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Joins of C_f/C and C_f/SiC Composites to Metals

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1. Introduction

Composite is a combination of a reinforcing material within a matrix material that act together to provide enhanced properties unobtainable in either single material. Often the matrix provides protection from damage and gives mechanical stability to the reinforcement under loading; at the same time the reinforcement can enhance the mechanical properties of the matrix [Messler, 2004].

Ceramic Matrix Composites (CMCs) combine reinforcing ceramic phases within a ceramic matrix to overcome the intrinsic brittleness and lack of reliability of engineering ceramics (monolithic ceramics) while retaining their most favourable properties. The ceramic matrix composites (CMCs) considered in this study consist of carbon ceramic fibers (arranged in multidirectional preforms) embedded in a C- or SiC-matrix. These CMC materials have the potential for being used at high temperatures, as thermo-structural materials, in different fields including heat exchangers used in severe environments such as rocket and jet engines [Schmidt et al., 2005], gas turbines for power plants, heat shields for space vehicles, inner walls of the plasma chamber of nuclear fusion reaction [Nozawa et al., 2009; Schlosser et al., 2005], aircraft brakes, heat treatment furnaces, etc. The main advantages of CMCs lie in the fact that they present superior mechanical properties and resistance against high temperatures and at the same time they are lightweight and cost-effective [Lamouroux et al., 1999; Naslain, 2004].

The key property of the CMCs is achieved through a proper design of the fiber/matrix interface arresting and deflecting cracks formed under load in the brittle matrix and preventing the early failure of the fibrous reinforcement [Evans & Marshall, 1989]. Crack deflection is controlled via the deposition of a thin layer of a compliant material with a low shear strength, on the fiber surface, referred to as the interphase and acting as a mechanical fuse (to protect the fiber) [Naslain, 2004]. Carbon fiber reinforced carbon composites (C_f/C) have excellent high temperature properties; they maintain high strength and high toughness even at temperatures above 2273 K [Goto et al., 2003; Schmidt et al., 2005]. The strength to weight, in particular at high temperatures, compared with metal materials is just one special feature that make them attractive as a construction materials. On the basis of these attributes C_f/C composites are used in the nose cone and leading edges of the space shuttle, solid propellant rocket nozzles and exit cones, heat shield, and other components for ballistic missiles, and aircraft braking...
Carbon fiber reinforced SiC ceramic matrix composites (Cf/SiC) are lightweight, hard, and wear resistant and stable in oxidizing environment up to a high temperature. Owing to the embedded carbon fibers, they have an excellent combination of mechanical properties. Therefore, Cf/SiC composites are promising new structural materials for a variety of high-temperature burner environments, including hypersonic aircraft thermal structures, advanced rocket propulsion thrust chambers, cooled panels for nozzle ramps, turbo pump blisks/shaft attachments, and brake disks [Ishikawa et al., 1998].

Most such applications in aerospace and nuclear industry require joining CMCs to metals, ceramics or composites. Fabrication of complex large-scale structural components requires robust integration technologies capable of assembling smaller, geometrically simple CMC parts. Thus, advances in joining science and technology are important in order the benefits of these advanced materials to be realized. Generally the requirements for CMC-metal joints are high mechanical strength at high temperatures and in aggressive environments, high oxidation resistance, high stability under service and low production cost.

In general, there are four basic joining methods, mechanical, adhesive, diffusion bonding and brazing (or combination of them) which rely on mechanical, chemical and physical forces. The mechanical joining, although simple in its realization, can present a plethora of weak points which can make it unreliable. The adhesive method is mainly used for joining CMC to CMC or CMC to polymer. The two latter techniques have been developed for application in extreme environmental conditions.

For a successful fabrication of CMC-metal joining that performs well at elevated temperatures and under the application of loads there is a series of aspects which have to be addressed and successfully coped with. Both materials to be bonded are inhomogeneous and have very different coefficients of thermal expansion (CTEs) which lead to high residual stresses. Moreover, the difference in Young’s modulus may introduce stress concentrations at the interface between the dissimilar materials. To cope with the mismatch of the usually widely differing CTEs, a number of approaches could be used [Razzell, 2004]:

(i) Functionally graded joints in which the strain differences are spread gradually through intermediate layers by altering ratios of constituents.
(ii) Strain isolation systems in which a flexible (e.g., metallic) interlayer accommodates the strain mismatch by elastic deformation.
(iii) Variation of geometry (angled or domed shapes) to minimize stress concentrations.

The inhomogeneous surface structure can be addressed by the application of a coater which bonds well with all the constituents or by an appropriate surface modification. In some cases the rough surface may be advantageous if it is made to act as an interlocker.

A strong bonding can not rely on the weak Van der Waals forces but to 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 CMC/metal bond for operation at high temperature [Nicholas & Peteves, 1994]. 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 [Peteves et al., 1998; Ashworth et al., 2000].

Another important aspect is the diffusion of species from the metal to the CMC and vice-versa. The diffusion has implications in both the fabrication of joints, if high temperatures
are employed and also in the service conditions. The diffusion paths can be very complex as many species are involved but also porosity and microcracking would play an important factor. These effects are expected to be detrimental to both the joining and the joined materials and they can be addressed by choosing a joining technique which can be applied at lower temperatures and creates homogeneous, dense and free of porosity layers. The diffusion of species, in high temperature service conditions, can be handled by the application of a diffusion barrier. A diffusion barrier would also be needed when a combination of techniques are employed e.g. sputtering and diffusion bonding. For a successful metal-ceramic joining the ability to grow both metallic and ceramic layers is of most importance.

In the current review paper first are discussed the main aspects of mechanical joining, adhesive and diffusion bonding and these are presented in sections 2, 3 and 4, respectively. Since brazing is the most common method for ceramic-metal joining and there is an increasing interest for its application in CMC/metal joining, special emphasis is given and its scientific principles as well as the most interesting applications of CMC/metal brazed joints are presented in section 5. A short description of the most significant aspects concerning the wettability and the different brazing alloys used for C/C and C/SiC joining to metals are discussed in paragraph 5.1. The various brazing parameters, such as temperature, holding time, surface preparation and mostly important the difference in the thermal expansion coefficient (CTE) in the metal/filler/ceramic structure, as well as ways to cope with the different limitations are examined in paragraph 5.2. The chemical interaction of the brazing alloys with the CMC substrate and the formation of different compounds are discussed in section 5.3. In section 5.4 examples of successful joining of C/C and C/SiC composites to metals for mainly aerospace and nuclear applications are given. Finally, in section 6 characterization techniques assessing the structure and quality of the joint are briefly described.

2. Mechanical joining

Mechanical joining is the oldest and the simplest way to join ceramic matrix composites (CMCs) to metals using either fastening or mechanical attachment. In this type of joining only forces of mechanical origin enable the joining. The materials that comprise the joined pieces remain distinct and separate at the atomic or molecular level. The principle of fastening in mechanical joining is based on drilling holes in the two materials to be joined and then placing a mechanical fastener through the holes and fixing the fastener in place. This type of joining, although simple in its realization, can present a plethora of weak points such as a) deformation of the CMC materials due to the compressive forces at the joints, b) delamination due to drilling, c) failure of the CMC material due to localized forces (stress concentration) and d) fatigue after long term use of the mechanical joint.

In mechanical attachment, no supplemental devices (or fasteners) are needed. Joining is accomplished by interference or interlocking between designed-in or fabricated-in geometric features integral to the parts being joined. Examples include dove-tails, tongues-and-grooves, T-slots, wedges, and integral snap-fit features molded into plastic parts, as well as elastic thermal shrink-fits, elastic or plastic mechanical interference fits, and plastic staking, crimping, folding and hemming all also found in plastic (especially thermoplastic) parts [Messler, 2004]. Snap-fit integral features are beginning to appear in metal extrusions and
castings (to allow the snap assembly of the space-frame in aluminum-intensive automobiles) and in composites (to allow the snap assembly of power transmission towers (Goldsworthy et al., 1994)).

In general, mechanical joining may present a number of disadvantages which can make it unreliable. Issues such as stress concentration, positions of bores, performance under high temperature of joining parts (for instance, bolts) and their match properties with base materials etc, renders the application of mechanical CMC/metal joining, limited [Zhang et al. 2006]. Another issue is the possible intrusion of a fluid which may be prevented by using appropriate seals or gaskets. In addition, it is difficult to bore through the ceramic matrix composites, and the machining process often produces defects, degrading the mechanical behaviour of the composites.

In aerospace applications, and specifically for the re-entry demonstrators currently being developed in Europe thermal protection systems (TPS) based on C/SlSiC mechanically fastening is used for their joining to the metallic panels [Pichon et al., 2009]. TPS of CMC material may be connected to the space vehicle by CMC fasteners [Böhrk & Beyermann, 2010]. However, examination after the re-entry tests showed that these CMC fasteners may present loss of torque which can be mission critical [Reimer, 2006].

One method of making a joint with a metallic bolt and a CMC is by arranging the thermal expansion to cause sliding between the two components, rather than loosening the joint [Razzell, 2004]. A 45º conical head metallic fastener can be used in a matching countersunk hole in the CMC. The arrangement can be adapted for linear joints as well, with metallic inserts used to provide the angled surface. The above joint is limited to moderate temperatures by the capabilities of the bolt, a typical upper temperature being ~800 ºC for typical superalloys. Fretting between CMCs and between CMCs and metals is a component specific problem.

3. Adhesive bonding

Adhesive bonding is a process of joining materials with the aid of a substance able to hold those materials together by surface attachment. The forces that enable the surface attachment are a combination of substantial secondary (and, occasionally, primary) chemical bonding, often the result of some chemical reaction, and, at least for rough-surfaced or porous adherends, some mechanical locking at the microscopic level between the adhesive and the adherends [Messler, 2004].

The most common structural adhesives are: epoxies, polyurethanes, acrylics, cyanoacrylates, anaerobics, silicones, and phenolics. The adhesives to be successful have to ensure good wetting and chemical compatibility with the surfaces to be bonded. Their advantages rely on the weight saving, the more homogeneous distribution of forces compared to mechanical joining, ability to join complex shapes and capability for sealing, insulating, damping, and resisting fatigue. However, it is problematic that the bonded joint cannot be disassembled without damage. Their use and performance can be limited or degraded by a number of environmental factors, such as temperature, humidity, UV-light exposure and attack by solvents and fungus. The most serious problem for adhesive bonding, however, is that design engineers are uncertain regarding long-term structural integrity and, further, bonded joints tend to fail instantaneously, not progressively [Kweon et al., 2006]. Even if a bonded joint meets strength requirements in laboratory testing, it is doubtful whether the bonding will work with the designed target performance throughout the whole life span of the joint.
Also hybrid joints have been proposed which combine mechanical fastening and adhesive bonding [Kweon et al., 2006]. It is pointed out that hybrid joining is effective when the mechanical fastening is stronger than the bonding. On the contrary, when the strength of the bolted joint is lower than the strength of the bonded joint, the bolt joining contributes little to the hybrid joint strength.

Currently used thermal protection systems (TPS) in aerospace applications utilize epoxy for the composite matrix. Epoxy matrices are known to be unstable and consequently can decompose during re-entry. Another problem with currently used TPS is the adhesives that are used to bond the composite to the metal panels of spacecraft. The adhesives which have good behaviour at high temperature are brittle, and the adhesives with better mechanical behaviour are not adequate for high temperatures and can degrade and lead to devastating consequences.

Different adhesives have been used to join C/C–SiC composites to Ti–6Al–4V alloys [Srivastana, 2003]. The author analysed the effect of glueline length, glueline thickness, etching time, temperature, exposure time in distilled water and strain rate on adhesive joints. The bond strength was found to decrease about 40–50% with increase of temperature and exposure time simultaneously. Also, they lose their strength in hot water and even their strain rates decrease.

4. Diffusion bonding

Diffusion bonding is a solid state welding process in which two materials can be bonded together through the interdiffusion of atoms across the interface. The two materials are pressed together at an elevated temperature usually between 50 and 70% of their melting point. In most cases the surfaces of the materials to be joined have to be of very low roughness. The pressure is used to relieve the void that may occur due to the different surface topographies. The diffusion of atoms at the interface is carried out by several mechanisms, such as the replacement of near atoms, movement of vacancies etc. Diffusion bonding can be achieved with or without the use of an interlayer. The interlayer can reduce cracking, relax the thermal residual stress and improve the joining strength [Zhang et al., 2006].

In literature there is limited information about the use of diffusion bonding in joining CMCs to metals, whereas there is able information in the case of joining monolithic ceramics, especially SiC, to metals [Li J. & Xiao, 2004; Matsuo et al., 2011; Zhong et al., 2011; Liu H.J. et al., 2000a]. W was diffusion bonded to SiC at 1500°C for 0.5 h under high purity Ar flow atmosphere [Matsuo et al., 2011]. The reaction phase was amorphous with a gap from 500 to 600 nm in which precipitates having a size of several tens of nanometer were formed. The shear strength of the W-SiC joint strongly depends on its amorphous layer existing between SiC and W and the shear strength of the each interface.

Reaction-bonded Si-SiC (RBSC) was diffusion bonded to Inconel 600 superalloy at temperatures from 900 to 1080°C [Li J. & Xiao, 2004]. It was shown that the interfacial reaction products at 900 and 950°C were various silicides with some voids formed in the RBSC. As the bonding temperature increased to 1000 °C, the superalloy/RBSC reactions become more intensive, although some pores in the RBSC were filled by the reaction products. With the bonding temperature increasing to 1080 °C, a thin layer of CrSi2 was formed at superalloy/SiC interface without formation of any pores in the RBSC and of excessive brittle silicides. The shear strength of this joint was measured as 126 MPa.
SiC was diffusion bonded to F82H steel using a double W/Cu and a multiple W/Ni/Cu/Ni interlayer to reduce the residual stress [Zhong et al., 2011]. Diffusion bonding was used to join SiC to a Ti-43Al-1.7Cr-1.7Nb (at %) cast alloy at 1473–1573 K for 15–240 min under a pressure of 35 MPa [Liu H. J. et al., 2000b]. Two kinds of reaction products or new phases have formed during the diffusion bonding, a face-centered cubic TiC and an hexagonal Ti$_5$Si$_3$C$_x$.

Successful bonding of three-dimensional C$_f$/SiC to a niobium alloy has been reported using a Ti–Cu bi-foil interlayer by a two-stage joining process: at 800°C for 30 min under 6 MPa (solid state diffusion bonding) and at 1020°C for 8–120 min under 0.01–0.05 MPa (transient liquid phase diffusion bonding) [Xiong J.H. et al., 2006]. These results showed that the residual Cu layer at the joining interface relaxed the thermal stress of the joint effectively, and the Ti–Cu eutectic liquid, formed by the contact melting of Ti–Cu, not only infiltrated into C$_f$/SiC, but also reacted with the SiC coating of C$_f$/SiC. Liquid-phase diffusion bonding was also used for the successful joining of two-dimensional C$_f$/C to Nb alloy using again a Ti/Cu interlayer [Li J. et al., 2008]. The shear strength of the joint reached a value of 28.6 Mpa.

5. Brazing

Brazing, principally used for metal-metal joining, is now increasingly used for the fabrication of metal-ceramic and ceramic-ceramic couples. It employs a brazing alloy with a low melting point which as it melts wets the two solid surfaces and during the solidification the bond is established between the two parts.

There is a broad knowledge base on brazing monolithic ceramics to metals but the information in the literature concerning the brazing of CMCs to metals is rather limited. The scientific principles involved in the brazing of monolithic ceramics to metals have been discussed by Akselsen where the mechanical properties of directly brazed ceramic-metal joints are discussed as a function of key parameters such as temperature and time [Akselsen, 1992].

For a ceramic-metal brazed joint to be successful, a crucial point is wettability of the ceramic by the liquid metals since in the majority of ceramic-metal systems direct wetting is not observed [Naidich et al., 2008]. The limitation of poor wettability can be overcome by the incorporation of an “active metal” into the braze or to precoat the ceramic with a wetting promoter or the metallization of the ceramic prior to the brazing process [Dixon, 1995; Moutis et al., 2010]. The issue of wettability and the different brazing alloys used for C$_f$/C and C$_f$/SiC joining to metals are discussed in paragraph 5.1. Brazing parameters as temperature, holding time, surface preparation and mostly important the CTE difference between metal/filler/ceramic and ways to cope with are examined in paragraph 5.2. The introduction of an active metal has as a result the strong chemical interaction of the filler alloy with the ceramic substrate and the formation of different compounds and locally different distribution of the alloy elements and these effects are discussed in section 5.3. Finally in section 5.4 examples of successful joining of C$_f$/C and C$_f$/SiC composites to metals for mainly aerospace and nuclear applications are given.

5.1 Brazing alloys

During brazing the liquid alloy must come into complete contact with the solid surfaces and must be able to enter all cavities and porosities or in other words it should “wet” the solids
Joining of Cf/C and Cf/SiC Composites to Metals

245

to be joined. The contact angle and work of adhesion are the primary parameters which define the interaction of a brazing alloy with the surface of the materials to be joined as well as the quality of the joint. Wettability is affected by many factors, such as atmosphere, temperature, thermodynamic stability of liquid and solid, alloying constituents, and the surface condition of the solid (surface roughness, surface stress and crystallographic orientation). Thus, in order to obtain high quality joints controlling of the wettability is necessary. The typical method to promote the wettability in metal/ceramics is to introduce in the liquid metal a so-called adhesion-active element -titanium, hafnium and others- which are characterized by high chemical affinity to the atoms of the solid phase. The liquidus temperature of the braze is important as, for work pieces to be used at lower temperatures, a high processing temperature might result to the ceramic deterioration. On the other hand, for joints to be used at high temperature applications, a high solidification temperature is required. The CTE and yield strength of the filler metal are of importance for the fabrication of a sound joint and some of these aspects are discussed in section 5.2. Brazing alloys in the form of paste, foil or powders can be used. Complex joint configurations are often better accommodated by use of braze foils than pastes [Morscher et al., 2006]. Powders and pastes containing organic binders often leave contaminants (binder residue) at the interface and impair the joint strength.

Brazing Cf/C and Cf/SiC composites to metals, as generally ceramics to metals, has to tackle the problem of poor wettability of metals on ceramics [Akselsen, 1992]. In order to improve the wettability interfacial chemical reactions between the ceramic and braze are put into play by the introduction of an active metal to the braze. Thus, brazing fillers for metal/ceramic joining are obtained by modifying a conventional filler by the addition of an active element promoting the wetting of the ceramic surface [Nicholas, 1998]. It has also been found that the reactive wetting correlates with the final interfacial chemistry of the system, not with the intensity of the interfacial reactions [Eustathopoulos, 1998]. Unfortunately at present, the experimental estimation of reliable equilibrium contact at high temperatures remains a major challenge and a serious obstacle to the development of scientific approaches to wetting phenomena [Sobczak et al., 2005]. The concentration of the active metal is crucial for a successful brazing. High content of the active metal ensures better wetting but might lead to brittle intermetallic phases or could harden the filler alloy which is detrimental to residual stress relief. The active metal interacts with C or SiC to form different compounds. Active metals in the form of foils have been used to join ceramics to ceramics as Ti or Zr foils for joining SiC [Morozumi et al., 1985].

The brazing fillers mainly consist of two groups of alloys, i.e. Cu-X or Ag-Cu-X brazes where X is the active element typically a group IVB element (Ti, Zr, Hf). In many cases, active brazes also contain additions of Ni, Be, Cr, V, In and Co. The addition of tin to copper does not enhance its ability to wet ceramics, but the addition of titanium does, and the simultaneous addition of tin and titanium is particularly beneficial. The commercially developed Cu-10.3at%Sn–12.8at%Ti brazing alloy wets very well carbon [Standing and Nicholas, 1978]. The binary Cu-Ti alloys for Ti content above 10at% solidify over a narrow temperature range which improves the flowability and reduces the risk of liquation and brittleness during solidification. The initial contact angle of the alloy of 145° on carbon is reduced almost instantaneously to 50°, that of pure Cu. Before the final reduction to 0° there is a plateau lasting of about 3 mins. This plateau indicates the presence of an incubation period needed for the initiation of the chemical reactions between the absorbed Ti and
carbon [Li J.G., 1992]. The same effect is achieved by the addition of Ti to the eutectic composition of Ag-Cu (78at% Ag -22at% Cu).

For brazing using the Ti-Ag-Cu system the isothermal section of the ternary phase diagram is used [Petzow & Effenberg, 1988]. The miscibility gap divides the liquid braze into solutions of low and high Ti content [Pau lasto et al., 1995] and has a significant effect on the mechanisms of active brazing. The very large values of the surface tension of Ag and Cu of the braze at their melting points show that these metals in pure state do not wet the carbon based materials. The high chemical affinity of Ti towards C, which promotes wetting and bonding, results in the segregation of Ti at the composite/braze interface. Also Ti additions to Sn, Ag, Cu, and CuSn alloys sharply decrease the contact angle on carbon. The addition of Ti and/or Si improves the wetting through the formation of carbides TiC and SiC at the interface [Grigorenko et al, 1998].

The very large values of the surface tension of Ag, Ni and Cu of the braze at their melting points show that these metals in pure state will probably not wet the C. However, the wettability of TiCuNi brazing alloy (70Ti-15Cu-15Ni, wt%) on C is very high. A joint, of about 30–35 μm thickness formed at the interface between the C and the braze alloy, is continuous, free of micro-defects, independently from the carbon fibre orientation (parallel or perpendicular to the surface) [Salvo et al, 2010]. A thin titanium carbide layer of about 2 μm close to C substrate causes beneficial near-interfacial changes which promote wetting and bonding [Singh et al., 2007].

The operation temperature of C composites to metal joints fabricated using the fillers discussed above is limited to around 500 or 600 °C. Therefore in order to fully exploit the high temperature potentials of C composites high temperature brazes are required. PdNi alloys offer such a possibility and PdNi alloys and with different Cr-active content have been examined and the alloys PdNi-(12–25)Cr and Ni-33Cr-24Pd-4Si (wt%) showed excellent wettability [Chen et al., 2010].

In terms of SiC brazing, research progress has so far been rather slow. According to the reactivity of SiC with metals two groups can be defined: a) metals (Ni, Co, Fe, etc.) which react only with silicon and b) metals (Zr, Ti, Hf, Mn, etc. . . .) able to react with both silicon and carbon. It is known that a banded structure would form at the interface between SiC and elements Ni, Co or Fe, consisting of alternating bands of silicides and of randomly distributed graphite precipitates in the silicide matrix which has as a consequence the weakening of the joints [Chou, 1993; Mehan et al., 1976]. Therefore, taking also into account the presence of carbon fibres in a C/SiC composite the second class of metals are the most appropriate for C/SiC to metal joining. For example brazing alloys of 22Ti–78Si (wt.%) and 21Ti–74.2Si–4.8Cu (wt.%) exhibit both good wettability and cohesion with SiC after cooling [Li J. et al., 2009]. Cu-Cr and Cu-Ni-Cr alloys wet well SiC and the addition of Si suppresses the formation of a duplex layer of Cr23C6 [Xiao & Derby, 1998]. For high temperature applications of SiC joints the addition of V in Co and Pd–Ni based alloys eliminated the periodic band structure of the interfacial reaction layer controlling thus effectively the interface reaction [Xiong H.P. et al., 2007].

5.2 Brazing processes

Once the brazing alloy has been chosen the brazing temperature is more or less defined by the liquidus of the braze. A little higher temperature might improve braze-ceramic substrate interactions as well as the penetration of the braze into the ceramic. The holding time at the brazing temperature controls the reaction layer formation. Both the brazing temperature and holding time should be optimized so as to achieve a controlled thickness of
Joining of Cf/C and Cf/SiC Composites to Metals

the reaction layer without the development of brittle reaction phases. Heating and cooling rates are important for the thermal stresses minimization but also on the formation of secondary phases. The conventional brazing process is characterized by slow heating and cooling cycles while the whole component is placed in a uniform heat zone. Another important parameter is the composite ceramic surface preparation. Ceramic composite surfaces are generally rough but additional surface roughness and sub-surface are damage may be introduced while vacuum heating and opening-up of partially closed pores during heating under vacuum has been observed [Sobczak & Asthana, 2001]. Decreasing the brazing temperature and time are always recommended with the advantages of decreased interfacial reactions, decreased erosion of substrates and minimum loss of base-metal properties. The application of brazing alloys which contain reactive metals requires that joining is performed in a vacuum with a very low oxygen potential, or in a dry inert-gas atmosphere with a low dew point to prevent the active elements from reacting with the atmosphere. If these requirements cannot be met, the ceramic surfaces should be metallized prior to brazing.

The effect of brazing temperature and time are very important on the quality and shear strength of the brazed joint. This is very nicely demonstrated by the brazing of Cf/C to TC4 alloy [Qin & Feng, 2009]. The maximum shear strength of the joint has a temperature window of about 20 °C while the holding time window is of about 5 min at the best brazing temperature. The temperature controls which phases will occur between the active metal(s) of the filler and the composite whereas temperature and time the thickness of the reaction layer. Formation of brittle phases is also a consideration for the brazing temperature adjustment. Thus, both brazing temperature and time have to be optimized for improved joint strength [Paiva et al., 2000; Tillmann et al., 1996].

Residual stresses developed during the cooling process will be sufficiently high to influence the strength and properties of the brazed joint during subsequent mechanical or thermal loadings, and in some cases will lead to catastrophic failure during the fabrication process. Careful design with, for example, the employment of finite element analysis (FEA) can minimize the residual stresses developed during the brazing. Increasing the braze thickness generally leads to higher peak residual stresses, but plastic behavior within the joint reduces this effect. There is the possibility of introducing an efficient stress-relaxing procedure, in which, during cooling, the temperature is held constant at an intermediate level at which stresses are high but not catastrophic, to allow for stress relaxation through creep [Levy, 1991].

The critical defect size, \( d_c \), at the interface or within the ceramic can be calculated from the equation

\[
d_c = \frac{4K^2}{\pi\sigma^2}
\]

(1)

where \( K \) is the fracture toughness of ceramics and \( \sigma \) is the residual stress (no external load applied) which depends on the CTE difference given by [Ning et al., 1989]

\[
\sigma = \frac{E_1E_2}{E_1+E_2}(a_i-a_i)(T_b - T_o)
\]

(2)

where \( E \) is Young’s modulus, \( a \) the CTE, \( T_b \) the brazing temperature and \( T_o \) the temperature of the surroundings. For small CTE mismatch the critical crack length is of the
order of tenths of mm whereas for large CTE mismatch could be in the order of μm. Defects of this size may be present in ceramics in the form of pores. This strongly suggests that ceramic surface processing prior to brazing is important for adequate joint mechanical properties. Young's modulus and strength [Ryshkewitch, 1953] and hence strain at fracture, are found to be exponentially dependent on the volume fraction of pores [Moulson, 1979]. Therefore, it is not surprising that failure may occur in metal/ceramic joints even without application of an external load. Thus, evaluation of the joints also requires testing for porosity and internal cracks.

Composite surface polishing prior to brazing might promote chemical reactions which the interfacial roughness of the unpolished substrate could reduce by hampering braze spreading and physical contact. Surface roughness could result in an increase of the contact angle in non-wettable systems whereas in wettable systems in a decrease. Such a surface treatment has been proven beneficial in the case of monolithic ceramics, however, its beneficial effects in the case of composites has not yet been established. A disadvantage in the case of composites is that polishing very likely might introduce surface and sub-surface damage such as grain and whisker or fiber pull-out as well as porosity.

One of the main reasons for the metal-ceramic joint to fail either during its fabrication or during service is the different CTE between metal and ceramic (see equation (2) above). The CTEs of C/C and C/SiC composites are normally much smaller than those of most alloys (e.g. steels or superalloys) with which need to be joined together (CTE mismatch). When constrained to cool together either through the process of joining or work thermal cycle, residual stresses resulting from the differences in thermal expansion can compromise the integrity of the joint. This intrinsic failure mechanism of the joint can be alleviated by the introduction of an interlayer between the metal and the composite. In addition, complex interlayers with incremented thermal expansion coefficients may be used which, through a gradual transition of CTE, relieve the thermal stresses.

Ductile metallic interlayers as Cu (yield strength of about 50 MPa) provide significant reduction of residual stresses, but their applicability in real systems is limited due to their low resistance to corrosion and oxidation at elevated temperatures. Mo thermal expansion coefficient is very low (about $4.8 \times 10^{-6} \, \text{K}^{-1}$), very close to that of the ceramic and can be used as CTE matching interlayer. Using a double foil of Mo adjacent to the metal and Cu adjacent to the C/C thermal stresses can be minimized and cracks during brazing or cooling from a working temperature to be avoided. When the thermal stress of the joint is over the yield strength of Cu, the Cu foil yields releasing part of the stress. Moreover, part of stress diverts to the Mo foil resulting to a decrease of stress at the composite and the filler metal interface.

Stress release can also be accomplished by the incorporation of few interlayers (compensated interlayer) as in the case of a triple layer Kovar/tungsten/nickel used for brazing SiC to a nickel-based superalloy [Xiong H.P. et al., 2007] or by a layer with linearly or non-linearly varying CTE (functionally graded interlayer). Another approach is that of a flexible interlayer which uses a thin, dimpled or corrugated sheet of metal brazed to the metal and ceramic parts. In this context it has been proposed the use of metal foam for joining ceramics to metals. This has been applied in brazing aluminium nitride to Inconel 600 and it has been demonstrated that the joints are tolerant to severe thermal cycling tests [Shirzadi et al., 2008]. Relief of the residual stresses could also be accomplished by the combination of reinforced and un-reinforced filler alloy layers and for example...
Incusil®ABA™ (Ag59Cu27.25In12.5Ti1.25) brazing filler was reinforced with SiC particles [Galli et al., 2006]. Properly designed multiple interlayers can reduce the strain energy in the ceramic-metal joining more effectively than a single interlayer [Park J.W. et al., 2002] and the most desirable gradation of interlayer properties is not a simple linear decrease from one base material to the other. The use of rigid layers with increasing CTE away from the ceramic interface and insertion of ductile layers between each rigid layer can reduce the strain energy most effectively. Also a very effective way to decrease the strain energy at the ceramic/metal interface and to provide a better solution for larger area joints is through the control of porosity at the interlayer [Park J.-W. et al., 2004]. This has been confirmed by shear tests which proved that the joint strength is increased up to a certain level of porosity due to relaxation of residual stresses. Generally multiple interlayers play an important role in reducing the strain energy in the ceramic and in increasing the strength of the joint and their designing should be based on material properties and numerical or analytical calculations.

5.3 Surface Interactions
The brazing alloy at the brazing temperature is in liquid form thus the liquid-metal/ceramic interfaces play a central role in the brazing of metals to ceramics. As mentioned above, the decisive parameters determining the chemical and physical interactions that take place at the interface is the wettability of the solid substrate by the liquid alloy, characterised by the contact angle, and the interface adhesion strength. The width, $w$, of the reaction zones can be estimated by the following relationship:

$$w = c_i t^n \exp(-Q / RT)$$

where $n = 0.5$, $t$ the holding time, $T$ is the brazing temperature, $R$ the gas constant and $Q$ the activation energy for diffusion. The activation energy for diffusion depends on the diffusing species and the chemical and structural form of the substrate (e.g. porosity, fibre versus matrix). If the constituents of a filler alloy have different activation energy for diffusion (which usually will be the case) the ceramic composite will assist in their separation and different activation zones will be observed. Also faster or slower diffusion can occur dependent on the path of the melt which could be through or around a fiber or through an open porosity channel. In addition, some of the elements of the filler metal might react with the ceramic and as the content of the filler alloy changes the activation energy will also change. Thus, the filler ceramic surface interactions can be very complicated and the phases formed will depend not only on the phase diagram but very strongly on the changing concentration of the penetrating filler versus depth. The surface structure, both chemical and morphological, is what will determine the joint quality and strength and has thus to be controlled by the filler and process choice. In fact, interfacial reactions can affect every stage of the formation of a joint from the onset of bonding through the development of equilibrated microstructure to the optimization of the mechanical properties. An important point is that all investigations related to interface compound formation are carried out at room temperature and it could be contemplated whether the compounds are formed when the metal filler is in the liquid state or are formed as a result of crystallization when the more refractory component of the alloy solidifies. Notwithstanding that it is thought that most of the compounds are formed at
the brazing temperature the importance of the cooling from the brazing temperature to room temperature should not be ignored. Further work in this area is needed as sometimes holding the cooling at some specific temperature improves the joints and this could be connected with the formation of beneficial phases [Naidich, 2005]. Also it is not quite clear the mechanism of the spreading of a liquid on a ceramic at high temperature which is usually accompanied by chemical reactions and diffusion [Saiz & Tomsia, 2005]. Theoretical calculations on the energetics of liquid metal/ceramic interface based on statistical mechanics [Novakovic et al., 2003] will be of great help for understanding brazing interface phenomena and guiding developments in controlling the interface interactions and thus the fabrication of sound joints for demanding applications.

5.3.1 Carbon and filler metal interactions
Carbon strongly interacts with the active metals (Cr, Ti) in the filler to form carbides. Different stochiometric or sub-stochiometric carbides can be formed of which their chemical formula and mixture will depend on the Gibbs free energy. Bulk thermodynamics of different alloys and carbon could be a guide as to what compound might be formed. However, there are severe limitations of bulk thermodynamics as the interaction occurs in surfaces and the surface energy has to be taken into account. In addition, the filler alloy concentration changes in time and in depth and during cooling, phases formed at higher temperatures might be transformed. Further, it should be remembered that we are far away from thermodynamic equilibrium and the products of the interactions are mostly diffusion controlled.

An approach to study surface interactions is to deposit an active element on the surface of carbon and by X-ray diffraction measurements to determine the phases formed at different temperatures or by imitation of the brazing process thermal cycle [Moutis et al., 2009]. Cr deposited on carbon was completely transformed into a mixture of the Cr$_7$C$_3$ and Cr$_3$C$_2$ phases after the thermal cycle of brazing. Generally, when Cr is the active element in a brazing filler it reacts strongly with C to form different carbides Cr$_{23}$C$_6$, Cr$_4$C, Cr$_7$C$_3$ and Cr$_3$C$_2$ and spreading kinetics are limited by the Cr diffusion [Voitovitch et al., 1999]. The Cr carbide formation promotes the reaction of brazing fillers with C/C composite, resulting in the improvement of wettability on carbon matrix. Cu poorly wets carbon but the liquid Cu-Cr alloys (Cr 0.5 and 2 at.%) show improved wettability on vitreous carbon substrates which is due to the formation of a 1-5 μm thick layer of the compound Cr$_7$C$_3$ [Voitovitch et al., 1999]. The high temperature filler Ni-33Cr-24Pd-4Si forms a 15-20 μm in width homogeneous diffusion layer at the C/C composite interface. Close to the C/C surface Cr reacts with carbon to form a Cr-C reaction layer. Subsequently, Pd and Si participate in the reactions and form Pd$_{2}$Si and Pd$_{3}$Si phases, and in this reaction zone, the residual brazing alloy became Ni-rich and Pd-depleted [Chen et al., 2010].

Wetting by the Ti-Ag-Cu braze is due to the formation of Ti carbide. Only one stable intermediate phase is formed in the Ti-C system: TiC, with a face centered NaCl type structure. The TiC has a wide composition range which extends from 29 at% C to 50 at% C with the lattice parameter increasing from 4.303 to 4.330 Å with increasing carbon content. As the Ti is depleted from the alloy the wetting behaviour will change as Ag and Cu do not wet carbon or TiC [Frage et al., 2002]. Whenever carbon fibers are used for CTE matching or for increasing joint strength, Ti in the braze alloy reacts with the fibers bonding them to the structure [Zhu & Chung, 1994]. Usually different interaction zones are observed in the C/C substrate when Ti-Ag-Cu braze is used. The closest to the substrate zone is divided into a
TiC layer and a layer which mainly consist of Ti and Cu [Qin & Feng, 2007]. The second layer consists of Cu-rich and Ag-rich phases. In the next zone a mixture of Ag-rich phase and a phase mainly consisting of Ti and Cu are observed. The formation of the TiC phase near the C/C interface is also observed in the brazing of the C/C composites with a Ni superalloy [Moutis et al., 2010] and the second layer consists of separated Ag and Cu rich phases. Ti carbide formation is not only observed on the composite surface but also around the carbon fibers. The Ti-Ag-Cu melt and composite interactions are mainly determined by the TiC formation at the composite/filler interface. As the Ti interacts with the carbon its concentration in the melt adjacent to the composite surface decreases. Ti from the bulk melt diffuses to the depleted zone and interacts with the underlying carbon increasing the carbide layer thickness. As the melt is depleted from Ti and probably during cooling separation of Ag and Cu occurs. Also TiCu phases have been observed and probably their formation would be possible in cases in which the formation of TiC is not the prevailing compound. In addition, the mutual exclusion between the Ag and Ti elements have a significant influence on the joint microstructure [Wang et al., 2010].

The nickel in TiCuNi also has a higher affinity for carbon than Cu, Au and Ag, and has been found to segregate at the carbon/metal interface. There are no stable Ni carbides however there is some evidence on the formation of metastable ones. However, as the principal constituent of TiCuNi is Ti (~70%), which strongly reacts with the carbon, formation of nickel carbides is less probable.

A foil filler metal Ti–37.5Zr–15Cu–10Ni (wt%) forms a 2 μm reaction layer with a C/C composite which consists probably of Zr and Ti carbides [Qin & Feng, 2009]. When Cu is used as a stressed reliever three layers between C/C composite and Cu are formed. A Cu9Zr11 compound is formed at the Cu-filler interface (10 μm). At the composite site (Ti,Zr)C reaction layer is formed which changes from discontinuous at lower temperatures (850 °C) to continuous at higher brazing temperatures (920 °C) and its thickness increases. In the third layer (50 μm ) many phases (Ti2(Cu,Ni) + Ti(Cu,Ni) + TiCu + Cu2TiZr) coexist. As the temperature increases the plethora of phases is reduced and only Cu and Ti(Cu,Ni)2 remain. The phases present and the joint microstructure determine the shear strength of the joint which increases from 7 MPa for the brazing fabricated at the lowest temperature to 21 MPa for that fabricated at the highest temperature.

5.3.2 SiC and filler metal interactions

The brazing of C/SiC to metals is mainly based on processes and methodologies developed for brazing monolithic SiC to metals. Therefore, in order to put the discussion of the brazing of C/SiC to metals in the right perspective and assist in the expected future intense activity in this area the interaction of SiC to filler metals is outlined in this section. Designing and controlling the chemical reactions between SiC and metals is an important issue in the fabrication of the C/SiC to metal joints. Formation of various reaction products at the SiC/metal interface during the joining process may lead to completely different mechanical properties of the joints. Thus, the understanding of reactions between SiC and different metals is substantial for the realization of a successful joining between C/SiC and metallic alloys. In addition, the control of interface reactions between the SiC matrix and the brazing alloys is a significant matter and should be considered in the design of new brazing alloys for joining SiC based materials.

The reaction kinetics of SiC/metal can be indentified into two modes i) formation of silicides and free carbon (type I) and ii) formation of carbides and silicides (type II) [Park J.S. et al.,

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Ni, Co, Fe, etc. metals react with SiC to form brittle silicides which are accompanied by carbon precipitation in the form of graphitic layers which weaken the joint of the ceramic to a metal. Zr, Ti, Hf, Mn, etc., that react with both silicon and carbon, can lead to a high reactivity with SiC that must be controlled in order to select the nature of the reaction products and the thickness of the reaction zone. Bhanumurthy & Schmidt-Fetzer studied the interface reactions of SiC with Ni, Cr, Pd and Zr [Bhanumurthy & Schmidt-Fetzer, 2001]. It was observed that none of these metals are in thermodynamic equilibrium with SiC. The interface reactions lead to the formation of complex structures in the reaction zone. The interface reactions in SiC/Ni, SiC/Pd form periodic bands and SiC/Cr, SiC/Zr form layered structures. C and metal atoms are the most dominant diffusing species in SiC/Cr, SiC/Zr and C is almost immobile in SiC/Ni and SiC/Pd. Therefore development of brazing alloys will rely on employing combinations of these metals in order to control the intensity of the interactions and chemical composition of the products. Other elements (Si, Ag, Al, etc.) may be added in order to control the strength of the interactions and the final products. Nickel’s strong interaction with SiC can be controlled by the addition of, for example, Ag or Si. An Ag coating, about 2 μm thick, significantly reduces the reaction of SiC with Ni and this approach has been used in joining SiC to Ni super-alloys for high temperature applications [Hattali et al., 2009]. A Ni-56Si filler alloy was used to join SiC to Kovar alloy (Fe-32at%Ni-15at%Co) [Liu G.W. et al., 2010]. McDermid & Drew used solution thermodynamic theory to compute an optimum composition of Ni–Cr–Si alloy for brazing SiC ceramics [McDermid & Drew, 1991] and they conducted brazing experiments in order to assess the effect of changing the Si content away from the optimum composition on the joint microstructures. They pointed out that the alloy’s containing less than 36 at% Si lead to the formation of a porous reaction zone at the brazing alloy/SiC interface due to the excessively vigorous joining reaction between brazing alloy and ceramic. The best microstructures were attained for 40 at% Si alloy joints, closely agreeing with the thermodynamic model, whereas higher Si content alloys exhibited localized debonding of the brazing alloy from the SiC.

The AgCuTi filler poorly wets SiC [Südmeyer et al., 2010]. Titanium and silicon carbide in the temperature range between 1250 and 1500 °C form the ternary phase Ti3SiC2 [Gottselig et al., 1990] which could improve the wettability if the chemical potential is appropriate for its formation. Good wettability with a contact angle less than 30° on SiC is observed when using as a braze filler SnAg3Ti pellets with a Sn content above 30 wt%. Standing and Nicholas pointed out that the solubility of Ti in ternary systems was reduced by the addition of an element with a low surface energy like Sn [Standing and Nicholas, 1978]. In that manner the activity of Ti, which is necessary for the diffusion process at the ceramic–braze interface, can be increased so that the ceramic–braze interface is strengthened. Moreover the low solidus temperature (200 °C) and the small Young’s modulus of Sn leads to a reduction of residual stresses, which has a positive effect on the compound strength. Ti reacts with the carbon in the C/SiC composite substrate to form stoichiometric carbide (TiC) as well as sub-stoichiometric carbides (e.g., TiC0.95, TiC0.91, TiC0.80, TiC0.70, TiC0.60 and TiC0.48). In addition, formation of silicide phases at the interface from the reaction of Ti and Si (from the SiC) is a distinct possibility.

5.4 Fabrication of brazed joints of C/C and C/SiC to metals
5.4.1 C/C-metals brazed joints
Semi-3D C/C has been brazed to TC4 (Ti-6Al-4V (wt. %)) aerospace alloy [Donachie, 1982; Roger et al., 1993] using a Ag-26.7Cu-4.6Ti (wt.%) 50 μm thick foil [Qin & Feng, 2010].
Notwithstanding the thickness of AgCuTi foils is 50 μm, joining zones of about 60–80 μm are formed indicating inter-diffusion of the filler metal and base materials. Within the three zones (metal/braze, intermediate, braze/composite) different layers are formed. In the braze/composite zone TiC+C and TiCu layers are formed. In the intermediate zone there is the formation of Ag (s.s) phase and the TiCu + Ti₃Cu₄ phases. Whereas in the metal/braze zone the layers of phases Ti₃Cu₄, TiCu, Ti₃Cu and Ti₃Cu + Ti (s.s), are observed. Brazing at 900 °C for 5 min using Ti-Zr-Cu-Ni foil results in the formation of a reaction layer of 2 μm thickness which is probably (Ti,Zr) carbides. The formation of (Ti,Zr)C between Cf/C composite and the filler metal speeds the wettability of the liquid brazing alloy. A good joining is observed but there is also a crack arising from the thermal stresses. Thus, a pure Mo foil (0.1 mm thick) next to the TC4 and the pure Cu foil (0.3 mm thick) next to the Cf/C were used as composite interlayer in order to release stresses (Cu) and provide a matching (Mo) CTE to the composite. Samples brazed at 900 °C for 5 min have the maximum shear strength of 21 MPa, a four fold increase in comparison to samples (5 MPa) without the Mo/Cu interlayer. This strength corresponds to that of the Cu/filler/Cf-C system which is the weakest and fracture occurs in the composite when carbon fibers are parallel to the joining surface and the fracture surface lies in the composite/filler metal interface when the fibers are vertical. In order to reduce the CTE mismatch between the Cf/C composite and the TC4 metal, SiC particles were introduced in the Ag-26.7Cu-4.6Ti (wt.%) filler alloy. SiC particles as reinforced phase had an average particle diameter of 4.6 μm. The best shear strength was attained for volume fraction of SiC particles of about 15%. SiC particles have reacted with the brazing alloy, forming a new phase, probably a Ti–Si–C compound [Qin & Yu, 2010].

Ti-metal/Cf-C composite joints were formed by reactive brazing with three commercial brazes, namely, Cu-ABA, TiCuNi, and TiCuSil [Singh et al., 2005]. Ti-rich phases such as TiC₁₋ₓ which bond well to both the carbon and the braze, were formed at the Cf-C/TiCuNi and Cf-C/TiCuSil interface. At the braze/Ti interface some dissolution of the metal in the molten braze has occurred. The highest joint strength was obtained by the Cu-ABA braze material. Joining of Ti tubes to Cf/C composite plates provide a test of the joined structure in tension. The Cu-ABA braze composition had the highest load-carrying ability in comparison to TiCuNi and TiCuSil. Fracture always occurred within the surface ply of the Cf/C composite which indicates a stronger bond between the braze material and the Ti-tube or Cf/C composite than the strength within the outer ply itself. The interlaminar tensile strength of these Cf/C composites was an order of magnitude higher than the bond strength measured based on the failure load and bonded area of the surface ply. Probably the brazing process introduces defects in the outer ply reducing its interlaminar tensile strength or the loading condition induces stress-concentrations and other fracture modes. The fiber orientation is also a factor that dictates the load-bearing capability of the joint [Morsch et al., 2006]. Titanium aluminate is regarded as an excellent material for high-temperature applications [Li Y.L. et al., 2006] and its joining to Cf/C could further elevate the operating temperature of thermal structures. The interfacial structure of the Cf-C/AgCuTi/TiAl braze joint was greatly influenced by the mutual exclusion between the Ag and Ti elements with typical interface structure TiAl/Ti₂Al + AlCuTi/AlCu₂Ti/Ag(s.s)/TiC/Cf-C [Wang et al., 2010]. Copper-clad-molybdenum and copper-clad-invar because of their thermal conductivity and low thermal expansion are used for thermal management applications. A joined Cu-clad-Mo/Cf-C composite system can provide excellent heat dissipation capability at reduced
weight. The Cf/C composites made from T-300 C fibers and resin-derived carbon matrix have been joined to Cu-clad-Mo using four brazes (Cu–ABA, Cusin-1 ABA, Ticuni, and Ticusil) [Singh et al., 2007]. Cu–ABA (92.8Cu–3Si–2Al–2.25Ti) microstructure consists of needle-like precipitates that are a Cu(Ti,Si) phase, and a Cu-rich homogeneous matrix. Mo is dissolved in the molten braze and diffuses within 20 μm in the composite. Redistribution of alloying elements because of dissolution and interdiffusion was also observed with the other brazes and the surface active element Ti preferentially segregated at the Cf-C/braze interface in all joints. Also 3D Cf/C composites having CVI carbon matrices were joined to Cu-clad-Mo for heat rejection applications using two Ti-containing Ag–Cu active braze alloys (Ticusil and Cusil-ABA) [Singh & Asthana, 2008]. Both Cusil-ABA and Ticusil have infiltrated the inter-fiber regions in the 3-D Cf/C composite of several hundred micrometers. The TiC reaction layer that forms is known to be discontinuous and this permits extensive infiltration of porous carbon by the melt even in a short time interval.

Cf/C composites (CARBOTEX) have been joined to a Nimonic alloy using Ticusil (Ti-Cu-Ag) filler metal [Moutis et al., 2010]. In order to accommodate the different linear coefficients of thermal expansion between ceramic composite and metal as well as to provide compatibility between the surfaces to be joined, the Cf/C surface was metallized through the deposition of a chromium layer. Heat treatment at 700 °C for 1 h results in the transformation of part of the deposited Cr to chromium carbide Cr7C3. During brazing with Ticusil filler it is found that the Ti penetrates into Cf/C in depth of about 100 μm and coats the carbon fibers. This deep Ti penetration in the carbon substrate has also been observed in Cf/C composites brazed to Cu clad Mo [Singh & Asthana, 2008], and in graphite brazed to Nimonic alloy [Moutis et al., 2009]. Layered structures of different compounds are observed and these arise from the Ti carbon interaction to form TiC and the separation of Ag and Cu in the remaining filler melt. The surface metallization with chromium improves the reactivity of the elements of the filler metal and the carbon.

The use of metallic glass brazes to join ceramic composites, notwithstanding their high strength and excellent corrosion resistance, has been limited. Cf/C made from T-300 C fibers and resin-derived carbon matrix CVI SiC matrix reinforced with T-300 carbon fibers was brazed to Ti using two Ni-base metallic glass braze foils (MBF-20 Ni–6.48Cr–3.13Fe–4.38Si–3.13B–0.06C–0.07Co–0.01Al and MBF-30 Ni–4.61Si–2.8B–0.02Fe–0.02Co–0.01(Al, P, Ti, Zr)) [Singh et al., 2008]. The very large Ti concentrations in the vicinity of the Cf/C composite surface in both MBF brazes suggest that Ti from the substrate had actually dissolved in molten braze during joining, and segregated at the Cf/C surface. The joints show large internal stresses and inter-laminar shear failure within the composite matrix was also noted in some joints. Cf/C composites as low neutron activation materials are considered as excellent materials for nuclear fusion reactors because they also have very low atomic number and very high melting and sublimation temperatures. For fusion applications the joining material and process must satisfy certain criteria as not using high pressures, the braze should contain low activation materials and present thermomechanical stability at least 600 °C [Salvo et al., 1997].

The general configuration of the ITER high heat flux components consists of armour material, which directly faces the thermonuclear plasma, and the heat sink, which transfers the heat loads from the armour to the water coolant [Merola et al., 2002; Liu J.Y. et al., 1994]. Cf/C is the reference design solution for the armour material as it can withstand high heat loads, has high thermal shock and thermal fatigue resistance as well as high thermal conductivity. For this application Cf/C material has to be joined to Cu interlayer. The main
problems in the development of the Cf-C/Cu joints are the large thermal expansion mismatch and the fact that Cu does not wet carbon. Plansee AG developed a methodology which consists in the casting of pure copper on the CFC laser machined surface which previously has been activated by titanium and Ansaldo Ricerche developed a brazing alloy with good wetting characteristics on CFC surface [Merola et al., 2003].

Also direct joining of the CFC to Cu was performed by modifying the surface of the composite by a solid-state reaction at high temperature of a transition metal of VI B group (chromium and molybdenum) deposited on the CFC surface by a simple slurry technique (metal powder suspension in ethanol) [Appendino et al., 2004]. The direct joining of copper (in form of slurry or foil) to CFC was performed at 1100 °C for 20 min. The direct joining could be performed as the wetting angle of copper on the modified CFC was lower than 20° at 1100 °C [Appendino et al., 2003].

5.4.2 Cf/SiC -metals brazed joints

Brazing is the main method for joining SiC ceramic to metal [Liu H.J. et al., 2000a]. Carbon fiber-reinforced SiC matrix (Cf/SiC) composites present higher fracture toughness than SiC monolithic ceramics and also combine the merits of the SiC ceramics such as low density, excellent oxidation resistance and high-temperature strength. Therefore, they are excellent potential candidates for application in the aerospace industry [Jian et al., 2005]. Reliable joining of the composite to a metal, especially to the Ti-alloys widely used in aerospace field, is essential for full exploitation of the composite properties and saving weight of the overall structure. As these composites are reaching maturity a recent effort has been devoted in the development of brazing them to metals [Lin G. et al., 2007; Liu Y.Z. et al., 2011; Singh et al., 2008; Singh et al., 2010, Xiong J.H. et al. 2010a; Xiong J.H. et al., 2010b; Xiong J.H. et al., 2006].

For aerospace applications joining of Cf/SiC composite to aerospace alloys, as Ti-6Al–4V, is required. For the brazing of the Ti rich alloys is apparent that Ti as an active metal in the braze would be the best choice. Also Ti reacts with both the matrix (Si, C) and the fibers (C) and therefore stronger joints are expected. Cu-Ti or Ag-Cu-Ti alloys have been the base of brazing Cf/SiC to Ti alloys and in some cases carbon or carbon fibers have been introduced in the braze. Lin G. et al. used carbon fiber-reinforced brazing material (67.6Ag-26.4Cu-6Ti, wt%) to braze Cf/SiC to Ti alloy [Lin G. et al., 2007]. The volume fraction of the carbon fibers in the braze defines the strength of the joint, controls the reaction between the Ti element and the brazed composite and it is associated with the brazing parameters. The reactive products include TiC thin layers covering the fibers and TiC small particles distributed near these fibers in the brazing layer. With the increase of the brazing temperature and dwell time, more Ti dissolves into the brazing layer from the Ti-alloy and the extent of interfacial reaction of Ti with the composite increases. However, excessively high brazing parameters and dwell times incur the formation of pores in the brazing layers.

Using brazing alloys in a powder form, being cheaper in principle, could also permit the mixing of different elements for which brazing foils or pastes are difficult to be fabricated. As an interlayer a mixed powder of Ag-Cu-Ti-W was used for joining Cf/SiC to a Ti alloy [Lin G.B. et al., 2006]. The results showed that W grains mainly distributed in Ag phase in the brazing layer provide the effects of reinforcement and lowering residual thermal stress at the joint. The room temperature and 500 °C shear strengths of the joints performed at 500°C for 30 min with Ag-Cu-Ti-50W (vol.%) are remarkably higher than the optimal strengths of the joints brazed with Ag-Cu-Ti. Successful joining of Cf/SiC composite to TC4.
alloys (Ti–6Al–4V (wt%)) was realised using 94(72Ag–28Cu)–6Ti (wt.%) alloy powder with particle size of 320 mesh [Xiong J.H. et al., 2010b]. The joint interfaces were microstructurally sound, well bonded, and without cracks and voids. Ti₃SiC₂, TiC and Ti₅Si₃ phases were formed in the reaction layers between the composite and the interlayer whereas TC4 dissolved in the braze and Cu diffused into the TC4. The best strength of the joints, 102 and 51 MPa at room temperature and 500 °C, respectively, was obtained for brazing at 900 °C and with dwell time of 5 min.

Also mixed powders of Cu, Ti and graphite were used for brazing C₁/ΣC composite to a Ti alloys [Ban et al., 2009; Xiong J.H. et al., 2010a]. Formation of TiC around surplus graphite and TiC particles in the bonding layer reduced the thermal stress significantly. The reaction rate was controlled by the diffusion rate of C from graphite particles to the liquid bonding layer. The shear strength was remarkably higher than the optimal shear strengths of the joints brazed with pure Cu-Ti.

A Ti-Ni-Nb (39.4-39.4-21.2 at%) brazing alloy [Liu Y.Z. et al., 2011] or a Ti–Cu bi-foil interlayer [Xiong J.H. et al., 2006] were used to join C₁/ΣC composites and Nb alloy (rocket propulsion). The brazing using Ti-Ni-Nb was performed at 1220 °C for 20 min and the ductile filler metal released the thermal stress in the joint. Both Ti and Nb elements in the filler reacted with C₁/ΣC during the brazing process, and a well bonded C₁/ΣC-Nb joint was obtained with shear strength of 149 MPa. The Ti–Cu bi-foil interlayer was used together with a two-stage joining process: at 800 °C for 30 min under 6 MPa and at 1020 °C for 8–120 min under 0.01–0.05 MPa. The results showed that the residual Cu layer at the joining interface relaxed the thermal stress of the joint effectively, and the Ti–Cu eutectic liquid, formed by the contact melting of Ti–Cu, not only infiltrated into C₁/ΣC, but also reacted with the SiC coating of C₁/ΣC. These characteristics were beneficial to the joint, of which the shear strength was as high as 34.1 MPa.

C₁/ΣC composites were vacuum brazed to Ti and a Ni-base superalloy using Ni-base metallic glass braze foils (MBF-20 and MBF-30) [Singh et al., 2008]. For the Ti joint, the results showed that the braze/composite interfacial contact, in both braze foils, is intimate. However, significant cracking through the braze region was observed in the case of MBF-20 braze foil, whereas in the case of MBF-30 there was no evidence of interfacial microvoids and cracks in the joint region. The cracking in MBF-20 was attributed to the higher boron content of MBF-20 (3.13%) than MBF-30 (2.8%), and the presence of ∼6.48%Cr in MBF-20 opposed to MBF-30 that does not contain any Cr. For the case of the Ni-base superalloy the joints for both braze foils are sound, but in the case of MBF-20 shrinkage cavities had been formed. It is pointed out that compositional changes due to substrate dissolution led to secondary-phase precipitation which aided interfacial bonding although inter-laminar shear failure occurred within some composites. Residual thermal stresses in the joint led to hardness gradients; however, stress accommodation by the braze prevented interfacial cracking.

C₁/ΣC composites reinforced with T-300 carbon fibers in a CVI SiC matrix were joined to Cu-clad Mo using two Ag-Cu active braze alloys, Cusil-ABA (1.75% Ti) and Ti-Cu-Ag (4.5% Ti) [Singh & Asthana, 2010]. The brazed joints revealed good interfacial bonding, preferential precipitation of Ti at the composite/braze interface. The Knoop microhardness distribution across the joints revealed hardness gradients at the interface, and a higher hardness in Ti-Cu-Ag than in Cusil-ABA. The effect of composite surface preparation revealed that joints made using ground samples did not crack whereas un-ground samples cracked due conceivably to amplification of residual stress at surface imperfections.
Theoretical predictions of the effective thermal resistance suggest that composite-to-Cu-clad-Mo joints may be promising for lightweight thermal management applications. Also interlayers have been used in order to achieve bonding and relieve strain mismatch between the composite and steel or Ti or Ni alloys. Brazed joints using an interlayer which accommodates strain mismatch have been successfully produced between a SiCf/cordierite CMC and Ti-6Al-4V alloy, and between SiCf/cordierite and Fe-18Cr-8Ni stainless steel (Dixon, 1995). Ductile interlayers of Ni, Cu, W, and SiCf/Ti-6Al-4V metal matrix composite were used between the metals and the CMC. The CMC was coated with 1μm Ti in order to induce wetting and bonding and a Ag-28Cu eutectic braze or aluminium braze was used. Joints brazed normal to the CMC layup plane were generally much stronger than those brazed parallel to the layup plane. Li S. et al. used Cu/W/Cu/W/Cu multiple interlayers to bond Cf/SiC to Ni-based superalloy [Li S. et al., 2003]. The bending strength of the joints has been improved by using the active metallic filler contacted with Cf/SiC. The strength of the joints was remarkably affected by the welding temperature. The maximum value 102.1 MPa has been obtained at 970°C (dwell time: 10 min, welding pressure: 34.3 MPa).

6. Characterization techniques

The characterization techniques can be categorized into two groups, those assessing the joint structure, thermal and mechanical properties and are in general destructive in nature and those assessing the quality of a specific joint and for a specific application which have to be non destructive (NDT). The first type can be performed at the different stages of joint fabrication or after a service cycle, real or laboratory. NDT on composite/metal joints has an inherent difficulty as the response of these complex structures to the excitations used are difficult to be appraised with regard to the component performance in service conditions. However, NDT techniques calibrated against metallographic examinations and mechanical tests can form a basis for reliable NDT test in manufacturing components for critical applications as in the aerospace and nuclear industry [Escourbiac et al., 2007; Ezato et al., 2002; Mergia et al., 2009; Merola et al., 2002].

The metallographic type examinations of the joints as well as mechanical tests are well known and will not be referred here [Kim & Lee, 1998; Park J.-W et al., 2002; Jadoon et al., 2004; Takahashi et al., 2003; Galli et al., 2009; Lee et al., 1995; Serizawa et al., 2006; Serizawa et al., 2007; Serizawa et al., 2008]. However, some advanced techniques not widely used and not well known need to be mentioned. Laboratory X-ray diffraction is well suited in identifying different phases in the joint. Taking into account that there are cases that we need locally to identify phases or that the amount of a phase present is below the laboratory X-ray detection limit, synchrotron X-ray techniques would be of an advantage. X-ray diffraction measurements near the ceramic interface can be used to determine the residual stress distribution [Eigenmann et al., 1987] as indentation fracture [Larsson 2011] or combination of them with finite-element analysis [Lee et al., 1997]. Residual stresses measured by X-ray diffraction in conjunction with finite element models predict very well the joint strength assessed by four-point bend tests [Gali et al., 2009]. Also neutron diffraction could be of great advantage for identifying phases and internal stresses in the joint. Neutron diffraction can be used as a NDT technique even for large components. Neutron diffraction has been applied in determining the stresses of Cf-C/Mo structures to be used for the ITER divertor [Ceretti et al., 1994]. Also strain field both in CFC graphite and in the brazing metal of Cu/Cf-C joints produced for fusion applications has been
determined by neutron diffraction in temperatures up to 600 °C, temperature at which these joints are going to be employed [Ceretti et al., 1998].

An interesting method for detecting weak or defective bonding areas within the brazed adjoining contact surfaces of composite ceramic-metal plates is the measurement by dynamic holographic interferometry of the response of transient flexural waves transmitted through the joint structure [Conrad & Sayir, 2001]. The quality of joints between CFC composites and Cu or CuCrZr to be used as high heat flux components of fusion machines has been tested by lock-in thermography, ultrasonic inspection, microtomography and micro-radiography [Casalegno et al., 2008]. The thermal diffusivity at the material interface of a C/C composite joined to Cu has been determined by the laser flash method. Subsequent calculation of the thermal conductivity and thermal contact resistance can be used as a qualitative assessment of the ceramic/metal joint integrity [Casalegno et al., 2010].

In conclusion, these NDT test need further evaluation and development in order to routinely screen the quality of joints.

In order to understand the filler/ceramic interactions and its wetting process is important its activity to be observed “in situ” as the filler metal interacts with the ceramic at the brazing temperature. A technique sensitive to the different interface formation with resolution of few Å is neutron reflectivity. In addition this technique can be used at high temperature and due to the high penetration of neutrons into the matter real interacting metal/ceramic sandwiches can be used [Derby et al., 1998; Xiao et al., 1997].

7. Conclusions

Ceramic-matrix composites (CMCs), and especially C/SiC and C/C composites, are attractive materials mainly for aerospace, thermonuclear fusion and other applications that require heat and wear resistance. Most of such applications require joining CMCs to metals which has been done using a number of approaches: mechanical joining, adhesive and diffusion bonding and active alloy brazing. Brazing is the method that presents the highest perspectives for the use of CMCs in advanced applications and demanding service conditions. The most critical issues related to the brazing process of CMC/metal are the poor wettability of ceramics by metals and the mismatch in the thermal expansion coefficient which induce residual thermal stresses at the joint. Different approaches to address the wettability issues include the development of brazing alloys, surface modification of the CMC by a wetting promoter of by direct metallization of its surface, and the promotion of certain chemical reactions in combination with the restriction of others through diffusion barriers. The relief of thermal strains at the joint is coped with by the use of ductile interlayers, the employment of carbon fibers or SiC particles reinforced brazing material and the use of an efficient stress-relaxing procedure, such as intermediate holding times during cooling for stress relaxation through creep.

However, notwithstanding sound joints between CMCs and metals have been produced, a lot of improvement in brazing is required in order to address the standards imposed by aerospace and nuclear applications. For this a better understanding of the liquid-metal/ceramic wetting and the underlying physics and chemistry has to be achieved. This will help in the development of predictive models of liquid-metal/ceramic substrate interactions and also of new brazing alloys. The brazing thermal cycles need to be optimized by finite element analysis for the induced thermal stresses and by incorporating predictive models determining the compounds to be formed at elevated temperatures through the
liquid-metal/ceramic interactions. Advanced characterization techniques such as synchrotron X-ray and neutron based techniques will be valuable for the joint characterization. In addition, standardization of existing and development of new non-destructive techniques are needed in order to assess the quality of the joints for the intended application.

8. References


Joining of Cf/C and Cf/SiC Composites to Metals


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This book contains chapters on nanocomposites for engineering hard materials for high performance aircraft, rocket and automobile use, using laser pulses to form metal coatings on glass and quartz, and also tungsten carbide-cobalt nanoparticles using high voltage discharges. A major section of this book is largely devoted to chapters outlining and applying analytic methods needed for studies of nanocomposites. As such, this book will serve as good resource for such analytic methods.

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