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One-step brazing process to join CFC composites to copper and copper alloy

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Abstract

The aim of this work is to develop a new single-step brazing technique to join carbon fibre reinforced carbon composite (CFC) to pure copper (Cu) and copper alloy (CuCrZr) for nuclear fusion applications. In order to increase the wettability of CFC by a copper-based brazing alloy containing no active metal, the composite surface was modified by direct reaction with chromium, which forms a carbide layer and allows a large reduction of the contact angle. After the CFC surface modification, the commercial Gemco® alloy (Cu/Ge) was successfully used to braze CFC to pure copper and pure copper to CuCrZr by the same heat treatment. The shear strength of the CFC/Cu joints measured by single lap shear tests at room temperature was (34 ± 4) MPa, comparable to the values obtained by other joining processes and higher than the intrinsic CFC shear strength.

1. Introduction

The ITER machine is an international effort aimed at demonstrating the scientific and technological feasibility of fusion energy. One of the most technically challenging components of the ITER machine is the divertor; it includes the cassette body (CB) and the plasma-facing components (PFCs). The PFCs are actively cooled thermal shields devoted to sustain the heat and particle fluxes during normal and transient operation conditions as well as during off-normal events. They consist of a plasma-facing material, the armour, which is made of either carbon fibre reinforced carbon composite (CFC) or tungsten (W). The armour is joined onto an actively cooled substrate, the heat sink, made of precipitation hardened copper alloy, CuCrZr.

The main problems in the CFC/Cu joint manufacturing are the large thermal expansion mismatch of the components and the bad wetting behaviour expressed by a very high contact angle of molten copper on carbon substrates. CFCs have excellent thermo-mechanical properties, such as high thermal conductivity, high thermal shock and thermal fatigue resistance. Thanks to these characteristics, the CFCs will be employed in ITER (International Thermonuclear Experimental Reactor) as plasma facing components, which interact directly with plasma [1].

This paper deals with the realization of the CFC/CuCrZr joint for the ITER divertor, which is the most critical step in the manufacturing of this component. This joint must withstand the thermal, mechanical and neutron loads, the cyclic mode of operation, while providing an acceptable lifetime and reliability. Due to the large thermal expansion mismatch between the CFC and the copper alloy, a thin (1–2 mm thick) soft interlayer made of pure copper is inserted between the CFC and the CuCrZr to alleviate the joint interface stress [2,3] generated during the working conditions. In the manufacturing process of the CFC to Cu joint,

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the very high contact angle of molten copper on CFC composites (θ ≈ 140°) forbids the direct casting of pure copper on CFC. Besides, the use of small amounts of active metals improves the copper wettability on carbon substrate [4–6] but it will also lead to the formation of brittle intermetallics or compounds with a low melting point.

At the moment, four possible solutions are available in Europe for CFC/pure Cu joints:

- The active metal casting (AMC®) has been developed by Plansee AG and consists in the casting of pure copper on the laser-machined CFC surface previously activated by CVD or PVD titanium [7]. Recently, beside titanium, silicon is also employed during the AMC process [8].
- The second method, developed by Politecnico di Torino, consists in the CFC surface modification by solid-state reaction with chromium (slurry deposition) followed by the direct joining of copper to CFC [9].
- A titanium–copper–nickel commercial brazing alloy was used by ENEA to activate the CFC surface and allow joining between the cast copper and the CFC matrix [10].
- Finally, the method developed by Ansaldo Ricerche foresees the use of a carbon fibre reinforced Cu–Ti active brazing alloy with good wetting characteristics on the CFC surface [11].

The subsequent Cu/CuCrZr joint can be obtained by:

- Hot isostatic pressing (900 °C/1000 bar) followed by a heat treatment to restore the overaged CuCuZr alloy [8].
- Brazing at the annealing temperature of 975 °C followed by a rapid cooling (>1 °C/s) and later ageing at 475 °C for 3 h to maintain the good mechanical properties of CuCrZr alloy [12].

In this work, the possibility to join simultaneously CFC/Cu/CuCrZr, by using the same brazing alloy and heat treatment, was demonstrated. This technology has advantages in terms of industrialization and cost reduction. The morphology and mechanical strength of the joined samples were investigated. Furthermore, preliminary thermal fatigue tests were performed.

2. Experimental

The carbon fibre-reinforced carbon composites, CFC NB31, used in this work were developed for the ITER divertor manufacturing by the French company SNECMA Propulsion Solide. The metal used to modify the CFC surface was high-purity chromium. The metal was deposited by the slurry technique on the CFC surface and a heat treatment at 1300 °C for 1 h (Ar flow) allowed the solid-state reaction between the metal and the composite. The carbide formation on the composite surface was detected by X-ray diffraction analysis (Philips PW1710).

The joining process between the surface-modified CFC, pure copper and CuCrZr was performed by using the Gemco® brazing alloy (87.75 wt% Cu, 12 wt% Ge and 0.25 wt% Ni; Wesgo Metals) for both the CFC/Cu and Cu/CuCrZr joints (Fig. 1). The brazing alloy foil thickness was 60 μm and three foils were used for each joint. The brazing process consists in a heat treatment at 970–980 °C for 30 min (heating rate 10 °C/min), a rapid cooling (>1 °C/s) from this temperature to 475 °C, an isothermal treatment at 475 °C for 3 h and finally an isothermal treatment at 350 °C for other 3 h in vacuum. In this treatment the precipitation hardening process for the CuCrZr alloy occurs at the same time with the brazing process itself in order to reach the maximum mechanical strength of the CuCrZr. Furthermore, to enhance the adhesion at CFC/Cu interface the joining process was performed with a low external pressure of about 1 kPa.

The joined specimens were morphological analysed by optical and electron microscopy (SEM Philips 525 M), by energy-dispersive analysis (EDS SW9100 EDAX) and electron probe micro-analysis (EPMA) using WDS (Jeol JXA 8600).

The CFC/Cu joint shear strength was measured at room temperature with a compression machine (SINTEC D/10), according to the method described in [13]. The fracture surface was examined to determine the fracture propagation.

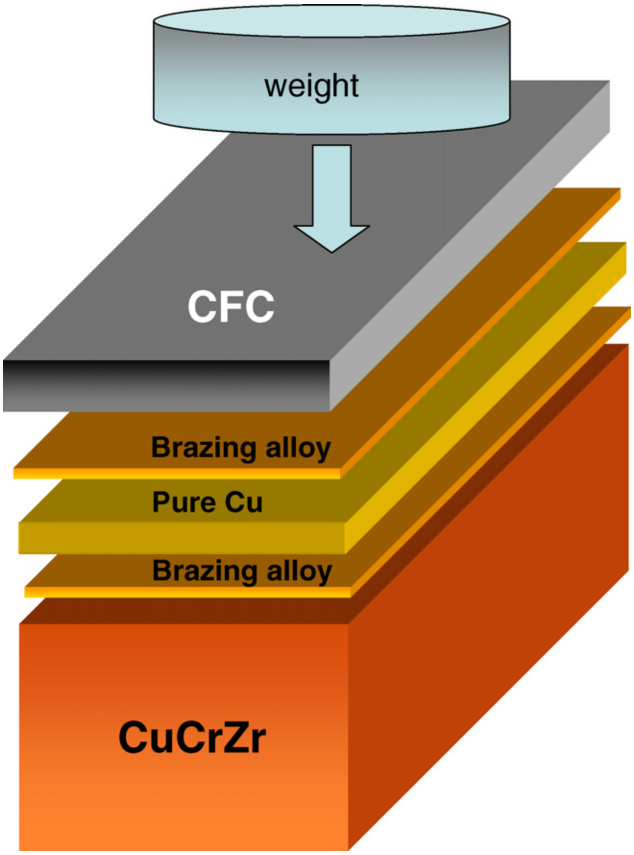

Fig. 1. Experimental setup for the CFC/pure copper/CuCrZr one-step brazing process.

These samples were submitted to preliminary thermal fatigue tests: heating of samples up to 450 °C was followed by fast cooling (>1 °C/s) from 450 °C to room temperature in air with water quench; the cycles were repeated 50 times for each sample.

3. Results and discussion

The joining between CFC, pure copper and CuCrZr was obtained during the same heating treatment by using a copper–germanium brazing alloy (Gemco®) for both the CFC/Cu and Cu/CuCrZr joints (Fig. 1). The Gemco alloy does not contain active metals, such as Ti and Si, and cannot be used to braze as-received carbon–carbon composites, but it was successfully used to join pure copper to CuCrZr for ITER application [11,14].

In a previous work [14], the authors demonstrated that the CFC composite surface leads, modified by direct solid-state reaction at high temperature with chromium, to a thin, coherent and adherent carbide layer (Cr_7C_3 and $Cr_{23}C_6$) which is very well wetted by pure copper. The same surface modification was performed in this work and the copper–germanium based brazing alloy (Gemco) showed an excellent wettability on the surface-modified composite. The basic idea is to activate the CFC surface using Cr without involvement of any active alloy; as a consequence, the brazing alloy does not contain any activating element.

The interfaces pure Cu/braze and braze/CuCrZr are defect free and almost undistinguishable also at highest magnifications by scanning electron microscopy (pictures not reported here).

Besides, Figs. 2 and 3 show the interfacial microstructure of the CFC/pure Cu joined sample: the thickness of the dense carbide layer is about 15–20 μm, the two interfaces (CFC/carbide and carbide/braze) are continuous and free of defects such as microvoids and porosity. The high wettability of the molten brazing alloy on the chromium carbide allows the penetration of the porous carbide-modified surface avoiding the formation of voids at the brazing alloy/carbide interface (Fig. 2). Furthermore, although the large thermal expansion mismatch between the brazing alloy and CFC, no cracks are present in the composite or at the interfaces after the very fast cooling from 980 °C (cooling rate >1 °C/min): the large ductility of the braze and of pure copper accommodates the thermal stresses, thus preventing interfacial cracks and debonding.

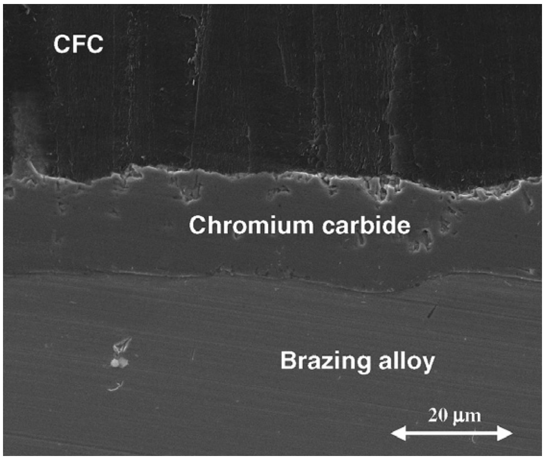

Fig. 3. Scanning electron microscopy of the chromium carbide modified CFC/braze interface.

The distribution of the elements across the two joint regions (CFC/Cu and Cu/CuCrZr) based on EDS and WDS analysis is shown in Figs. 4a and 4b. The Ni and Zr contents could not be determined because their concentrations are too low (0.25 wt% of Ni in the brazing alloy and 0.22 wt% of Zr in the CuCrZr alloy). The low signal of Cu in the CFC region (only detected on few samples) can be related to the metallographic polishing for SEM observation, during which small amount of soft copper can be accidentally moved on the CFC surface. Fig. 4a

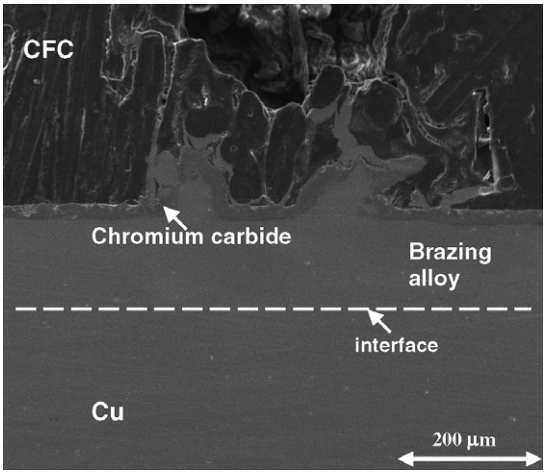

Fig. 2. Scanning electron microscopy of the cross-section of a CFC/Cu/CuCrZr sample brazed by Gemco alloy. The brazing alloy thickness after the brazing process is about 140 μm.

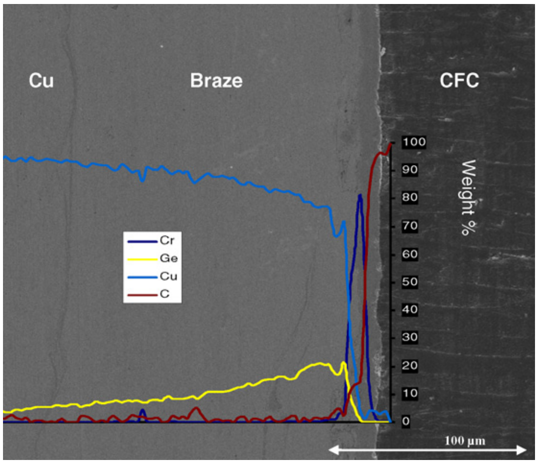

Fig. 4a. Element distribution (Cr, Ge, Cu and C) in the pure copper/braze/chromium carbide modified CFC composite joint region (wt%).

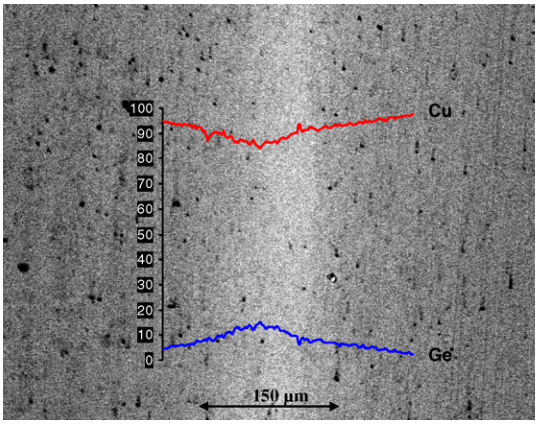

Fig. 4b. Element distribution (Ge and Cu) in the CuCrZr alloy/braze/pure Cu joint region (wt%).

relates to element distribution at the pure copper/braze/chromium carbide-modified composite interfaces; the stability of chromium carbide during the brazing treatment is demonstrated by the absence of Cr diffusion into the brazing alloy. The braze constituents (Cu and Ge) partially diffused in the chromium carbide layer but they did not diffuse across the carbide into the CFC composite. Besides, the brazing alloy/chromium carbide interface is enriched in Ge (Fig. 4a), while this segregation was not observed in the CuCrZr/braze/Cu joint region (Fig. 4b). The preferential segregation of Ge, near the chromium carbide interface, is consistent with the chemical affinity of Ge toward Cr, thus promoting wetting and bonding, but the presence of Ge_xCr_y intermetallic phases was not confirmed by XRD analysis and by the Cr diffusion pattern (Fig. 4a). Probably, if a reaction occurred at braze/chromium carbide interface during the brazing treatment, it should be limited at the region very close to interface.

Shear tests at room temperature were performed on CFC/Cu joined samples. The average shear strength of the joint is (34 ± 4) MPa, higher than the intrinsic CFC shear strength (15–20 MPa). The fracture surface analysis shows that cracks occurred inside the composite and/or the chromium carbide and not within the carbide/braze interface or the braze itself. Fig. 5(a) and (b) show typical fracture surfaces for a CFC/Cu joined sample: on both sides it is evident the presence of the composite (carbon fibres and matrix) that failed by interlaminar shear. In Fig. 6(a), the fracture mechanism involves fibre pull-out while in other fracture surface regions the presence of chromium carbide (porous phase in Fig. 6(b)) indicates that the cracks also propagated in the carbide layer.

Furthermore, the EDS analysis revealed on both the fracture surfaces only the presence of C (81–85 at.%), Cr (15–19 at.%) and Cu (2 at.%): the relative amount of these elements indicates that the failure did not occur within the braze, thus indicating a joint strength higher than the interlaminar shear strength of the composite itself.

The increase of the shear strength of the CFC composite near the joint interface (about 15–20 MPa higher than the one of the 'as received' CFC) can be justified by the braze partial infiltration into the porosity of the composite surface, thus obtaining a less porous and stronger surface layer with metal/ceramic composite behaviour and an additional mechanical bonding.

In order to qualify the manufacturing route for the subsequent development of mock-ups, the CFC/Cu/CuCrZr joints were also characterized by preliminary thermal fatigue tests in air with water quench. After 50 cycles (from 450 °C to room temperature; cooling rate about 60 °C/s), the micrograph analysis of the samples did not reveal any damage: there was no separation at CFC/Cu and Cu/CuCrZr interfaces and no cracks in the composite or in copper (picture not reported here).

Due to these promising preliminary results, the effectiveness of this joining technique is going to be tested by high heat flux facilities and some flat-tile mock-ups were produced. A flat-tile mock-up obtained with the one-step process is shown in Fig. 7.

Besides, the 'One-step brazing' process described above was also used to produce joined CFC/Cu in the monoblock

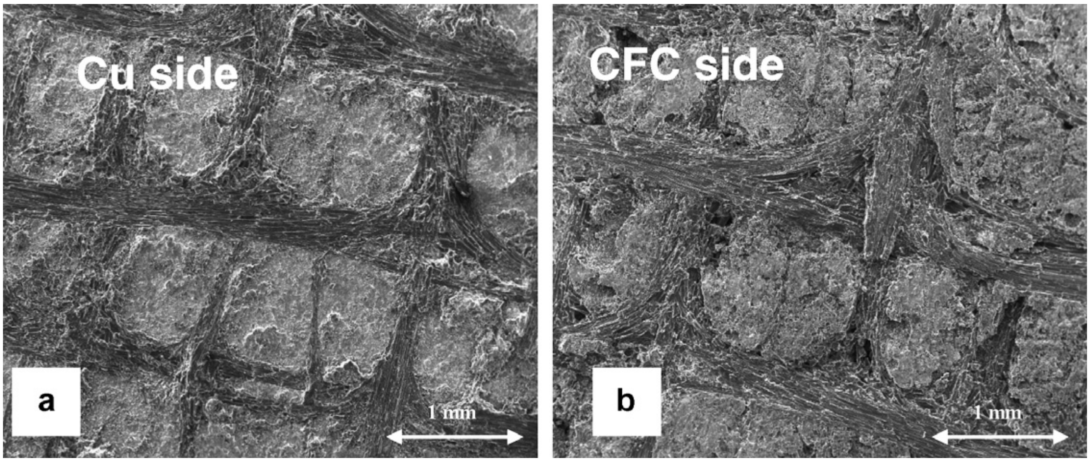

Fig. 5. Typical joint structure fracture surfaces: (a) Cu side and (b) CFC side.

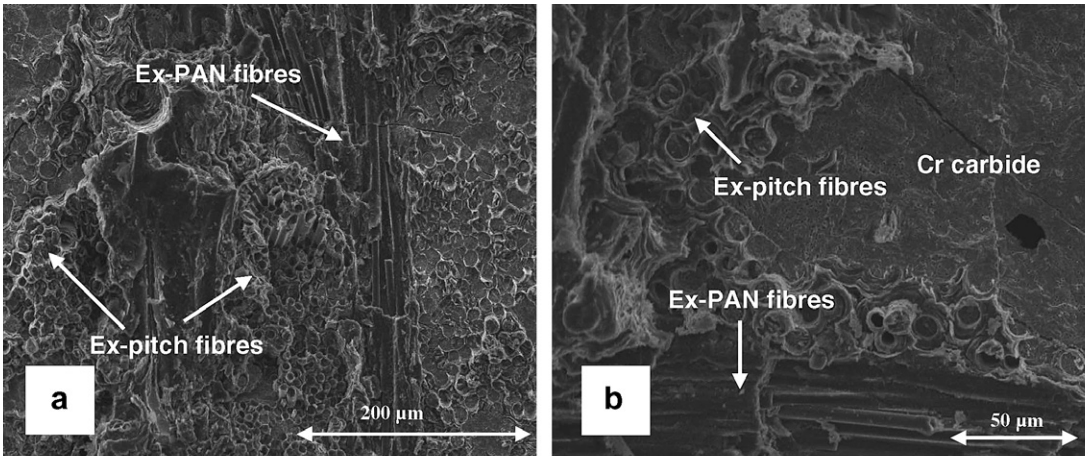

Fig. 6. Magnification of the fracture surface on the Cu side: (a) Fracture in the CFC composite with fibre pull-out. (b) Fracture through CFC and chromium carbide layer (porous phase).

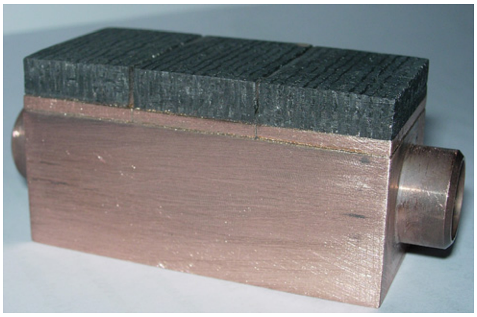

Fig. 7. Flat-tile mock-up produced by the one-step brazing process.

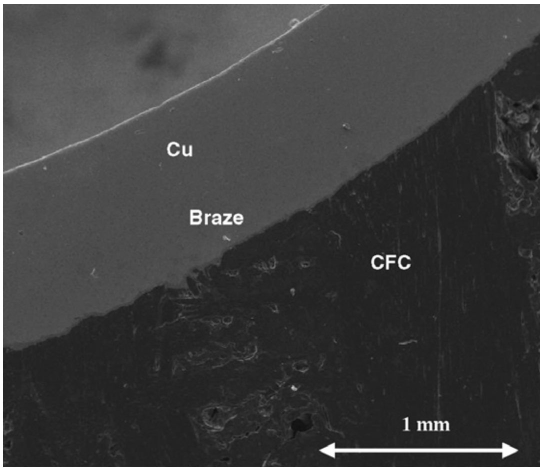

Fig. 8. CFC/Cu sample brazed in the mono-block geometry.

configuration. Fig. 8 shows the curved CFC/Cu interface of a monoblock sample. Also with this geometry the interface was continuous and the braze was free of microvoids and cracks. Further investigations will be performed on joined samples in monoblock geometry in order to validate the brazing process for this configuration.

4. Conclusions

The one-step brazing method described in this paper is a simple and low cost technique to join CFC composite to copper and to CuCrZr alloy in both flat tile and monoblock geometries. It does not require pressure and involves a temperature lower than that necessary for the joining process based on Cu casting. An excellent wettability of the brazing alloy on the CFC composite was obtained after the composite surface modification by high-temperature solid state reaction with chromium. The mechanical strength of the joined samples is higher than the interlaminar shear strength of CFC. Preliminary thermal fatigue tests reveal that they can be promising candidates for the manufacturing of heat-sink mock-ups to be tested in high heat flux thermal fatigue tests.

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