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Journal of Nuclear Materials 348 (2006) 102–107

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Proposal for a new technique to join CFC composites to copper

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Received 13 April 2005; accepted 12 September 2005

Abstract

The divertor design of the ITER fusion machine comprises the joint between CFC composites and the copper alloy heat sink. The main problem of the CFC–Cu joint manufacturing is the large thermal expansion mismatch of the components and the very high contact angle of molten copper on carbon substrates. The aim of this work is to develop a new technique to join CFC composite to pure copper. In order to increase the wettability of CFC by molten copper, the composite surface was modified by direct reaction with group VI transition metals which form a carbide layer and allow a large reduction of the contact angle. A morphological analysis and the mechanical and thermal shock tests were performed to characterize the CFC–Cu joined samples.

1. Introduction

Carbon fibre reinforced carbon matrix composites (CFC) have excellent thermo-mechanical properties, such as high thermal conductivity, good thermal shock and thermal fatigue resistance. Due to these characteristics, the CFC will be employed in ITER as plasma facing components, which interact directly with the plasma [1].

This paper deals with the realization of a high heat flux component formed by an armour (CFC) and a heat-sink material (copper alloy, CuCrZr grade), which transfers the heat from the armour to the water flowing in the cooling channel of the heat sink. One of the most critical steps in this component manufacturing is the joint between CFC and the copper alloy (CuCrZr): the joints must withstand cyclic thermal, mechanical and neutron loads to provide an acceptable design lifetime and reliability. In particular, the divertor shall sustain 3000 cycles at 10 MW/m^2 plus 300 cycles at 20 MW/m^2. The main problem related to the CFC–Cu alloy joints is the large thermal expansion mismatch between the two materials, which generates large residual stresses at the interface during the joining process [2,3]. These residual stresses can partially relax by the introduction of a very ductile layer of pure copper between the CFC composite and the Cu alloy [4]. The very high contact angle of molten copper on CFC composites ($\theta \approx 140°$) does not

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doi:10.1016/j.jnucmat.2005.09.007

allow the direct casting of pure copper on CFC. The C–Cu system is a non-reactive system: C and Cu are not soluble in the solid state and they do not form stable carbides.

The study of wettability of copper on carbon fibre reinforced carbon composites (CFC) is of great importance in several applications such as coating and joining processing.

In early 1970s, Mortimer and Nicholas [5] studied the improving of copper bonding to vitreous carbon and graphite with small amounts of active metals. Their investigation focused on segregation of active metals at the interface and subsequent carbide production, being able to improve copper adhesion to the reaction layer. From literature, it is known that transition metals react strongly with carbon to form carbides and some of these carbides are wetted by copper. The metal-like carbides of the transition metals are wetted better than the covalent carbides; in fact, these carbides have a partly metallic bonding which improves the interfacial adhesion to metals. Furthermore, these ceramics have metal-like behaviour such as good electrical and thermal conductivities; the latter is one of the main requirements in divertor CFC–Cu joints [5–9].

Up to now, two possible solutions are available in Europe for CFC-pure Cu joints. The first one has been developed by Plansee AG (Active Metal Casting, AMCR) and consists in the casting of pure copper on the laser machined CFC surface previously activated by titanium [10,11]. The second method, developed by Ansaldo Ricerche, comprises the use of a brazing alloy with good wetting characteristics on CFC surfaces [12].

In order to develop a new technique to join CFC composite to pure copper [13], the CFC composite surface was modified by different metals of the VIB group and the wettability of molten copper on the modified surface was investigated. The main differences between the new technique described in this paper and the AMCR – process consist in the use of new activating materials (Cr, Mo, W), a simpler deposition method (slurry technique instead of plasma spray) and the use of as-received CFC (laser machining of the CFC surface is not necessary).

2. Experimental

The carbon fibre reinforced carbon matrix composites used in the experimental study were developed for the ITER divertor by the French company SNECMA Propulsion Solide. Two different kinds of CFCs were utilized: CFC NS31 and CFC NB31. They are 3D composites obtained from a preform with ex-pitch fibres in one direction and ex-PAN fibres in the other direction, which are needed in the perpendicular direction. This 3D structure is densified with pyrocarbon through a CVI process; the densified material is submitted to heat treatment in order to make it highly conductive. NS31 is obtained by an additional injection of liquid silicon under pressure leading partly to the formation of silicon carbide (silicon content is about 8–10 at.%) [2]. The metals used to modify the CFC surface were high purity transition metals of the VIB group. The metals were deposited by the slurry technique on the CFC surface and a heat treatment initiated the solid-state reaction between the metals and the composite. Chromium and molybdenum were tested both on CFC (NB31) and on silicon doped CFC (NS31), while tungsten was utilized only on undoped CFC. The heat treatments were performed under vacuum at 1400 °C for 2 h with Mo, at 1300 °C for 1 h with Cr and 1600 °C for 1 h with W. The carbide formation on the composite surface was detected by X-ray diffraction analysis (Philips PW1710).

A hot stage microscopy (Leitz GmbH All), was used to study the wettability of copper, in a flowing Ar atmosphere, using the sessile drop technique.

The joining process between the surface modified CFC and pure copper was performed at 1100 °C for 1 h, Ar flow (more experimental details in Ref [14]). The pitch fibres which represent the direction with the highest thermal conductivity were oriented perpendicular to the joint interface. The joined specimens were morphological analysed by optical and electron microscopy (SEM Philips 525M) and by energy-dispersive analysis (EDS SW9100 EDAX). The joint shear strength was measured at room temperature with a compression machine (SINTEC D/10) [15]. The mechanical tests were performed at least on five samples for each kind of joint.

Some CFC–Cu samples were brazed to CuCrZr by Gemco brazing alloy (Wesgo Metals) at Ansaldo Ricerche. The brazing process involves a heat treatment at 975 °C (30 min), a rapid cooling (>1 K/s) from this temperature to 450 °C and finally, an isothermal treatment at 450 °C for 3 h in vacuum [16]. These samples ($19 \times 22 \times 8$ mm^3) were subjected to thermal shock tests: heating of samples up to 450 °C in air was followed by water quench to room temperature. The cycles were repeated 50 times for each sample.

3. Results and discussion

In this work, the composite surface was modified by direct solid-state reaction at high temperature between the CFC and a transition metal of VIB group. The reaction between CFC and a transition metal leads to a composite surface modification: the new modified carbide based surface is wetted by molten copper. The most desirable form of reaction product between the metal and the composite is a coherent and adherent carbide layer, which can be wetted by copper.

The reaction products between CFC and the transition metals were detected by X-ray diffraction analysis. The X-ray pattern of undoped CFC composite is shown in Fig. 1(a). On the composite surface modified by Cr, the Cr_7C_3 and $Cr_{23}C_6$ were found, while no graphite was detected (Fig. 1(b)). In the case of surface modification by Mo and W, the metal carbides were Mo_2C and WC, respectively and a residual quantity of unreacted graphite and metals was found (Fig. 1(c) and (d)). These two carbides are well wetted by copper at 1100 °C as reported in Ref. [6], while the presence of residual graphite on the surface can lead to an increase of the contact angle. Besides, metal silicides can be present on the silicon doped CFC modified surface. Anyway, a chemical etching on silicon doped CFC can partly remove silicon at the composite surface and reduce the formation of brittle intermetallic compounds at CFC NS31-Cu joint interface [17].

The carbide layers, obtained after the modification by Mo and Cr, were continuous and have a thickness of about 15–20 μm, as it is shown in Fig. 2 for the chromium carbide, while the W carbide coating appeared as a non-coherent layer (Fig. 3).

The wetting experiments were performed at 1100 °C for 30 min, but the contact angle of molten copper on the substrate did not change after the first

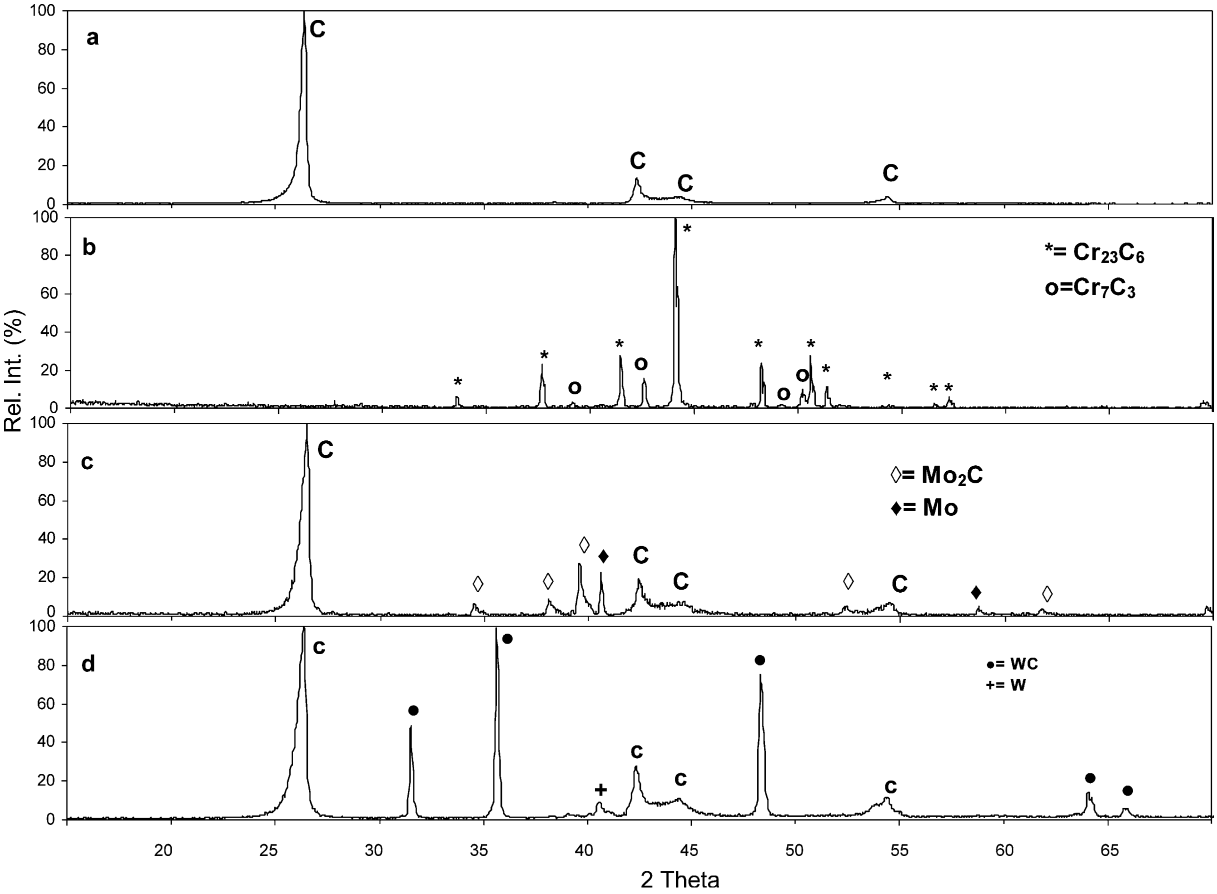

Fig. 1. XRD pattern of undoped CFC (NB31): (a) as received; (b) after modification by chromium at 1300 °C for 1 h; (c) after modification with molybdenum at 1400 °C for 2 h; (d) after modification with tungsten at 1600 °C for 1 h.

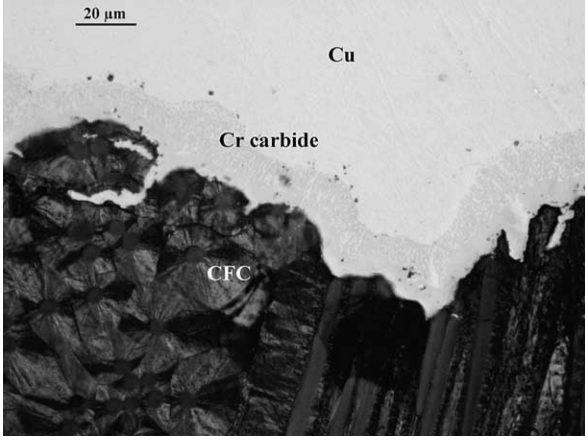

Fig. 2. Optical micrograph of the cross-section of a chromium modified CFC–Cu joint; the total thickness of the carbide layer is about 20 μm.

two minutes. Fig. 4 shows the contact angles of copper on as-received CFC (NB31) and on the surface modified CFC (NB31): in each case, the copper wetted the substrates but copper did not spread homogeneously on the composite modified by molybdenum and the adhesion on the WC coated CFC was very poor because of the carbide layer inconsistency.

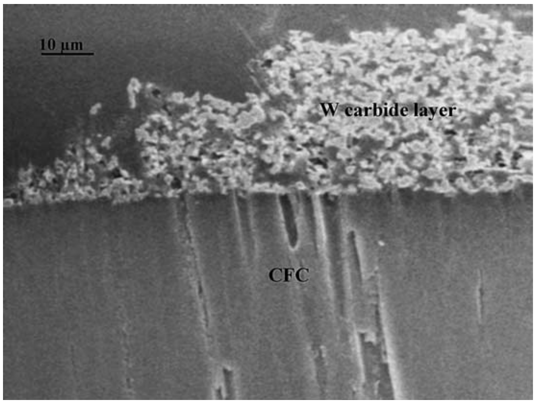

Fig. 3. Scanning electron micrograph of a tungsten carbide coating on CFC substrate.

The contact-angle measurements gave results coherent with literature data: pure copper did not spread over the as-received CFC substrates and the contact angle is >140° (Fig. 4(a)); copper on chromium carbide-modified CFC shows a final equilibrium contact angle of 40° (Fig. 4(b)), while on the molybdenum and tungsten carbide modified surfaces (Fig. 4(c) and (d)) the contact angle is respectively 35° and 30° (Table 1).

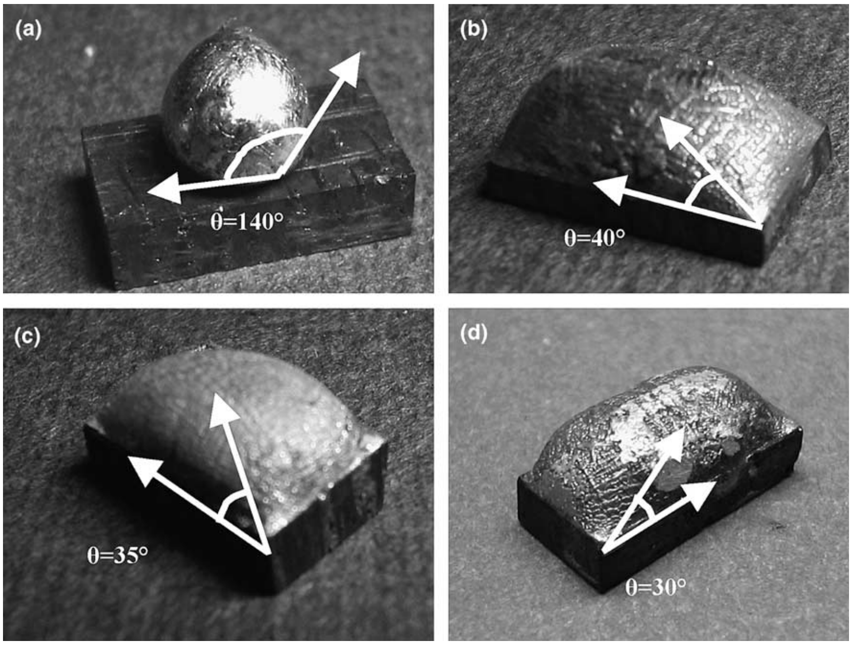

Fig. 4. Wettability of pure copper on CFC substrate (pitch fibres are perpendicular to the interface and the CFC surfaces were not machined) at 1100 °C for 30 min: (a) as-received CFC NB31; (b) Cr modified CFC NB31; (c) Mo modified CFC NB31; (d) W modified CFC NB31. Sample dimensions are about $12 \times 6 \times 3$ mm^3.

Table 1
Summary of wetting data and mechanical shear test results of CFC–Cu joined samples

CFC	Metal modifier	Mechanically machined surface	Average shear strength (MPa)	Contact angle (deg)
NS31	Cr	No	33 ± 6	40
NS31	Cr	Yes	32 ± 3	40
NB31	Cr	No	34 ± 6	40
NB31	Cr	Yes	31 ± 2	40
NS31	Mo	No	6 ± 3	35
NS31	Mo	Yes	11 ± 2	35
NB31	Mo	No	–	35
NB31	W	No	–	30

The contact angles were measured on machined and not machined surface CFC.

The good wettability of copper on the modified composite surface allows direct joining of pure copper to CFC, avoiding the use of brazing alloys that can cause metal diffusion into copper with the degradation of its thermal and mechanical properties [18]. Even low concentrations of alloying constituents can significantly reduce the copper thermal conductivity. Furthermore, to enhance the adhesion at the CFC–Cu interface, the joining process was performed with a low external pressure of about 1 kPa and the surfaces of some CFC samples were tool machined (machining depth of about 100–200 μm).

The cross-section of a chromium carbide-modified CFC–Cu joined sample is reported in Fig. 2: the chromium carbide layer follows the irregular profile of the composite surface, the copper wets uniformly the carbide layer and infiltrates the surface porosity of the substrate. Furthermore, the two interface (Cu-carbide and carbide–CFC) are continuous and without any cracks or pores and it is clearly observable a dense carbide layer (5–10 μm) and a less compact carbide layer (10 μm); the last one is completely infiltrated by copper. In the CFC–Cu joined sample where the composite surface was mechanically machined (Fig. 5), the high wettability of molten copper on the modified CFC allows the infiltration inside the cavities without the formation of any voids. Almost the same morphology was observed in the CFC previously modified with Mo.

In spite of the large thermal expansion mismatch between CFC and copper, no cracks are revealed in the composites or at the interface after cooling from copper melting to room temperature and no limitations are placed to the thickness of the copper layer casting on CFC (up to 5 mm have been successfully cast).

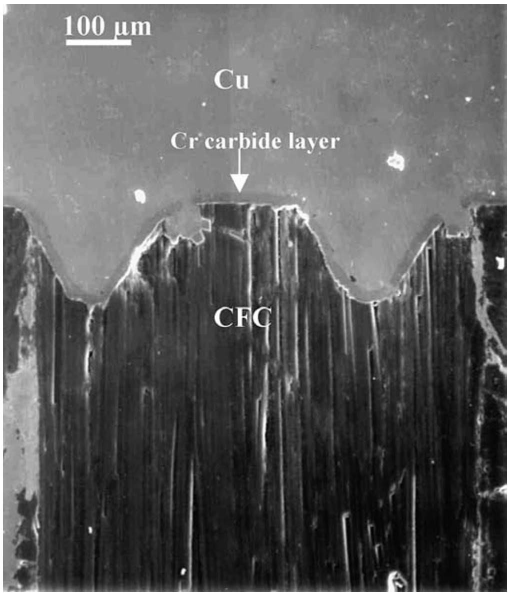

Fig. 5. Scanning electron micrograph of the cross-section of a chromium carbide-modified CFC–copper joined sample. The CFC was previously mechanical machined.

In the case of the WC modified CFC–Cu, the morphological analysis showed a porous carbide layer that corresponds to a weak interface: no mechanical tests were done for these samples. Besides, the joined samples produced by surface modification with Mo and Cr were submitted to shear strength tests. The chromium carbide-modified CFC–Cu samples resulted to have an average shear strength of 33 ± 4 MPa for both the two kinds of CFC composites (silicon doped and undoped) and the mechanical machining of the composite surface did not modify this result. In each case, the average shear strength is higher than the interlaminar shear strength, τ, of the CFC (τNS31 =

20–25 MPa; τNB31 = 15 MPa) [2]. On the other hand, the molybdenum carbide-modified CFC–Cu samples showed lower shear strength: 6 ± 3 MPa for not machined CFC surface and 11 ± 2 MPa for mechanically machined CFC surface (Table 1).

Then, the chromium modification seems to be the best solution to have a good wettability and a strong interface. Some of these samples ($19 \times 22 \times 8\ \text{mm}^3$) were brazed to the CuCrZr alloy: the brazing process consists in a very rapid cooling (>1 K/s) from 975 °C, which does not damage the joints. Furthermore, the same samples do not reveal any damage after the thermal shock test (50 cycles).

4. Conclusion

The joining method described in this paper is a simple and low-cost technique to join CFC composites to copper. An excellent wettability of copper on the CFC composite was obtained after the composite surface modification by high-temperature solid reaction with transition metals of the VIB group. Anyway, a very good adhesion between copper and CFC was observed only in the case of chromium carbide formation on the composite surface. The mechanical strength of the joined samples is higher than the interlaminar shear strength of CFC and thermal shock tests indicate that they can be promising candidates for the manufacturing of heat-sink mock-ups that are essential to demonstrate the reliability of the joints.

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