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Brazing of carbon–carbon composites to Nimonic alloys

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Abstract Industrially produced C_f/C ceramic composites have been brazed to Nimonic alloys using a TiCuSil filler metal. In order to accommodate the different linear coefficients of expansion between ceramic and metal as well as to provide compatibility between the surfaces to be joined, the C_f/C surface was metallized through the deposition of a chromium layer. Subsequent heat treatments were carried out to develop intermediate layers of chromium carbides. Crack-free joints have been produced and shear tests show that failure occurs within the composite. At the C_f/C-filler interface a layered structure of the metallic elements is observed. Titanium is depleted from the filler zone and interacts with the carbon to form carbides. In the filler region, Ag and Cu rich regions are formed.

Introduction

One of the key technologies which concern manufacturers of hypersonic engines and liquid rocket propulsion systems worldwide is the development of ceramic fiber-reinforced ceramic matrix composites (CMC) [1, 2]. Advances in joining science and technology are important for the benefits of these advanced materials to be realized [3]. A general requirement for aerospace applications is the joining of the CMC to a high temperature alloy which could be nickel-based alloys or Nimonic. A strong bonding cannot rely on the weak Van der Waals forces but on the chemical reactions which involve the main constituents of the work pieces. This can be achieved by either direct bonding or using interlayers. Whatever the joining process is, chemical equilibrium at the joint interface is needed to form a stable ceramic/metal bond for operation at a high temperature [4]. Interfacial reactions can affect every stage of the formation of a joint from the onset of bonding through the development of equilibrated microstructure and to the optimization of the mechanical properties [5, 6].

Diffusion bonding [7–13] and brazing [14–16] using different filler metals such as Cu-ABA, TiCuNi, and TiCuSil have been employed in joining C_f/C composites to metallic alloys or to themselves. Vacuum brazing compared to diffusion bonding has several advantages such as lower temperature and lower pressure requirements and the fabricated joints having low residual stress. It has been demonstrated that an adequate surface modification of the C_f/C could lead to improvements of the composite wettability by metals [17, 18]. C_f/C composites have been joined to Cu by surface modification obtained by direct chemical reaction between a transition metal slurry and the composite with heat treatment at 1300 °C [13, 19–21].

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In this study, C_f/C composites (CARBOTEX) are joined to a Nimonic alloy using TiCuSil filler metal. The wetting of the filler is enhanced with the deposition of a Cr film on the composite by magnetron sputtering and heat treatment before brazing. Ti or Cr enhances the metal–ceramic wettability by inducing chemical reactions at the joint during brazing [22–26] while the large ductility of Cu and Ag accommodates the thermal stresses that develop during joining. For high operating temperatures, the chemical inertness of Ag and Cu offers oxidation resistance. The purpose of this study is not only to produce sound joints but also to investigate the interface interactions as metal/ceramic joining for different applications and working environments that require control of the interface microstructure and its optimization.

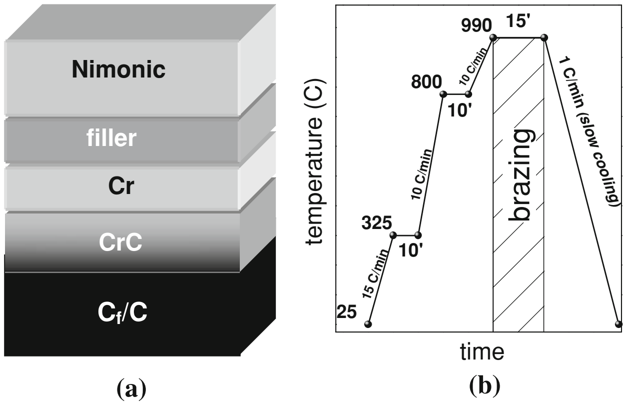


Fig. 1 **a** Schematic of the metal–ceramic joint and **b** the thermal cycle of brazing

Experimental

The CARBOTEX ceramic composites were supplied by EADS. They consist of carbon fibers embedded in a carbon matrix. The production process of this material is based on the combination of advanced textile techniques (braiding, weaving and stitching) and on rapid chemical vapor infiltration. From the supplied material, samples of 12 × 12 × 7 mm^3 were cut and used for all the experiments.

Chromium was deposited by magnetron sputtering at nearly ambient temperature (70 °C). A 2″-diameter Cr target of 99.95% purity was used. The base pressure before introducing the Ar gas was 1×10^{-6} mbar and the pressure during deposition was 4×10^{-3} mbar. Depositions were performed using a DC power of 120 W, resulting in a deposition rate of 17 Å/s. For the post-deposition thermal annealing, the CARBOTEX/Cr samples were enclosed in a quartz tube, and they were annealed in a tubular furnace for various periods and temperatures under high vacuum (10^{-6} mbar).

X-ray diffraction (XRD) patterns were collected by a Brucker D8 diffractometer using a Cu Kα radiation. The microstructure were examined using JEOL JSM 5910 LV scanning electron microscopy (SEM) coupled with INCA 300 energy dispersive X-ray spectroscopy (EDS).

The ceramic samples were brazed to a Nimonic 90 superalloy using an IPSEN VFCK-124 high vacuum furnace. Nimonic 90 is a wrought nickel–chromium–cobalt based alloy (Ni–20Co–18Cr wt%) strengthened by additions of titanium and aluminum. It combines high strength and creep resistance for service up to 920 °C. The superalloy samples were prepared in elongated sheets of 100 × 15 × 3 mm^3. The brazing was performed using as a filler metal TiCuSil alloy (Ag–26.7Cu–4.6Ti wt%) in paste form (Wesgo Metals), (Fig. 1a). The control of the quantity of filler metal was accomplished using a syringe and measured in weight, and excess of the filler metal was eliminated before the brazing process to avoid material that could modify the result of the mechanical tests. The thermal cycle used is presented in Fig. 1b. The heating was initiated at room temperature and follows a ramp with rates of 10–15 °C/min. Finally, the temperature of brazing was 990 °C. The slow cooling rate (1 °C/min) was selected to provide a thermodynamically stable configuration of constituent (molten) materials at the joint interfaces and to avoid premature cracking due to different CTE's.

For the shear strength mechanical tests, composite\Nimonic joints (Fig. 2a) and a mechanical device (Fig. 2b) were specially fabricated to assure the alignment of the sample during the test.

Results and discussion

SEM analyses of the cross sections of a series of CARBOTEX brazed to the Nimonic alloy samples show the successful brazing which is evidenced from the crack-free interfaces both at the Nimonic and the ceramic sides (Fig. 3). Overall, in all the samples, non-metallized and metallized by Cr, the interfaces appear to be microstructurally sound and well bonded due to interdiffusion of solutes and the formation of secondary phases. It should be noted that CTE difference between the TiCuSil and the CARBOTEX is very large and this would result in large thermal stresses due to differential expansion (contraction) at the CARBOTEX/braze interface during brazing. It appears that the relatively large ductility of the filler metal accommodated thermal stresses preventing interfacial cracking (Fig. 3).

In the following sections, the details of the brazing of CARBOTEX to the Nimonic are presented first. Next, the effects of the Cr layer on the joining and interface

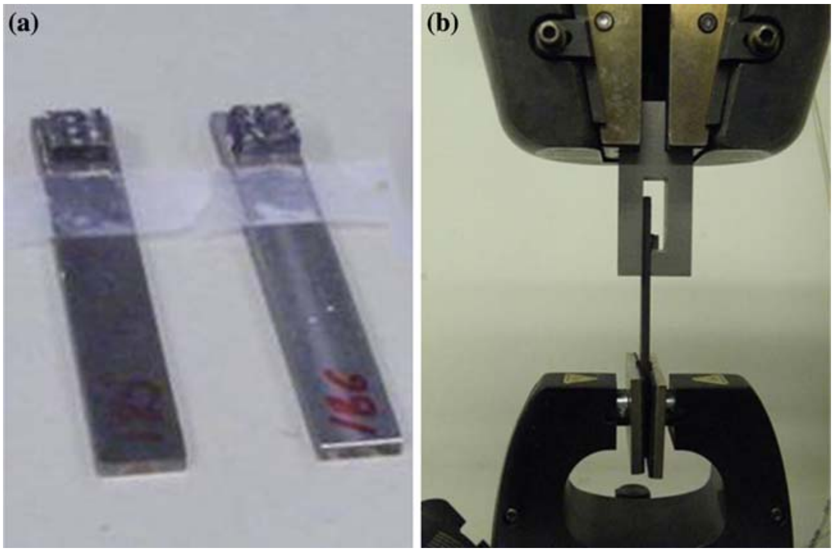


Fig. 2 **a** Brazed composites to Nimonic samples for the shear tests and **b** experimental setup for testing the shear strength of the joint

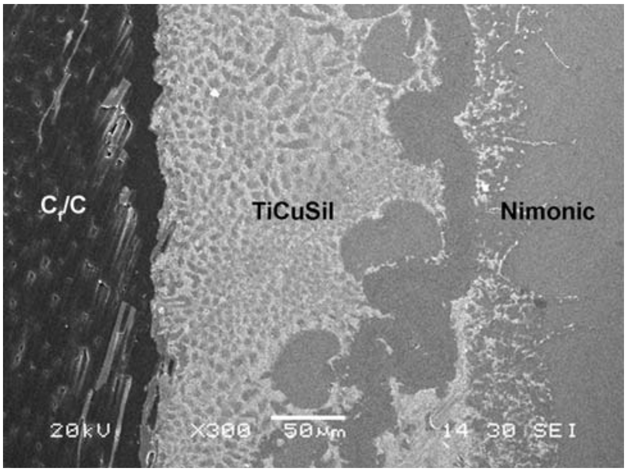


Fig. 3 SEM image of the cross section of the CARBOTEX/Cr/filler/Nimonic sample at the joint

microstructure are discussed. Finally, the results of the mechanical tests are described.

CARBOTEX/Nimonic brazing

At the ceramic–filler interface and adjacent to the C_f/C a Ti rich layer of 5-μm thickness is observed (Fig. 4). This Ti–rich interface bonds the C_f/C substrate to the brazing alloy. Cu and Ag do not interact with the carbon in the substrate, remain in the filler, and are separated with Cu forming islands with the sizes varying from 20 to 80 μm. The Ag–Cu–Ti system phase diagram at 950 °C contains a liquid miscibility gap which divides in a Ti-depleted and a Ti-rich liquid. The low concentration of Ti in the filler layer shows that the Ti-rich liquid on separation is on the ceramic part. This type of separation could be understood in terms of surface tension and contact angles. Pure Cu and Ag do not wet the graphite, but the addition of Ti [27–29] improves the wetting through the formation of carbides, and this behavior has been found in Ti-containing braze [30, 31]. As the Ti interacts with the carbon on the CARBOTEX surface, its concentration in the TiCuSil melt adjacent to the surface decreases. Ti from the bulk TiCuSil melt diffuses to the depleted zone and interacts with the underlying carbon increasing the carbide layer thickness and leading to the good physical contact shown in Fig. 4.

Ti carbide formation in this study is observed on the composites surface and around the fibers. Also, it has been observed on the surface and inside the pores of graphite brazed using TiCuSil [32]. From all these findings, we can conclude that the formation of Ti carbides takes place either on free surfaces or in regions in which there are free C bonds. The formation of TiC is thermodynamically favorable as the Gibb's free energy for the reaction $Ti + C \rightarrow TiC$ is -172 kJ. Thermodynamic calculations [27] also show that sub-stoichiometric carbides TiC_x could form from Cu–Ti alloys.

Summarizing the above findings, the filler-C_f/C composite interactions can be described as follows: At brazing temperature, TiCuSil melts (separation into in a Ti-depleted and a Ti-rich liquid expected from the phase diagram does not appear important in the process). TiCuSil melt permeates into the composite substrate, and the Ti interacts with the carbon at the surface to form TiC as it is thermodynamically favorable. From Fig. 5, we may assume that the main permeation of the liquid TiCuSil is about 5 μm which is the substrate/liquid braze interaction zone. As the liquid phase at the interaction zone is depleted from the Ti, new Ti from the filler zone diffuses into the interaction zone. This further interacts with the carbon forming TiC, and new Ti diffuses, and so on, up to the end of brazing process at 990 °C (Fig. 1b). The above described

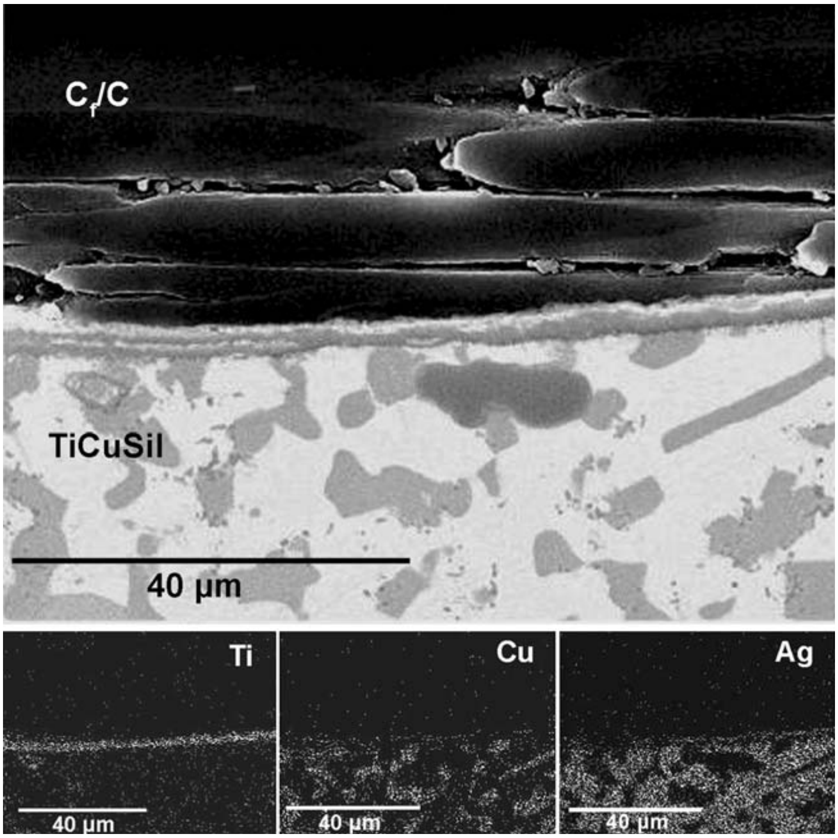


Fig. 4 SEM image of the cross section of the CARBOTEX/ filler interface (no Cr deposition) and the corresponding element mapping

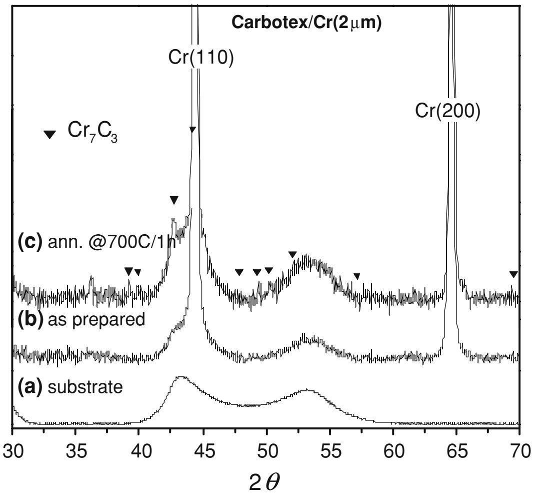


Fig. 5 X-ray diffraction spectra of the CARBOTEX/Cr(2 µm) structure: (*a*) CARBOTEX substrate, (*b*) CARBOTEX/Cr(2 µm) as prepared, and (*c*) CARBOTEX/Cr(2 µm) annealed at 700 °C for 1 h under vacuum. The triangular symbols indicate reflections from chromium carbide Cr_7C_3 [37]. The Cr peaks (110) and (200) are indexed

interaction process is supported by the facts that (a) the Ti concentration in the interaction zone is high whereas the Cu and Ag concentrations are low, and (b) the filler zone is almost completely depleted from Ti (Fig. 4).

In the Ti-depleted filler zone, grey and white areas are observed (Fig. 4). From the elemental analysis, it is found that the grey zones are Cu rich whereas the white zones are Ag rich. Similar separation of the TiCuSil filler metal have been observed in C_f/C composite joined to titanium alloy [15] or C_f/C composite joined to Cu-clad molybdenum [33]. As the filler zone is depleted from Ti the remaining Ag_xCu_{1-x} alloy separates into two phases Ag-rich and Cu-rich [34].

No carbon is observed in the Nimonic. The formed TiC is a good diffusion barrier to C diffusion since from its chemical diffusion coefficient [35], the temperature and the time of the brazing the calculated diffusion distance of carbon in TiC is few Angstroms.

Metallized CARBOTEX/Nimonic brazing

The CARBOTEX surface has been modified by the deposition of a Cr layer. Cr as a carbide former improves wettability and as it has been found in the case of graphite joining to Nimonic [32] the filling of the pores and the in depth formation of different carbides resulted in a mechanical type of joining i.e., a joint which its strength does not rely only on interface adhesion but also in substrate/braze interlocking.

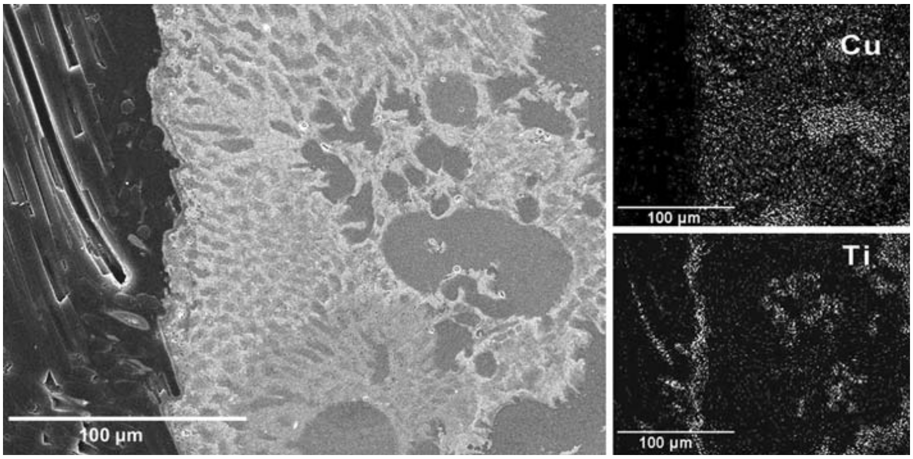


Fig. 6 SEM image of the cross-section of the CARBOTEX/Cr/filler interface and the corresponding element mapping

The XRD pattern of the CARBOTEX substrate is depicted in Fig. 6a. From the XRD pattern, we cannot discriminate whether it is hexagonal $P6_3$/mmc or hexagonal $P6_3$mc. The XRD of the as-deposited Cr layer (Fig. 5b) shows the strong (110) and (200) chromium peaks (space group *Im*-3*m*) on the top of the substrate pattern (Fig. 5a). There is no indication of any other crystallographic structure e.g., carbide formation. This is to be expected as the deposition temperature was 70 °C.

Heat treatment at 700 °C for 1 h results in the formation of the chromium carbide Cr_7C_3 (orthorhombic Pmcm) (Fig. 5c). There are three carbides of chromium: cubic $Cr_{23}C_6$, and orthorhombic Cr_7C_3 and Cr_3C_2. The metastable CrC phase, which should have a face-centered cubic lattice, is not explicitly mentioned in the phase diagram, although its existence is suspected. The interface reaction for carbide formation is probably controlled by the diffusion of carbon [36]. From Fig. 5c we observe that not all of the 2 µm Cr layer is consumed to the formation of carbide as the (110) and (200) Cr reflections remain after the heat treatment. Thus, the structure used for the subsequent brazing is that depicted in Fig. 5 i.e., a Cr_7C_3 adjacent to the C_f/C surface followed by a Cr layer. It is evident that sputtering deposition coupled with vacuum thermal annealing can be used to produce [C_f/C]/[Cr carbide]/Cr structures with different thickness of carbide and Cr. These types of structures might be useful in the employment of joining approaches different from the ones used here.

From the SEM image of the cross-section of the CARBOTEX/Cr/filler interface and the corresponding element mapping (Fig. 6), it is observed that Ti penetrates into C_f/C in depth of about 100 µm and coats the carbon fibers. Several hundred micrometer TiCuSil infiltration within C_f/C composites brazed to Cu clad Mo has also been observed [38]. It has been found that Cu–Ti alloys both wet and impregnate porous graphite [30]. A similar effect has been observed in the brazing of graphite to Nimonic using TiCuAg [32]. The Ti in the liquid TiCuAg system when in contact with a carbon surface interacts to form carbides. However, a part of the melt, probably through porosity channels, spreads out and decorates the carbon fibers to a depth from the composite surface of about 100 µm.

In Fig. 7, a high resolution SEM on a cross-section of a CARBOTEX/Cr sample brazed to a Nimonic (schematically depicted in Fig. 1a) using a TiCuSil filler is shown. It is deduced that the interactions of Ag, Cu, and Ti of the filler with the CARBOTEX substrate are the same, in general terms, as those observed in the case in which no Cr layer had been deposited (section 3.1). However, some crucial differences are observed which amplify the effect of the deposited Cr layer. From Fig. 7, we observe that the brazing process results in the formation of a layered structure at the carbon composite surface. The main features of the layered structure are a Cr layer adjacent to the CARBOTEX, followed by a Ti layer and, then, by another Cr layer which is between the Ti layer and the filler zone. Similar multilayered structures have been observed in the brazing of graphite to Nimonic using TiCuSil as filler metal [32].

For the interpretation of Fig. 7, it might be proposed that at 990 °C, the filler melt passes through the Cr layer and pushes into the substrate the Cr carbide formed on the top of the substrate thus generating the two Cr layers observed. Then, the Ti interacts with the carbon to form carbides. However, the details of the layered structure cannot be easily explained by a mechanical type action of the melt. Furthermore, the Cr and Ti layers there are: (a) an Ag layer between Ti and the Cr layer adjacent to the carbon composite, (b) a Cu layer between the Cr layer adjacent to the carbon composite and the composite surface and (c) a second Cu layer between the other Cr layer and the filler zone (Fig. 7). The main surface interactions of the brazed without surface metallization CARBOTEX (section 3.1) are the formation of Ti carbides, the depletion of the filler zone from Ti and the separation of the remaining alloy in the filler zone to Ag and Cu rich regions. These interactions have to be taken into account in explaining the structure

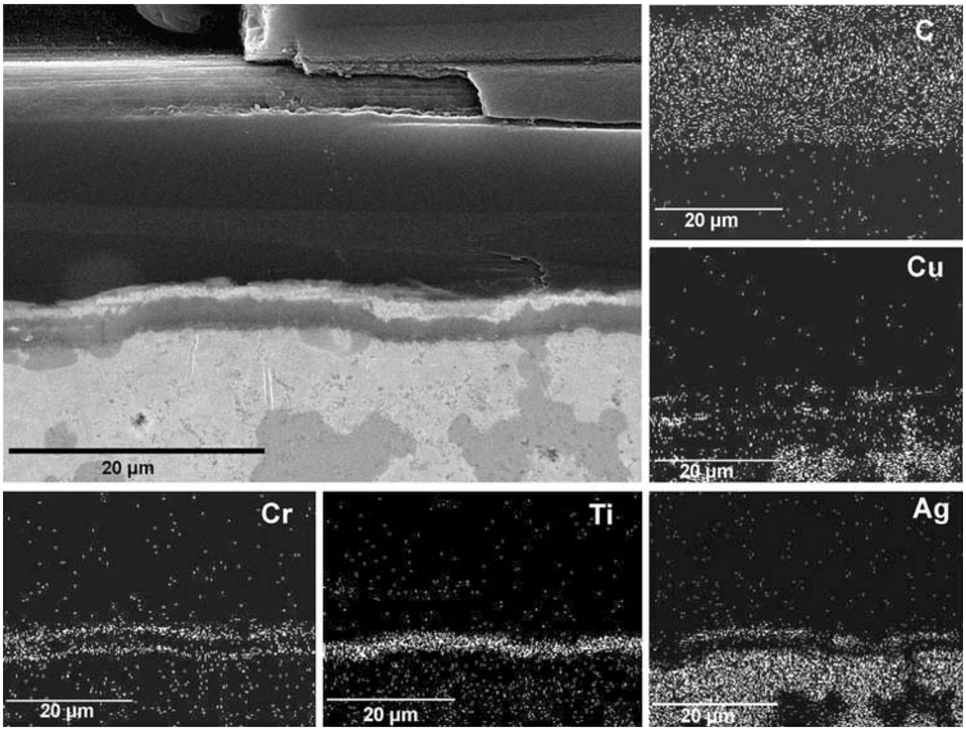


Fig. 7 SEM image of the cross section of the CARBOTEX/Cr/filler interface and the corresponding elements mapping

observed in Fig. 7. A possible mechanism arising from the features of Fig. 7 and consistent with the interactions outlined in "CARBOTEX/Nimonic brazing" section is as follows:

(a) During heating up (Fig. 1b) to 990 °C the Cr_7C_3 produced after the heat treatment at 700 °C transforms to Cr_3C_2 as it has been observed previously [32]. The main carbide formed at 727 °C is Cr_3C_2 as for high carbon content Cr–C mixtures has the lowest free energy [39]. Also, the Cr layer (see Fig. 1a) is to a large degree transformed to carbide.

(b) At the melting temperature of the filler, TiCuSil penetrates into the Cr carbide region (interaction zone). There is no evidence from SEM that the liquid filler mass transport occurs through micropores or microckracks of the Cr carbide layer. As it is apparent from the SEM pictures that the filler melt has transported through the Cr carbide layer, we have to suppose that this transportation occurs through nanochannels and atomic diffusion of the filler species.

(c) Ti from the filler alloy interacts with free carbon and replaces the Cr in the Cr_3C_2 forming TiC. The last reaction could be explained from the fact that the energy of formation for TiC (−172 kJ/mol) is lower than that of the Cr_3C_2 (−84 kJ/mol [39]). A similar effect has been observed in laser melting of powder mixtures from pure Ti and Cr_2C_3 in which titanium preferentially reacts with carbon to form TiC and releases Cr into the matrix [40]. The Ti layer thickness is about 2 μm, i.e., the same thickness as the deposited Cr layer.

(d) Cr diffuses out of the interaction zone. The two layers of Cr on either side of the Ti substantiate this process.

(e) As the Ti from the TiCuAg in the interaction zone forms TiC, its concentration in the alloy decreases. This generates diffusion flux of Ti from the filler zone which is between the interaction zone and the Nimonic alloy. The diffusing Ti forms new TiC in the interaction zone generating thus new flux of Ti from the filler zone. Finally, the 2-μm Ti-rich layer is formed and the filler zone is depleted from Ti (Fig. 7).

(f) As Ti is removed from the TiCuAg melt (both in the interaction zone and the filler region) the remaining metallic species Ag and Cu are separated as it has been observed in the brazing of CARBOTEX without metallization ("CARBOTEX/Nimonic brazing" section). In the filler region Ag and Cu rich regions are formed. In the interaction zone this separation takes the form of the layered structure. As Cu is released from the interaction zone and it is immiscible to Cr, moves outside the Cr layers. On the other hand Ag, being also immiscible to Cr, it has chemical affinity to Ti and forms a layer adjacent to the Ti layer.

Mechanical tests

For the mechanical tests, a new series of brazed samples were fabricated. The resulting brazed structures are shown in Fig. 2a. Subsequently, the joint structures were subjected to mechanical shear tests performed at room temperature, as depicted in Fig. 2b. In all the cases, the fracture has been produced through the ceramic part independent of the treatment performed (Fig. 8). Cracks are propagated parallel to the ceramic/metal interface. This type of failure also has been observed in the bonding of Ti-tubes to C–C composite plates using TiCuSil filler [41]. The interlaminar shear strength of C–C composites depends strongly on the test method [42], and these tests only show that the joining is stronger than the composite under the method of examination. The interfacial shear strength of C–C composite changes drastically by heat treatment [43, 44] and, possibly, the brazing process has modified the mechanical properties of the as-produced composite.

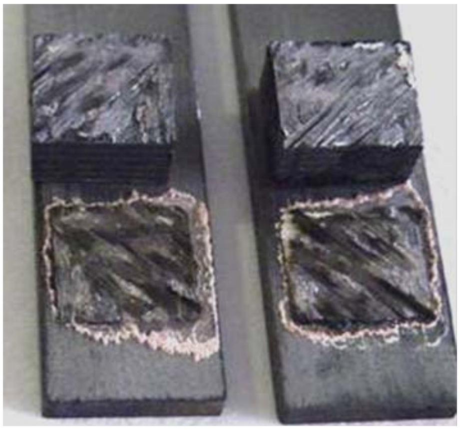
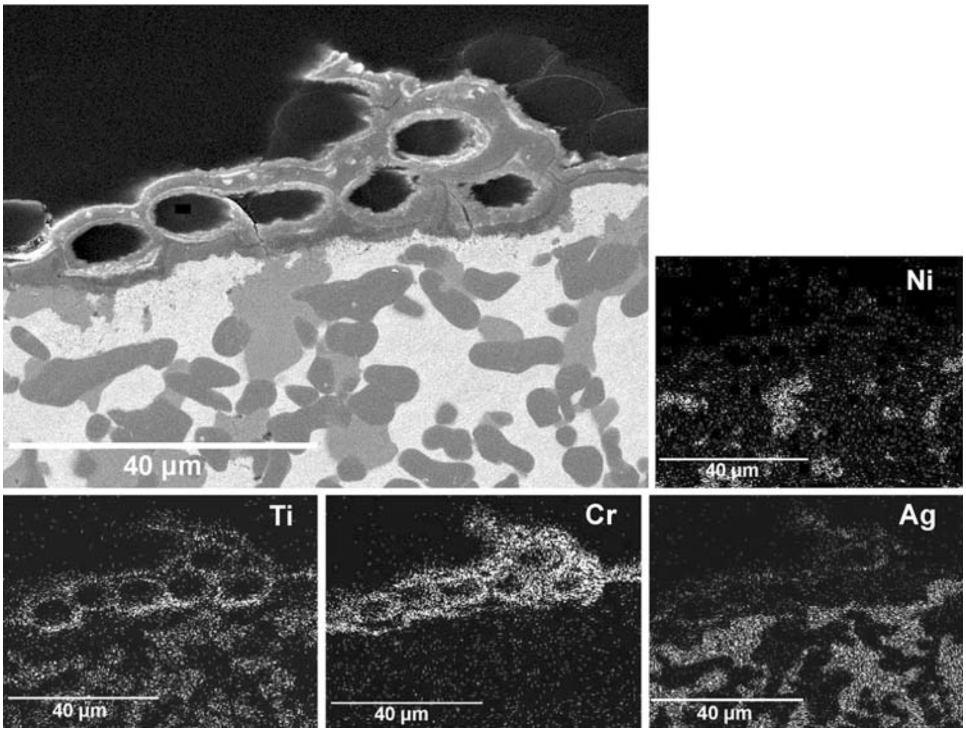


Fig. 8 Fracture surfaces after mechanical testing

Thus, from the shear stress results it can-not be concluded which brazing process gives the stronger joint. However, SEM observations of the fracture surface from metalized by Cr deposition CARBOTEX (Fig. 9) show that this process is the most promising for strength enhancement. In addition to the structure shown in Fig. 7, a decoration of the fibers is observed. Again in Fig. 9, the layer structure of Fig. 7 is observed, but in this case the layers are around the carbon fibers. This layered structure around the carbon fibers has also been observed inside the pores of graphite brazed to Nimonic under the same conditions as those described above. The Cr functions similar to a skin in a sandwich construction where the core is the titanium. This kind of interaction resembles to mechanical joining, and enhances the bonding between the filler and the composite.

In order to explain the features of Fig. 9, we can incorporate the mechanisms described in "Metallized CARBOTEX/Nimonic brazing" section. At 990 °C, the melted filler penetrates into the CARBOTEX substrate as the chromium carbides increase the wetting of TiCuSil. Apparently, the Cr carbides formed around the fibers channel the filler route around the fibers. Then, the interaction between filler and Cr carbides around the fibers are similar to those described in "Metallized CARBOTEX/Nimonic brazing" section.

Fig. 9 SEM image of the cross-section of the CARBOTEX/Cr/filler interface after shear stress mechanical tests and the corresponding elements mapping



Conclusions

1. Brazing using active filler metals such as TiCuSil leads to successful joints between the carbon composites and Nimonic alloys.
2. The surface metallization with chromium improves the reactivity of the elements of the filler metal and the carbon.
3. In shear tests, fracture was produced through the composite part.
4. At the CARBOTEX-filler interface, a layered structure of the metallic elements is observed. The same layered structure is observed around the fibers.

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