sufficiently controlled and limited to no more than a couple of fabric layers close to the joints (Fig. 4b).

EDX maps (Fig. 5) showed absence of Ti within SiC (close to the joint interface). No macroscopic reaction layers were visible at the interface SiC-Si.

In order to study the interface structure and the nature of the bonds between the eutectic and the SiC and SiC_f/SiC composites, investigations were performed by transmission electron microscopy (TEM) including high resolution or atomic plane imaging (HREM), and electron energy-loss spectroscopy (EELS) for chemi-

cal analysis (cf., e.g., [20–22]). The specimens were prepared in such a way that the interface between the joining body and the brazing material could be observed side by side on the same image (cross sectional preparation). These seen end-on interfaces are marked by arrows on most of the related images.

The EELS method allowed to estimate the kind and concentration of the chemical elements with a spatial resolution limited by the diameter of the measuring probe (1–2 nm). In particular, the analysis of the near-edge fine structures (ELNES) of the relevant ionisation edges, which are caused by excitations of core-shell

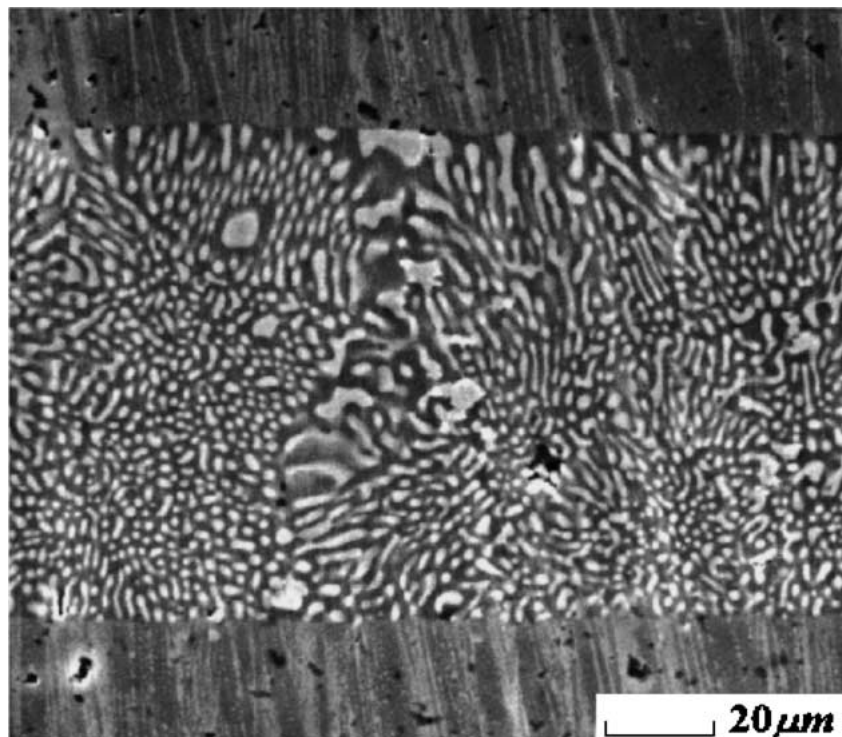


Figure 4 (a), (b) SEM images of a joint performed between SiC_f/SiC composites. (Continued.)

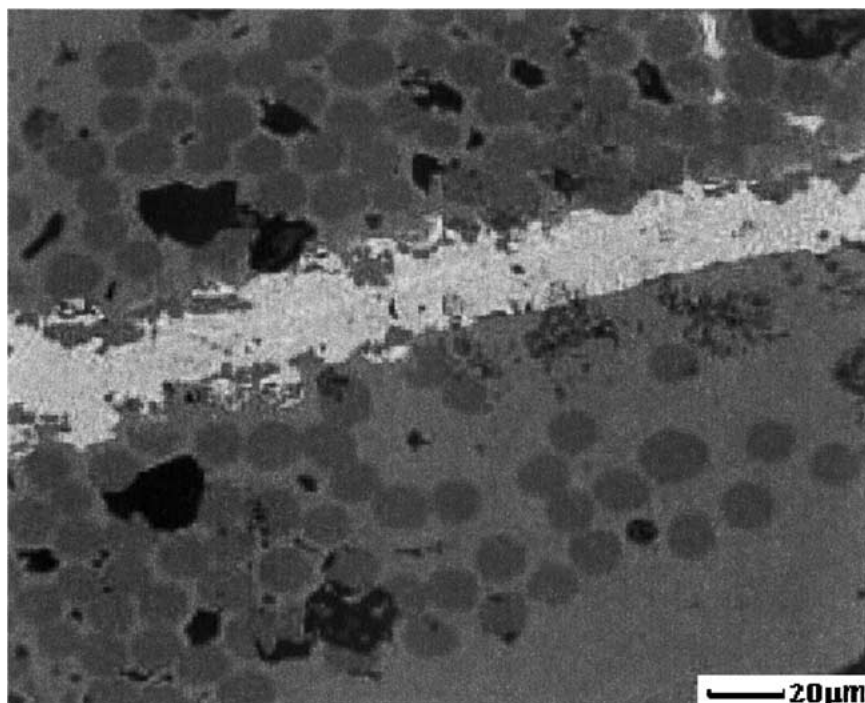


Figure 4 (Continued).

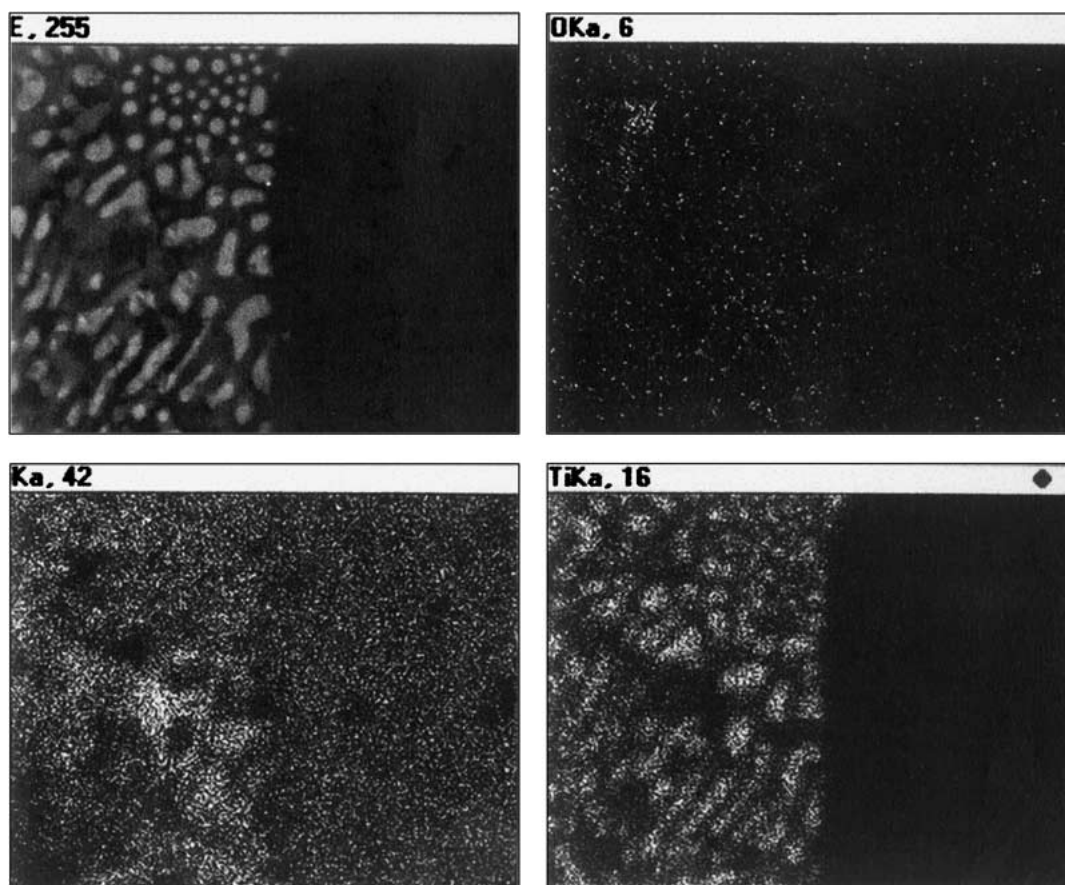
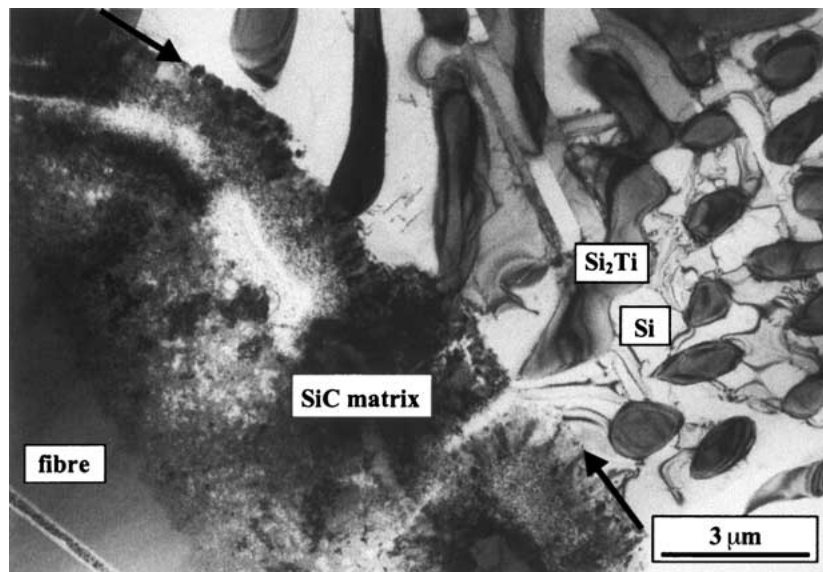


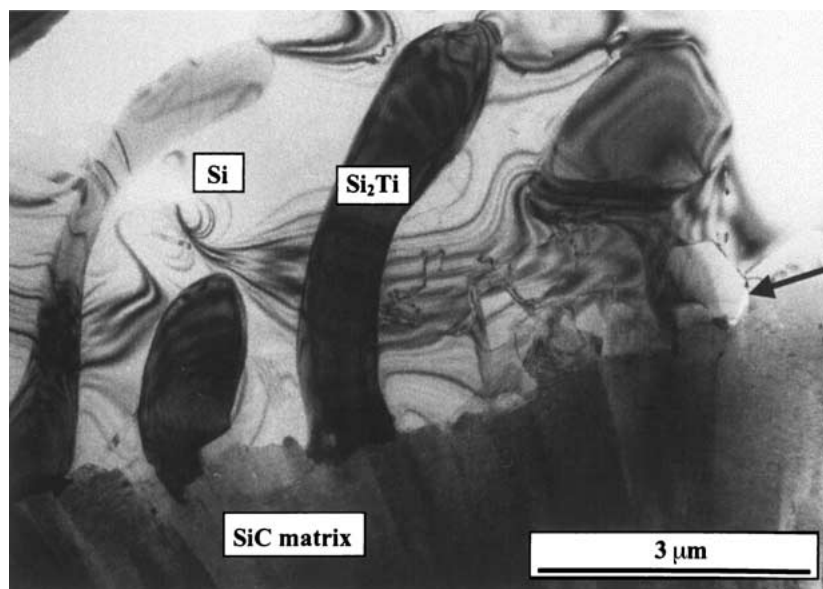
Figure 5 Oxygen, silicon and titanium mapping at the interface between joint and bulk SiC (EDX).

electrons into unoccupied states above the Fermi level, allows to characterise the chemical bonding state of individual elements with the same resolution. The characteristic ELNES details are the edge onset as well as the shape, the position and the intensity of individual peaks in the fine structure. The ELNES features were interpreted by comparing with related standard spectra.

Due to the limited spatial resolution, in the presence of an atomically sharp interface, the probe may detect the elements of both sides of the interface, i.e., a slight, virtual overlapping can not be excluded. In such a situation the EELS spectrum of the interface can be simulated by simple adding the spectra of both sides of it.



(a)



(b)

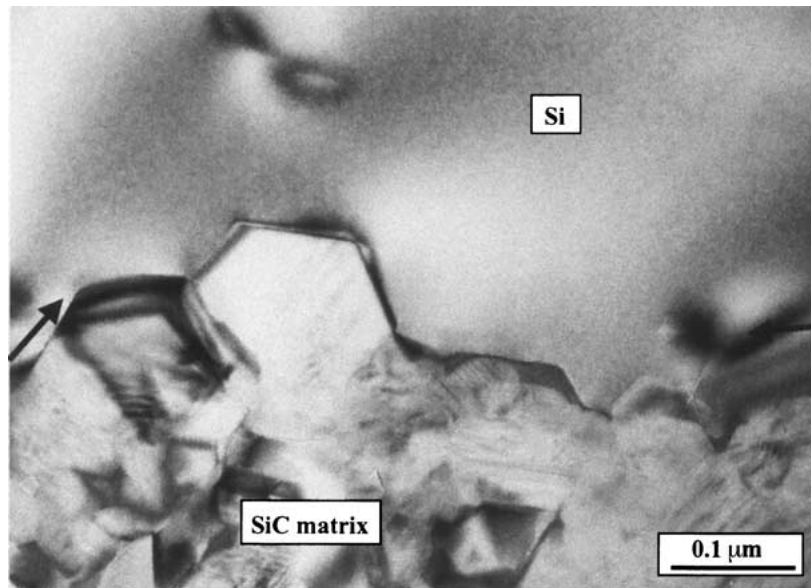
Figure 6 (a), (b) TEM overviews of the interface area between SiC_f/SiC and 84Si-16Ti brazing.

In case of SiC_f/SiC joints the separation of the eutectic alloy into Si and Si₂Ti is shown in the low magnification TEM overviews on Fig. 6a and b. The contact with the fibre reinforced SiC matrix is mostly performed by Si even if some Ti Si₂ particles also strike the interface. Substantial *hooking together* is clearly seen between brazing and the rough SiC matrix surface (cf. Fig. 6b). At medium magnification (Fig. 7a) and in the atomic plane HREM image (Fig. 7b) as well, no hint at any phase formation between SiC and Si is found, i.e., the *contact is atomically sharp*. On the left and right of the HREM image some overlapping between Si and SiC atomic planes occurred because of a slight tilting of the boundary. The chemical analysis of a SiC/TiSi₂ (cf. Fig. 8) and a SiC/Si (cf. Fig. 9) interface are shown in a nanometer scale as performed by a set of EELS spectra (a) across the individual interfaces (b). In Figs 8c and 9c the chemical bond specific ELNES of the Si-L₂₃ 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 TiSi₂ standard spectra and

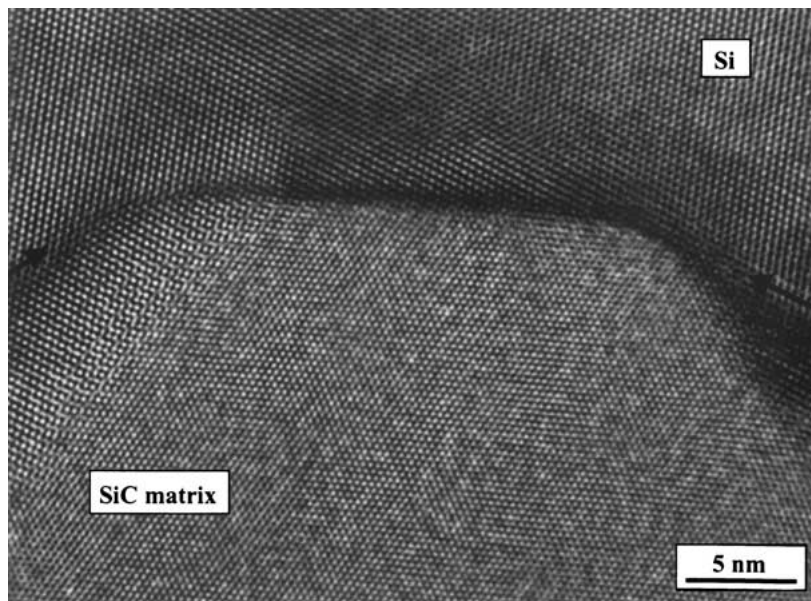
the sum of SiC and Si standard spectra, respectively. From these findings it must be concluded that in both cases *a sharp interface with no Ti diffusion into SiC and no other phases* has formed.

Also in the case of β-SiC joints (cf. Fig. 10), at medium magnification (a) and in the atomic plane HREM image (b) (here for the TiSi₂/SiC boundary), even at the atomic level *a sharp interface and no phase formation* could be observed. Similarly, in the β-SiC joints the EELS analysis results in the same interface situation as in the case of SiC_f/SiC joints. In particular, no Ti diffusion into SiC and no new phases were found in the related interfaces. In the TEM image on Fig. 10a along the interface some strain-contrast contours have formed. This mechanical strain could result from the thermal expansion mismatch between the SiC bodies and the brazing alloy and hints at strong bonding in the interface.

As a result of the above observations either from EELS measurements and HREM images, all the analysed interfaces between the substrate bodies and the



(a)



(b)

Figure 7 Microstructure of the interface area between SiC_f/SiC_f and 84Si-16Ti brazing, (a) TEM image, (b) High resolution TEM image.

brazing alloy could be proved to be nearly atomically sharp, i.e., there is no detectable interdiffusion or formation of new phases. Thus, the high strength macroscopically measured in these joining systems must be assumed to be caused by direct chemical Si–Si and Si–C bonds in case of a Si/SiC interface with additional Si–Ti or Ti–C bonds at TiSi₂/SiC interfaces. These considerations hold for SiC_f/SiC and SiC joints as well.

4. Shear strength

Among all the features of the joints obtained, the shear strength is the most important mechanical one. In fact, if the components to be joined are correctly designed, the joint will fail under shear strength instead of tensile or bending load. On the other hand, it is difficult to compare strength values from one study to another due to the different test methodologies generally used. There are several methods to test the shear strength of

joints [23] which are mainly based on the different sample typology (for example single and double lap joint, asymmetric four point bending bar, Iosipescu specimen etc); each of these methods exhibiting some advantages and disadvantages. In this work the joint performances were determined by means of shear tests, performed following “an ad hoc” modification of the ASTM D905-89 test procedure [24]. Even if the presence of a pure shear stress field was not assured by this procedure, it was however a simple method suitable 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. Two different sample-holder have been used for RT (Fig. 11a) and 600°C testing (Fig. 11b).

The strength values were computed by estimating the joint area for each sample. The crosshead speed was 0.6 mm/min, the tests were performed at room temperature and 600°C (the second temperature was obliged by testing equipment limitations). Remarkable results

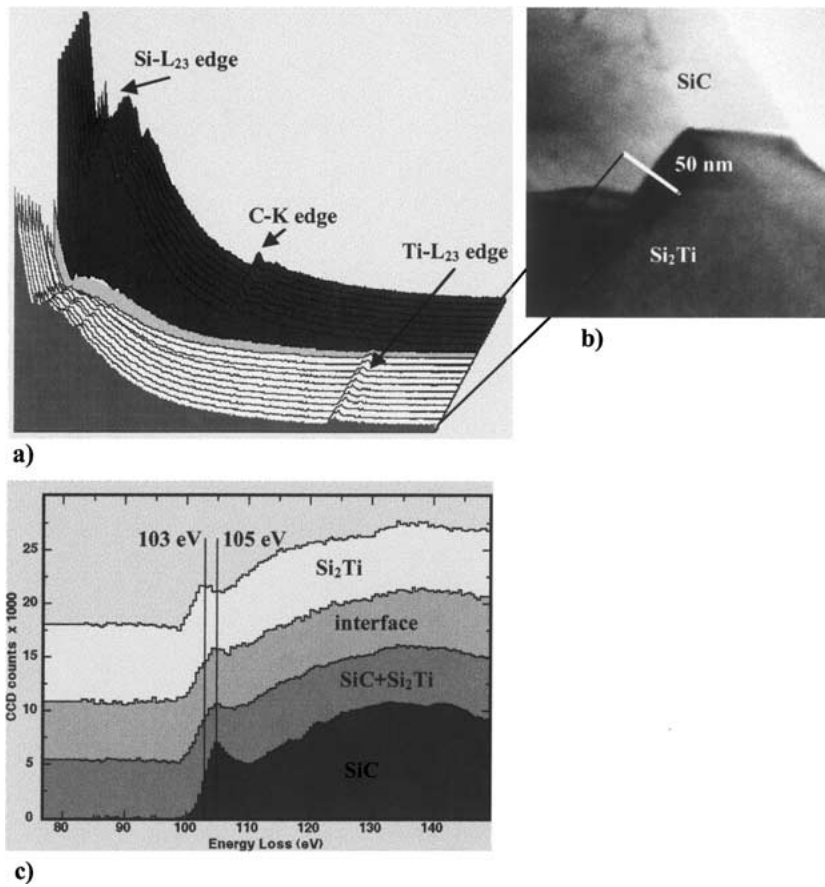


Figure 8 Nanochemistry of the interface between Si₂Ti and SiC, (a) series of EEL spectra (separation 2.5 nm), (b) TEM image, (c) Si-L₂₃ ELNES of selected spectra.

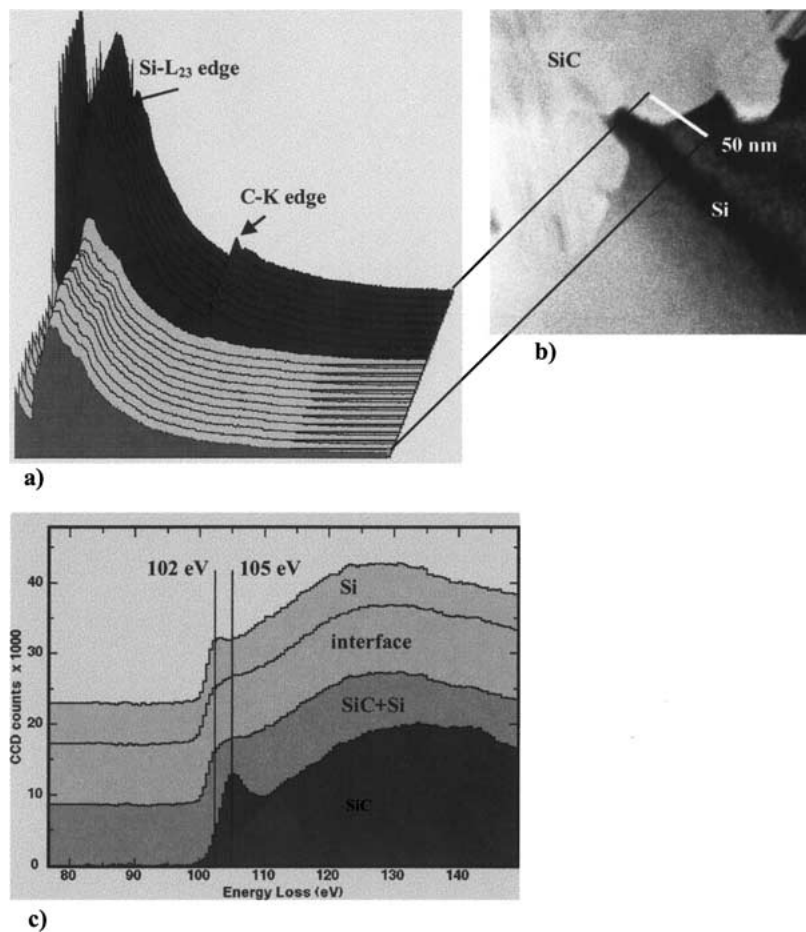
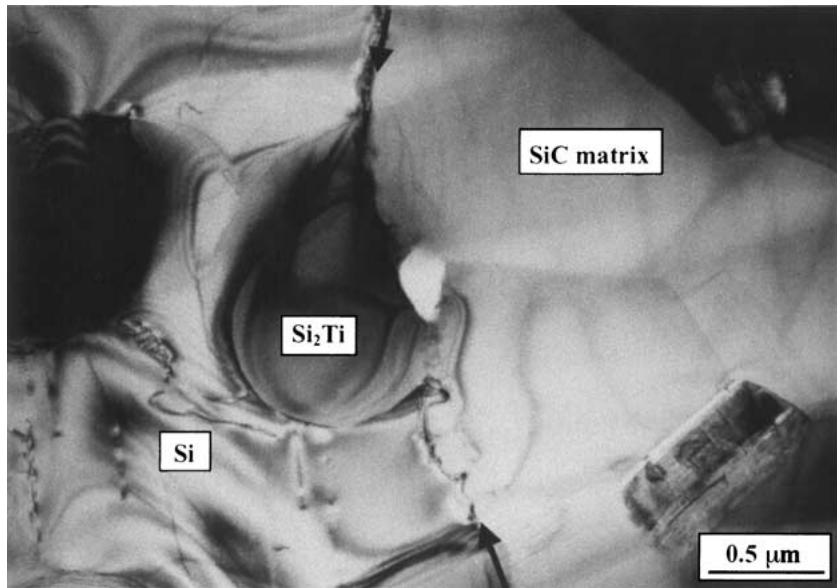
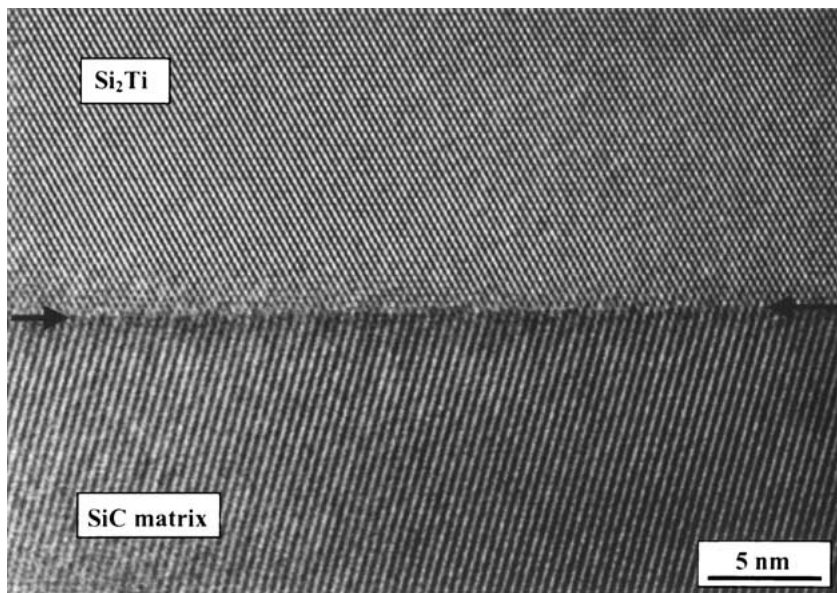


Figure 9 Nanochemistry of the interface between Si and SiC, (a) Series of EEL spectra (separation 2.5 nm), (b) TEM image, (c) Si-L₂₃ ELNES of selected spectra.



(a)



b

Figure 10 Microstructure of the interface area between β -SiC and 84Si-16Ti brazing, (a) TEM image, (b) High resolution TEM image.

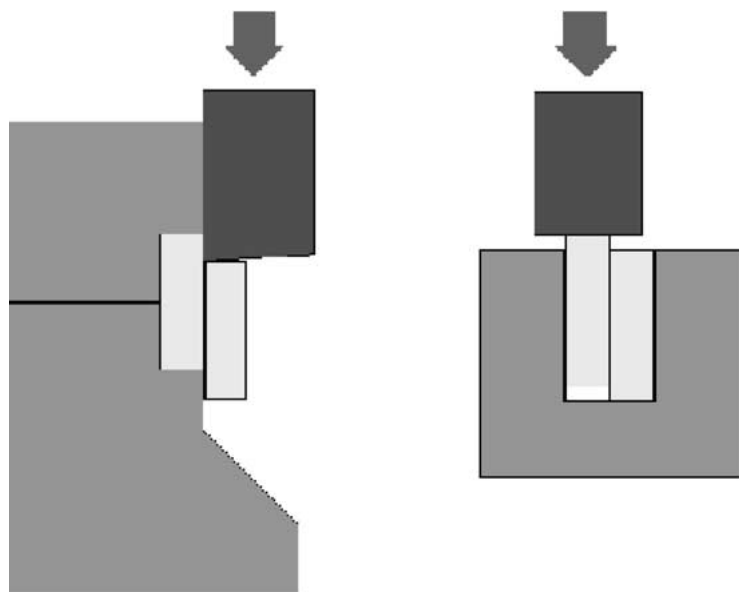


Figure 11 Scheme of the shear test arrangement at (a) RT and (b) 600°C.

were obtained: 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.

A typical shear load-displacement curve is shown in Fig. 12; the trend appears practically linear up to fail-

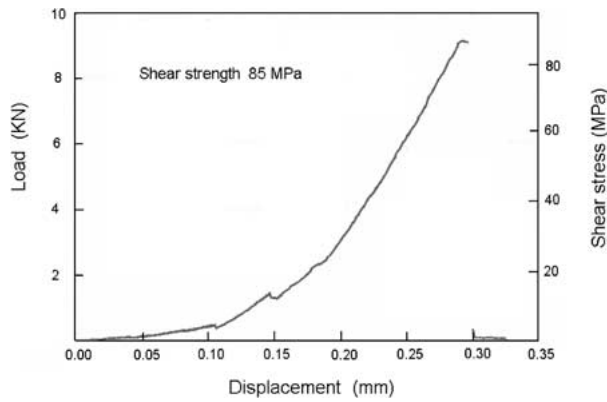


Figure 12 Typical shear load-displacement curve.

ure with a very limited toughness. All the tests carried out gave sufficiently reproducible results with a limited scattering.

Generally, the composite joints made in the vacuum furnace showed better performances probably because of the better control of thermal cycle possible in the facility used. The joint strength was slightly affected by the substrate roughness and the composite porosity. Observation of the fracture surfaces (Fig. 13) revealed that failure was always cohesive. In monolithic samples, the failure started sometimes at the joint interface but always propagated in the bulk SiC. In the composite samples, the failure always occurred in the composites (Fig. 14), leading to the conclusion that the limiting parameter of the performance was the shear strength of the composite itself.

5. Conclusions

The proposed joining technique, which employs an eutectic Si-Ti alloy, appears suitable for joining even large surfaces of SiC_f/SiC composites. In fact, in this

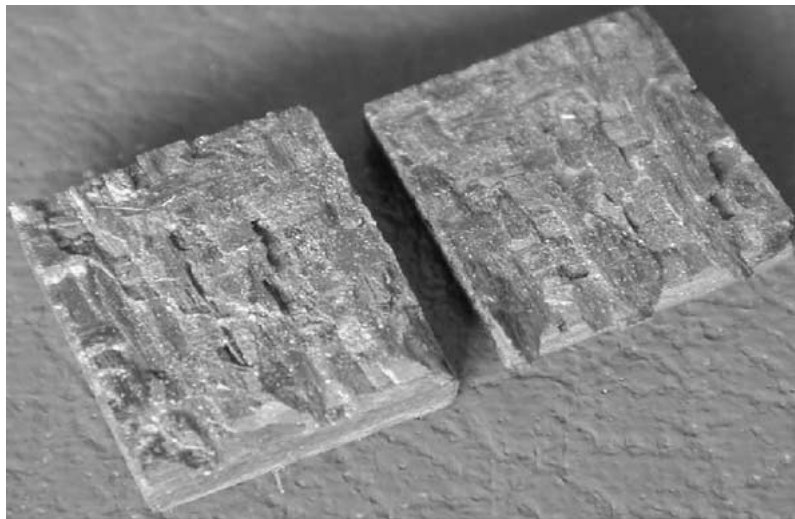


Figure 13 Composite joint fracture surface.

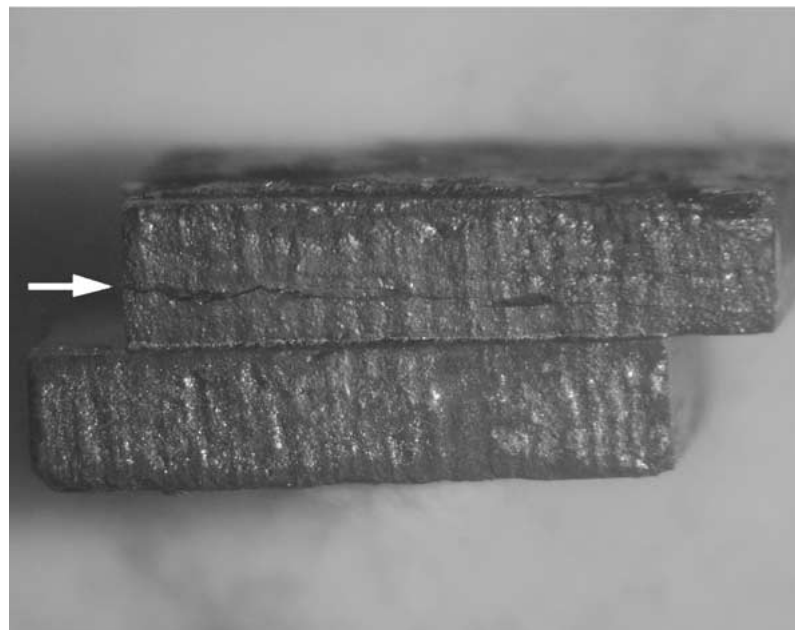


Figure 14 Typical composite specimen failure image.

way it is possible to obtain joints with reduced residual stresses and exhibiting thermo-mechanical properties similar to those of SiC and SiC_f/SiC composites.

All the joints obtained did not show any defects in the brazing layer which maintained, even after joining, a fine eutectic structure. Moreover, concerning the composites, the brazing alloy infiltration looked sufficiently controlled. Systematic investigations of the microstructure and of the nanochemistry (HREM, EELS, esp. ELNES) revealed atomically sharp interfaces without interdiffusion or phase formation at the interlayer leading to the conclusion that direct chemical bonds are responsible for the adhesion. Shear test results of the joints of SiC_f/SiC composites showed remarkable values (71 ± 10 MPa almost pure shear strength at RT and up to 70 MPa at 600°C).

Nevertheless, the technique has some disadvantages, namely the need of grinding the surfaces to joint in order to get tight tolerances and a joining thermal cycle that has to be tuned and strictly controlled around the eutectic temperature. The chemical stability of the joints with respect to oxidation is one of the important items still to be assessed, in order to demonstrate the suitability of the alloy for energy conversion application. The activity is continuing by investigating the performances of other eutectic alloys, such as for example Si-Cr.

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References

1. R. NASLAIN, *Adv. Comp. Mater.* **8**(1) (1999) 3.
2. A. MÜHLRATZER and M. LEUCHS, in Proceedings of the 4th International Conference on High Temperature Ceramic Matrix Composites, edited by W. Krukel, R. Naslain and H. Schneider, Munich, Germany, 1–3 October 2001.
3. M. ORTELT, F. RÜHLE, H. HALD, H. WEIHS, J. GREENWOOD and A. PRADIER, in Proceedings of the

4th International Conference on High Temperature Ceramic Matrix Composites, edited by W. Krukel, R. Naslain and H. Schneider, Munich, Germany, 1–3 October 2001.

4. O. M. AKSELSSEN, *J. Mater. Sci.* **27** (1992) 569.
5. A. T. J. MOORE, *J. Amer. Ceram. Soc.* **68**(6) (1985) C151.
6. M. SALVO, M. FERRARIS, P. LEMOINE, M. APPENDINO MONTORSI and M. MEROLA, *J. Nucl. Mat.* **212–215** (1994) 1613.
7. P. COLOMBO, B. RICCARDI, A. DONATO and G. SCARINCI, *ibid.* **278** (2000) 127.
8. E. PIPPEL, J. WOLTERS DORF, P. COLOMBO and A. DONATO, *J. Europ. Ceram. Soc.* **17** (1997) 1259.
9. P. COLOMBO, V. SGLAVO, E. PIPPEL and J. WOLTERS DORF, *J. Mater. Sci.* **33** (1998) 2405.
10. M. SINGH, *Scripta Mater.* **37**(8) (1997) 1151.
11. T. ISEKI, K. ARAKAWA and H. SUZUKI, *J. Mater. Sci. Lett.* **15** (1980) 1049.
12. M. NAKAMURA and I. SHIGEMATSU, *J. Mater. Sci.* **31** (1996) 6099.
13. M. M. SCHWARTZ, "Ceramic joining" (ASM International, 1990).
14. M. FERRARIS, C. BADINI, M. MONTORSI, P. APPENDINO and H. W. SCHOLZ, *J. Nucl. Mat.* **212–215** (1994) 1613.
15. J. G. LI and H. HUSNER, *J. Mater. Sci. Lett.* **10** (1991) 1275.
16. ASM Handbook, Volume 3: Alloy phase diagrams, ASM International, 1992.
17. ENEA Patent 478 (2001)–RM2001A000101.
18. HEXOLOY - S.A. Technical specification. Carborundum Italia s.r.l. (1998).
19. A. LA BARBERA, B. RICCARDI, C. A. NANNETTI, A. DONATO and L. F. MORESCHI, *J. Nucl. Mat.* **294** (2001) 223.
20. E. PIPPEL, J. WOLTERS DORF, G. PÖCKEL and G. LICHTENEGGER, *Mater. Charact.* **43** (1999) 41.
21. R. SCHNEIDER, O. LICHTENBERGER and J. WOLTERS DORF, *J. Microsc.* **183** (1996) 39.
22. E. PIPPEL, O. LICHTENBERGER and J. WOLTERS DORF, *J. Mater. Sci. Lett.* **19** (2000) 2059.
23. S. CORDEAU and C. TAFFAREL, Characterisation de la resistance au cisaillement de jonctions, Technical Note CEA-CEREM Grenoble (France) DEM n. 38/97 (1997).
24. B. RICCARDI, A. DONATO, P. COLOMBO and G. SCARINCI, Fusion Technology 1998-20th SOFT Marseille, edited by R. Beaumont, P. Libeure, B. de Gentile and G. Tonon.

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