JOINING DEVELOPMENT: PRODUCTION OF BRAZING ALLOYS AND JOINTS FOR IRRADIATION

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1. Introduction

Silicon carbide and SiCf/SiC ceramic matrix composites are attractive materials for energy application because of their chemical stability and mechanical properties at high temperature. Nevertheless, in order to manufacture complex components, the availability of suitable joining techniques is necessary. Among all the joining techniques under development the brazing is one of the most promising. The requirements of a suitable brazing material are: chemical compatibility and wettability with a SiC substrate, thermal expansion coefficient similar to that of the SiC substrate, high shear strength, and for the composite joints a brazing temperature low enough to avoid a degradation of the fibres and the fibre-matrix interface.

 The possibility to use pure silicon without an active metal filler as a braze for silicon carbide has been previously studied. The characteristics of Si are a good chemical compatibility and wettability with silicon carbide, in particular at 1480°C the contact angle between liquid Si and solid SiC is 38°. Moreover, the thermal expansion coefficient α is similar to that of silicon carbide: $\alpha_{Si}(RT) = 3.0 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{SiC}(RT) = 4.0 \times 10^{-6} \text{ K}^{-1}$. Unfortunately the use of pure silicon leads to serious problems because of the high melting point (T=1410° C) that may degrade the fibres or fibre-matrix interfaces, which results in a limited joint strength.

2. Preparation of the brazing alloys and joints

The Si-Ti and Si-Cr phase diagrams show the presence of two eutectics of interest Si-16Ti at.% and Si-18Cr at.% with melting points of 1330°C and 1305°C respectively. The Si-16Ti eutectic is contains free silicon and $TiSi_2$, while the Si-18Cr contains free Si and $SiCr_2$ intermetallic compound . The joining cannot be performed simply by mixing Si-Ti or Si-Cr powders because in this way it is not possible to get the above-mentioned eutectics. Therefore, the alloys have to be prepared previously, by means of a melting procedure, able to produce a fine eutectic structure.In particular, Si-Ti and Si-Cr mixtures were melted by a plasma torch and then re-melted several times by electron beam.

The joining was carried out by using monolithic polycrystalline α-SiC (Hexoloy-SA ®Carborundum) and a SiC$_f$/SiC composite produced by SNECMA (CERASEP® N3-1), with the latter consisting of a pseudo tri-dimensional weave of Nicalon^{TM} CG fibres, densified by chemical vapour infiltration (CVI) and finally SiC coated by chemical vapour deposition (CVD). The above materials have the necessary chemical stability at the brazing temperature. The typical properties of the monolithic and composite joining parts to be joined used are reported in Tables 1 and 2 .

The used samples were 12 x 10 x 3 mm^3 plates both of monolithic SiC and SiC$_f$/SiC composite. Bulk SiC samples didn't need any surface treatment since their roughness was in the order of 1 μm.The composite specimens were polished in order obtain a surface roughness in the range of a few microns. The mentioned CVD coating (> 100 μm) was partially removed

by surface preparation, thus some fibres remained uncoated and thus exposed to the brazing alloy. Anyway, even after grinding the composite surface did not assure an ideal contact.

Table 1. 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 2. 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)	$\geq$ 0.6 %	0.3-0.4 %
Trans laminar shear strength	(200 $\pm$ 20) MPa	--
Inter-laminar shear strength	40 MPa	30 MPa
4 points bending strength	600 MPa	--

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 1 N load. The first joinings were carried out in inert atmosphere (Ar+3% H$_2$) but then they were always performed in a vacuum furnace (10^{-6} mbar) because that facility allowed a better control of the thermal cycle. 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; cooling down to 600°C was performed at 20°C/min followed by natural cooling down to room temperature.

3. Microstructural and structural properties of Si-16Ti at.% and Si-18Cr at.%) brazing alloys

Fig. 1 shows a SEM picture of the Si-16Ti alloy prior to brazing; evidencing a fine and homogeneous microstructure composed of Si and TiSi$_2$. X-ray diffraction confirmed that no other phases than Si and TiSi$_2$ and Si and SiCr$_2$, respectively, were detected in the brazing alloys (Fig. 2). For the Si-18Cr eutectics the greatest part of CrSi$_2$ island have spherical shape with a mean dimension of about 1 μm. On the other hand, the islands of TiSi$_2$ have elongated shape with the length to depth ratio ranging from 1 to 20.
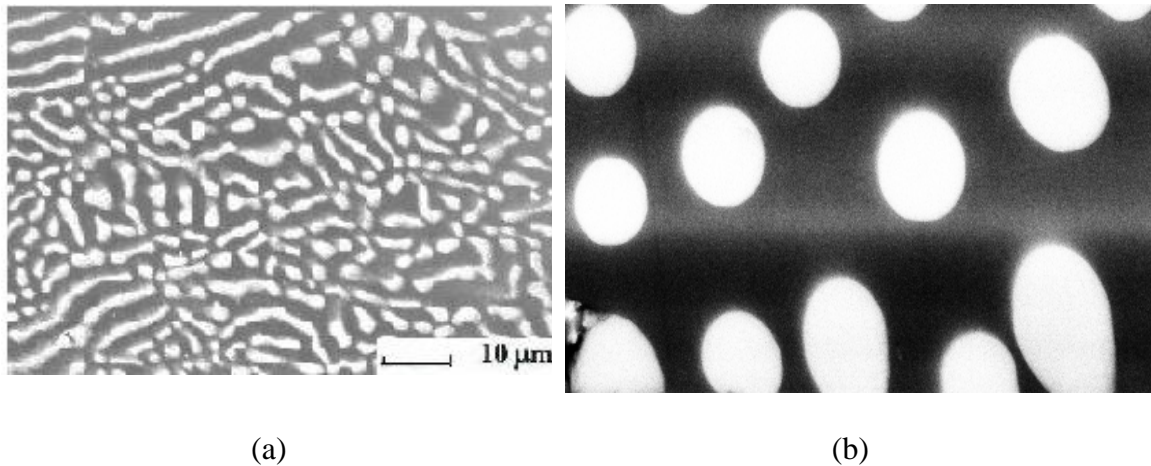
    (a)   (b)

Fig. 1: Micrography of a (a) Si-16Ti and (b) Si-18Cr brazing alloys before the joining process: grey zones = Si ; white zones=TiSi$_2$ and CrSi$_2$, respectively.
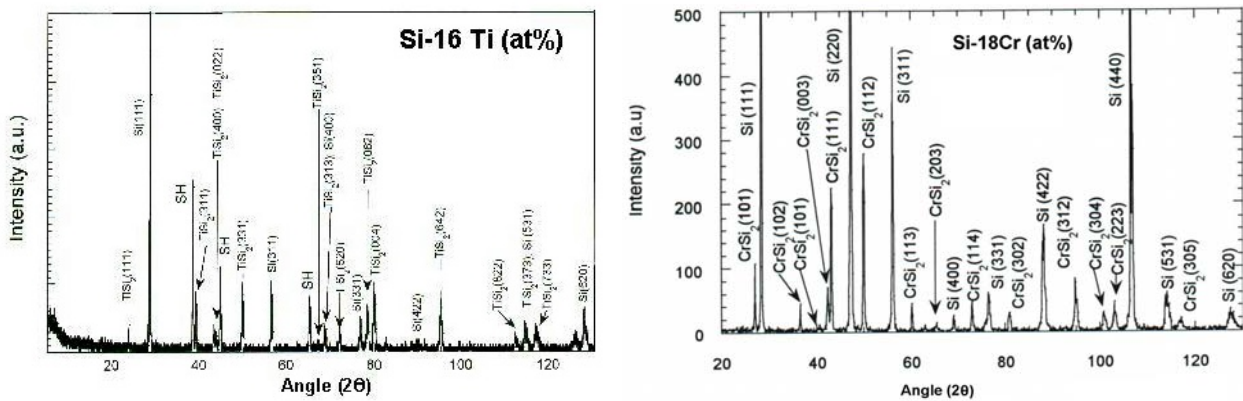

Fig. 2: XRD pattern of Si-16Ti and Si-18Cr alloys

4. Microstructure and nanochemistry of joints

Scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) examination have been performed on cross-sections of monolithic SiC and SiC$_f$/SiC composite joints to investigate their microstructure. As a first result, no flaws, unmelted particles and micro-cracks were detected in all joints. For Si-Ti and Si-Cr alloys, the thickness of composite joints was in the range of 20-30 μm, but a more pronounced local variation of the thickness could be observed depending on the surface roughness. The joint thickness of monolithic specimens was generally higher due to the absence of infiltration in the impervious SiC. The thickness values ranged from a few tenths of microns up to 100μm, depending on the amount of braze deposited between the pieces to be jointed. For both alloys the joints showed a fine size eutectic structure composed of a Si matrix and Ti or Cr silicides phases, comparable with that of the starting powder. The Si-18Cr microstructure was generally finer but less elongated than that of Si-16Ti. Due to the relatively short hold time at brazing temperature, the infiltration of the alloys in the composite joints looked sufficiently controlled.

The interface structure and the nature of the bonds between the eutectics and the SiC and SiC$_f$/SiC composites have been also investigated by transmission electron microscopy (TEM) including high resolution or atomic plane imaging (HREM), and electron energy-loss spectroscopy (EELS) for chemical analysis. The brazing alloy and the substrate could be observed side by side on the same image due to a specimen cross sectional preparation.

The EELS technique was able to provide an estimation of the type and the distribution 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 electrons into unoccupied states above the Fermi level, allows characterization of the chemical bonding state of individual elements with the same resolution. Characteristic ELNES details are the edge onset as well as the shape, the position and the intensity of individual peaks in a range of some 10 eV above the onset. The ELNES features were interpreted by comparing with related standard spectra. A slight overlapping of the detected elements from both sides of the interfaces cannot be excluded, although the interface is atomically sharp. This is why the spatial resolution is limited by the probe diameter. The EELS spectrum of the interface can be simulated by simply adding the spectra of both sides of the interface, thus, the formation of new phases can be excluded.

For example, Figure 3 shows TEM micrographs of SiC_f/SiC samples joined with Si-16Ti alloys indicating the separation of the eutectic alloy into Si and Si_2Ti. The two alloys are composed of a Si matrix with an intermetallic phase but the contact to the substrate is mostly performed by Si even if some $TiSi_2$ particles are linked to SiC. A consistent hooking together can also be seen between the brazing and the rough SiC_f/SiC matrix surface.
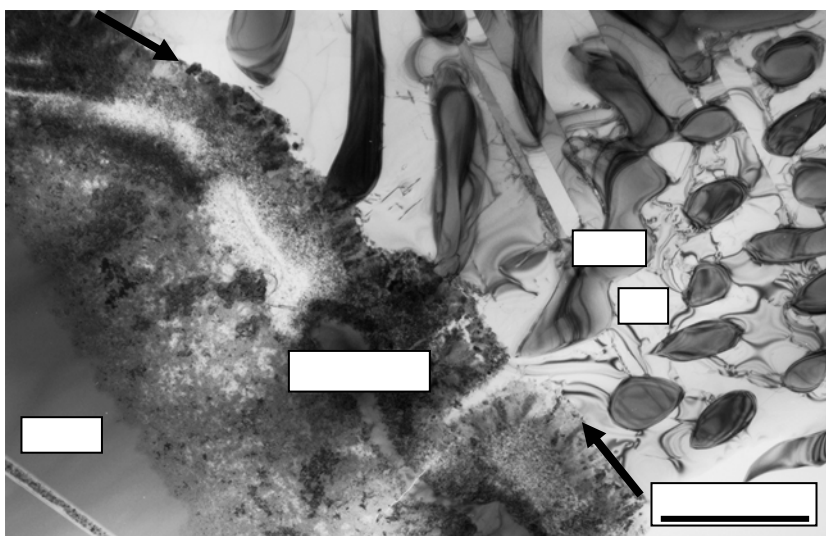

Figure 3. TEM image of the interface area between SiC_f/SiC and Si-16Ti brazing

From the atomic plane images it is found that no phases have formed between the SiC and Si and between the SiC and Si_2Ti or Si_2Cr, i.e., the contact is atomically sharp.
The chemical analysis of a SiC/Si , SiC/Si_2Ti and SiC/Si_2Cr interface (Figures 4 and 5) are shown in a nanometer scale as performed by a set of EEL spectra (a) across the individual interfaces (b). In (c) the chemical bond specific ELNES of the $Si-L_{23}$ edge of selected spectra are magnified with the background subtracted: it can be seen that the interface spectrum is almost the sum of those of the adjacent materials recorded far away from the interface.
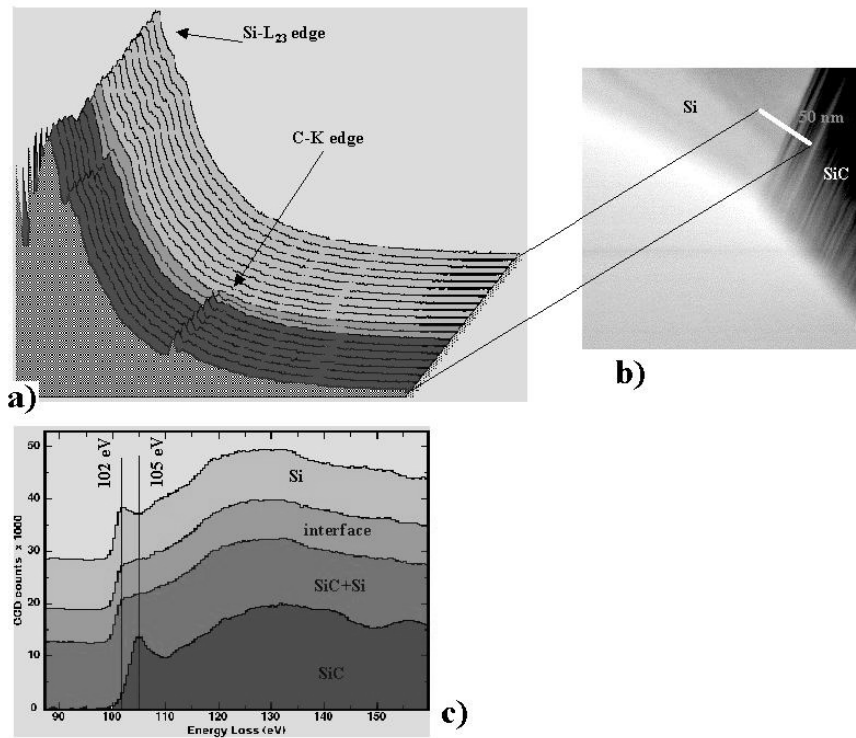
Figure 4. Nanochemistry of the interface between Si and SiC, a) series of EEL spectra (separation 2.5 nm), b) TEM image, c) Si-L$_{23}$ ELNES of selected spectra
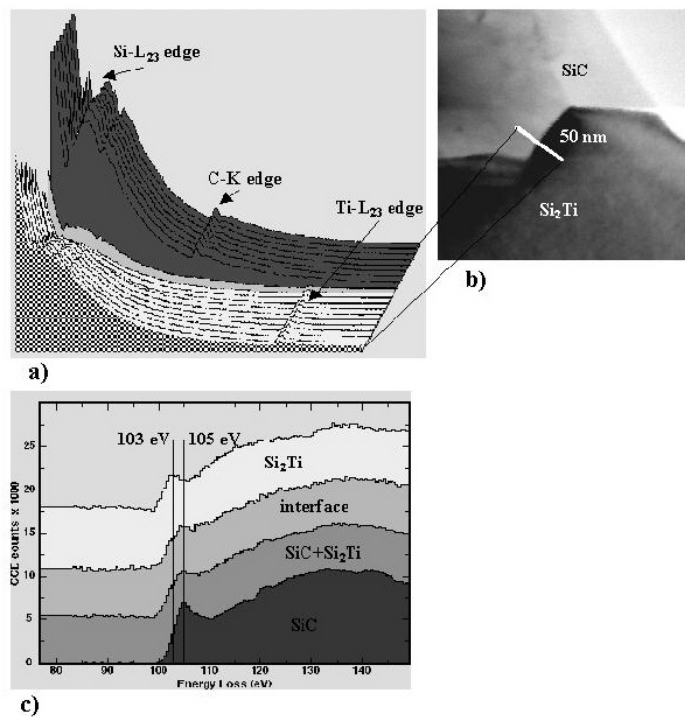

Figure 5. Nanochemistry of the interface between Si$_2$Ti and SiC, a) series of EEL spectra (separation 2.5 nm), b) TEM image, c) Si-L$_{23}$ ELNES of selected spectra

From these findings it must be concluded that in all cases no other phases have formed, i.e., the interface is sharp and no Ti or Cr diffusion into SiC occurs (within a resolution limit of 1-2 nm). All the analysis performed confirmed that the interfaces between the substrate bodies and the brazing alloy are nearly atomically sharp, therefore there is no detectable interdiffusion or formation of new phases. Thus, the high strength of the joints must be caused by direct chemical Si-Si and Si-C bonds in the case of a Si/SiC interface with additional Si-Ti and Ti-C or Si-Cr and Cr-C bonds depending on the alloy used.

5. Conclusions

The proposed joining technique, which employs the eutectic Si-16Ti and Si-18Cr alloys, appears suitable for joining of SiC and SiC_f/SiC composites. Joints with low residual strains and satisfactory shear strength were obtained. Following SEM analysis, all the joints investigated did not show any defects in the brazing layer which maintained a fine eutectic structure. Systematic investigations of the microstructure and of the nanochemistry (HREM, EELS, esp. ELNES) of both Si-16Ti and Si-18Cr joints led to the conclusion that direct chemical bonds are responsible for the adhesion with no interdiffusion or forming of additional phases. Shear tests of the joints of SiC_f/SiC composites showed remarkable values of the bonding strength (about 70-80 MPa) while joints of monolithic SiC (Si-18Cr) exhibited excellent strength (up to 140 MPa).