

# Wetting of silicon carbide by copper alloys

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This work reports on a study of the wetting of SiC by some Copper alloys. The work is intended to gain a deeper understanding on the wetting behaviour of selected CuTi alloys in contact with a polycrystalline silicon carbide substrate. Although the main body of this work deals with the CuTi/SiC system a few observations are also reported on the interaction between a CuZr alloy and a silicon infiltrated SiC grade. The contact angles established between the liquid alloys and silicon carbide at 1200°C were measured by the sessile drop method using a vacuum between  $10^{-4}$  and  $10^{-5}$  Pa. Since the interface generated between the metallic and ceramic phases in a composite material is a region that plays a critical role in determining its mechanical properties the obtained specimens were subsequently characterised using a SEM fitted with EDS facilities. X-ray diffraction was used to determine the phases formed while DSC analyses were employed to determine the temperatures for the formation of reaction products. © 2003 Kluwer Academic Publishers

## 1. Introduction

The need for new engineering materials with high strength, toughness and stiffness has produced an important research activity to investigate a wide range of metal-ceramic systems for obtaining composite materials which conveniently combine the attractive properties of ceramics (wear and corrosion resistance, hardness, stiffness and low specific weight) with the toughness and ductility characteristic of metals. In particular the development of Ceramic Matrix Composites (CMC's) will expand the application field of structural ceramics up to operation temperatures limited by the melting point of the metallic phase [1]. A first step towards obtaining adequate ceramic matrix composites is to study the physical and chemical interaction mechanisms between the metallic and the ceramic phases. Obviously, a good wetting of the ceramic by the metal during the manufacturing of composite materials is desirable and knowledge of the characteristic features of the metal/ceramic interphase thus developed is of major concern in relation to their final mechanical properties.

Basically, the interaction between a liquid metal and a ceramic substrate during processing may give rise to, either, physical or chemical bonding between them. For chemical bonding two main effects may be distinguished, one related to the formation of a solid solution and another leading to the formation of a reaction product. In these cases, the diffusion volume or the reaction layer formed is generally limited and its physical

properties such as thermal expansion coefficient, elastic modulus and strength, together with its formation rate determine the quality of the composite.

According to a previous report the contact angle between copper and SiC at 1373 K is 140° and the bonding is weak [2]. Furthermore, investigations of the wetting properties of molten copper with SiC have shown that Cu decomposes SiC to form Cu-Si alloys and graphite. The addition of small amounts of Si to copper has also been observed to inhibit the Cu-SiC reaction [3, 4], whereas, Ti and Zr additions are reported to improve wetting [5].

In the present work the SiC-Cu/Ti and SiC-Cu/Zr systems were studied focusing the analysis of the experimental observations on various aspects of the interfacial phenomena, the phases formed under the experimental conditions used, and the microstructures produced during the interaction at high temperature.

## 2. Experimental procedure

Three Cu based alloys, containing nominal additions of 3 and 5 wt% Ti or 5 wt% Zr were used in this study. The metallic alloys were prepared using a vacuum induction melting process with a vacuum level between  $10^{-9}$  to  $10^{-10}$  atm., while the ceramic rectangular substrates, with dimensions in mm of  $8 \times 3 \times 1$ , were obtained after pressureless sintering of  $\alpha$ -SiC green compacts constituted by micron size particles. After

sintering the substrates had approximately 5% residual porosity. The Differential Scanning Calorimetry (DSC) experiments were carried out at 1200°C in an argon atmosphere at a heating rate of 10°C/min. For these experiments the samples were prepared by mixing 50% wt SiC powder with 50% wt metal alloy fillings and subsequently heated in alumina crucibles. The specimens were maintained for 1 h at the treatment temperature and subsequently cooled at 2°C/min up to 850°C, where a faster cooling rate of 5°C/min was imposed. The study of the interaction between Cu-Zr and SiC was carried out using a commercial REFEL (silicon infiltrated) SiC grade. Before the wettability experiments were carried out every ceramic substrate was polished to 1 μm finish. The wetting tests were performed by the sessile drop method, at 1200°C for 10 min, using an ASTRO vacuum induction furnace with a vacuum level between 10<sup>-4</sup> and 10<sup>-5</sup> Pa, that is, 10<sup>-9</sup> to 10<sup>-10</sup> atm.

The interfaces were characterised using a Scanning Electron Microscope (SEM) fitted with Energy Dispersive Spectrometry (EDS) facilities. X-ray diffraction (XRD) was also used to determine the phases formed in metallic alloys melting and the samples of DSC analyses.

### 3. Results and discussion

As shown below, the addition of reactive metals to copper, specifically Ti and Zr, in order to improve their wetting behaviour and bonding characteristics with SiC leads to complex systems as revealed by the chemical reactions and the microstructures generated as a result of the interactions between the liquid metal alloys and the ceramic.

Therefore a systematic analysis of the events taking place at high temperature has been undertaken starting with the characterisation of the as-prepared metallic alloys, followed by a study of the interaction with polycrystalline SiC and ending with an inspection of the generated interfaces.

#### 3.1. Thermodynamic considerations and microstructural characteristics of the experimental copper alloys

The chemical composition of the experimental vacuum melted copper alloys was determined by X-ray fluorescence. Table I presents a summary of these results along with their experimental composition and the phases found in each case according to the obtained X-ray diffraction data.

As observed in Table I, there is a systematic discrepancy between the nominal and the experimental chemical composition of the alloys. In all cases the

TABLE I Chemical composition and phases present after vacuum melting of the experimental copper alloys

Alloys	Chemical analysis (wt%)	XRD analysis
Cu-3Ti	Cu: 97,03-Ti: 2.70	Cu <sub>3</sub> Ti; Cu <sub>2</sub> O; αCu
Cu-5Ti	Cu: 95,87-Ti: 4.13	Cu <sub>3</sub> Ti; Cu <sub>2</sub> O; αCu
Cu-5Zr	Cu: 95,58-Zr: 4.42	Cu <sub>5</sub> Zr; Cu <sub>2</sub> O; Cu

final composition shows a somewhat lower Ti or Zr content than intended. This loss may be the result of the formation of some volatile Ti or Zr oxides during the homogenisation of the alloys taking place by the dissolution of these elements in liquid copper.

Another important aspect shown by the data obtained by XRD is the presence of copper oxide (Cu<sub>2</sub>O) in the alloys and the absence, at least up to the detection limit of the diffractometer, of any stable refractory oxides. This might be the result of an increased reducibility of the oxides as Ti and Zr are dissolved in liquid copper thus forming an alloy and consequently decreasing their activity to a value of less than unity. In this case an increase in the oxygen partial pressure p<sub>O<sub>2</sub></sub> required to form a certain oxide would be expected.

This argument may be confirmed by an estimate of the modified p<sub>O<sub>2</sub></sub> as obtained from theoretical

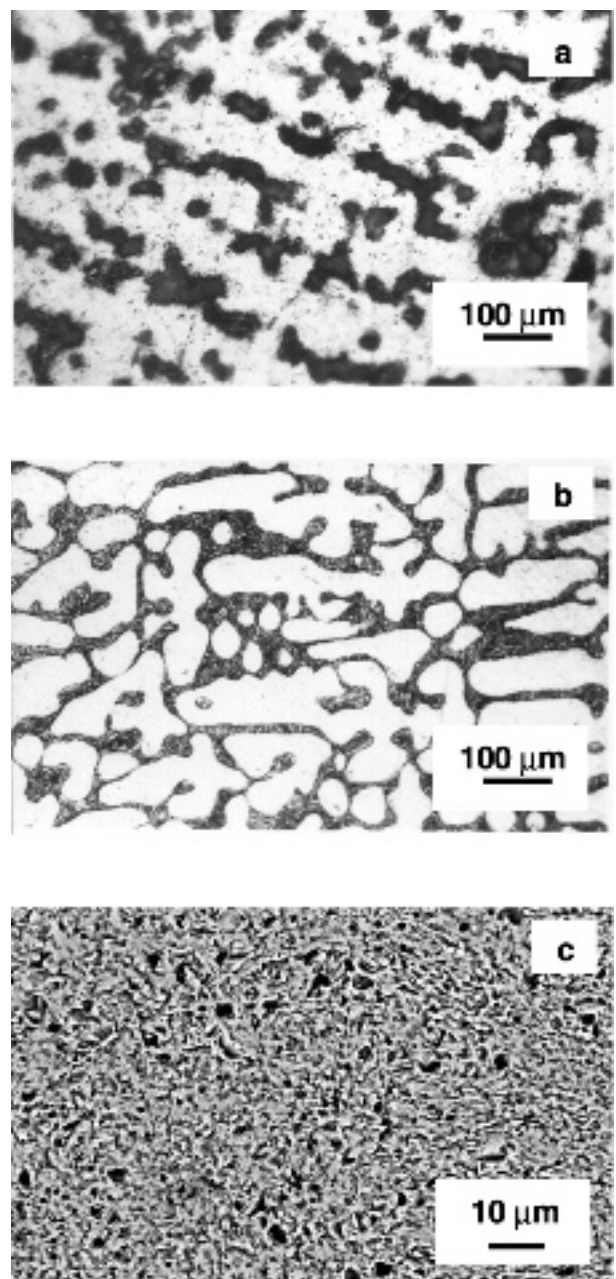


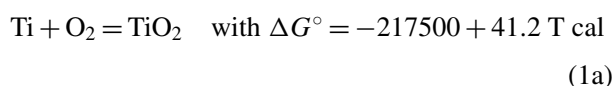
Figure 1 Optical micrographs corresponding to the as vacuum melted Cu alloys: (a) Cu 4.13 wt% Ti, (b) Cu 4.42 wt% Zr, and (c) SiC ceramic substrate.

calculations based on the fundamental concepts of Physical-Chemistry assuming ideality conditions as Ti or Zr form a solution with copper. On these bases it may be written that [6, 7]:

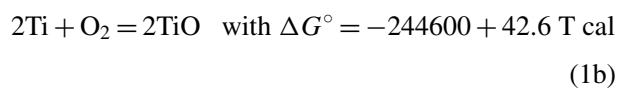
$$\log p_{O_2}(m) = \log p_{O_2}(p) - n \log N_{Me} \quad (1)$$

where  $p_{O_2}(m)$  and  $p_{O_2}(p)$  represent the equilibrium oxygen partial pressures for the alloy and the pure metal or oxide respectively,  $n$  is the activity exponent in the corresponding chemical reaction and  $N_{Me}$  is the activity of the metal or oxide according to Raoult's Law.

Taking the alloy containing 2.7 wt% Ti as a basis for the calculation the two possible reactions between Ti and  $O_2$  are:



and



Considering reaction (1a) as an example, the value of  $\Delta G^\circ$  at  $1473 \text{ K} = 1200^\circ\text{C}$  gives:  $\Delta G^\circ = -156812.4 \text{ cal}$ , and since

$$\Delta G^\circ = -RT \ln K = RT \ln p_{O_2} = 4.575 T \log p_{O_2}$$

upon substitution it results that

$$p_{O_2}(p) = 5.37 \times 10^{-24} \text{ atm.}$$

Now, for the alloy according to Equation 1,  $p_{O_2}(m)$  for  $TiO_2$  may be obtained assuming ideality, i.e.,  $N_{Me} \cong 0.027$ , with the exponent  $n = 1$  thus giving

$$\log p_{O_2}(m) = \log 5.37 \times 10^{-24} - \log 0.027$$

and therefore

$$p_{O_2}(m) = 1.9 \times 10^{-22} \text{ atm.}$$

Comparing these values with the experimental conditions during fabrication of the alloy it is clear that

$$p_{O_2}(p) < p_{O_2}(m) < 10^{-10} \text{ atm.}$$

Consequently, at least on Thermodynamic grounds, although the alloying of Ti forming a Cu-Ti alloy does show an increased reducibility of titanium oxide, since  $5.37 \times 10^{-24} \text{ atm.} < 1.9 \times 10^{-22} \text{ atm.}$  this value is still too low, as compared to the experimental conditions, to explain the absence of  $TiO_2$  in the alloy.

Also, taking reaction (1b) and following the same steps as above, with  $n = 2$  in this case, gives a similar result since the corresponding values now give that

$$1.03 \times 10^{-27} \text{ atm.} < 1.4 \times 10^{-24} \text{ atm.} < 10^{-10} \text{ atm.}$$

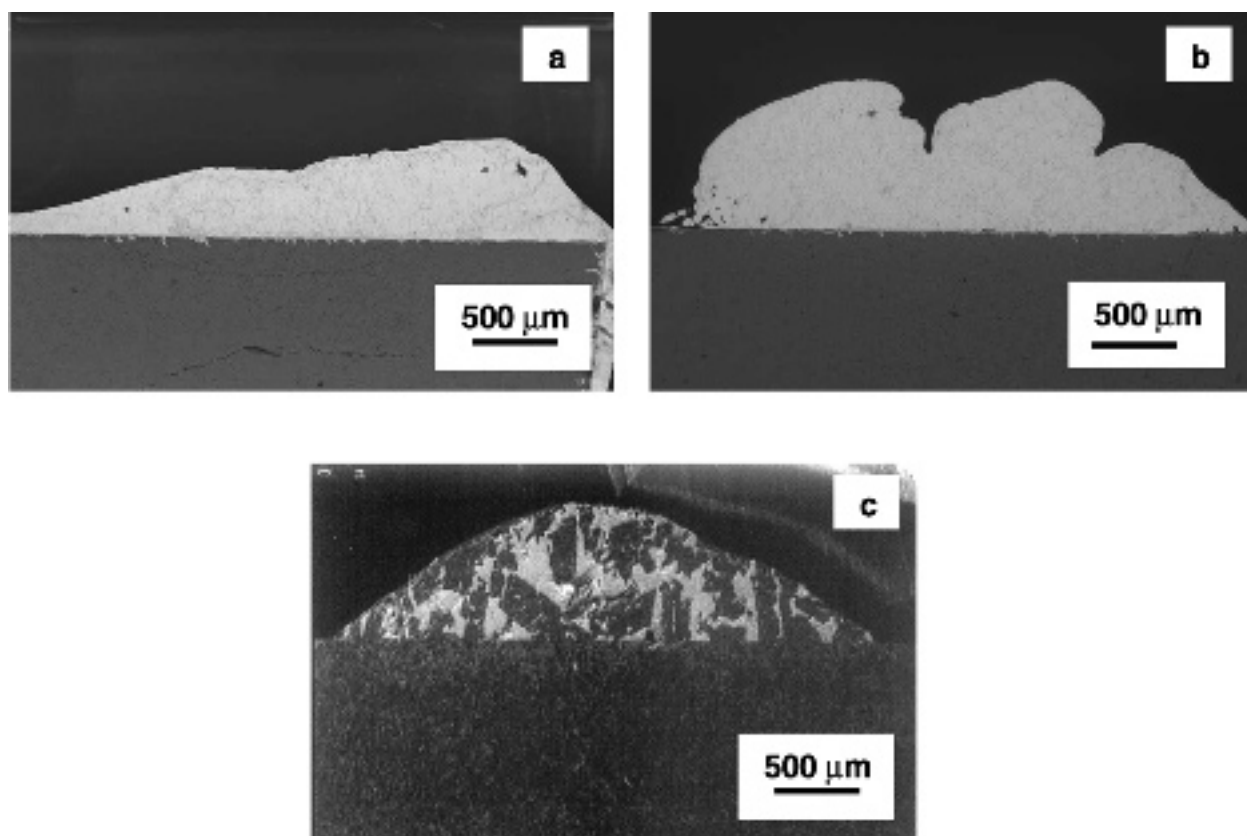


Figure 2 Optical micrographs illustrating the wettability tests carried out using: (a) Cu 2.7 wt%Ti on SiC, (b) Cu 4.13 wt%Ti on SiC, and (c) Cu 4.42 wt%Zr on Si infiltrated SiC.

At the light of these calculations it is clear that neither, the reduction of the stable oxide layer surely covering the titanium originally added to form the alloy, nor the protection of titanium from further oxidation will take place under the present processing conditions. However, since the amount of titanium oxides present is under the detection limit of the diffractometer it could only be argued that:

(a) Additional stable oxides do not form for kinetic reasons.

(b) The solution appreciably departs from ideality which does not seem very likely for a diluted solution.

(c) The Ti-oxides formed may be “unstable”, like TiO, and continuously volatilize during the homogenization time of the alloy taking place by diffusion of titanium into liquid copper.

(d) Alternatively, a combination of all these events cannot be ruled out as another possibility to understand the experimental results.

From these points, the argument indicated as (c) is consistent with the aforementioned Ti loss and is consequently considered as the most likely possibility to account for the experimental results in Table I.

Additionally, the presence of Cu<sub>2</sub>O as the only remaining oxide in appreciable amounts can therefore be reasonably accounted for since it may form during cooling of the alloy.

The microstructures of the metallic alloys and the SiC substrate, as viewed under the optical microscope, are shown in Fig. 1.

In the micrograph of Fig. 1a, corresponding to the Cu 4.13 wt% Ti alloy, two separate phases are distinctly appreciated. The light contrast areas correspond to the proeutectic Cu-rich solid solution and the dark phase may be identified as a eutectic structure containing the intermetallic compound Cu<sub>4</sub>Ti. This observation is in very good agreement with the expected phases from the Cu-Ti phase diagram [8] during the equilibrium cooling of an alloy with this chemical composition. This may therefore allow to conclude that the time given to the initial metal mixture at high temperature was long enough for the formation of a chemically homogeneous liquid by the complete diffusion of Ti into liquid Cu. It must be pointed out that a dispersion of small particles is also noticeable inside the Cu-rich solid solution. This oxide dispersion is thought to come from the irreducible titanium oxide layer (must probably TiO<sub>2</sub>) covering the surface of the titanium lumps added, which may have been fractured and detached from them as these undergo dilation due to thermal expansion. These oxides may therefore be dispersed by floating in the Cu-rich liquid and consequently trapped in the location seen in the micrograph as the alloy is cooled down.

Similarly, for the Cu-Zr alloy, the micrograph of Fig. 1b also shows two phases that correspond to the Cu-rich proeutectic and the eutectic mixture Cu + Cu<sub>5</sub>Zr. A dispersion of Zr oxides is also evidenced in the Cu-rich phase. Finally, Fig. 1c shows the typical fine grained microstructure of a nearly fully dense SiC.

TABLE II Contact angles measured for the experimental metallic alloys in contact with SiC at 1200°C under vacuum

System, 1200°C		
Cu-3Ti 27°	Cu-5Ti 30°	Cu-5Zr 28°

### 3.2. Wettability tests of Cu/Ti alloys on a polycrystalline SiC substrate

The contact angle between the liquid Cu/Ti alloys and SiC at 1200°C, corresponding to an average of the values at each side of the drop, are summarised in Table II. From the measured angles, and the corresponding micrographs in Fig. 2, it may be pointed out that both Ti-containing liquid alloys are seen to wet reasonable well the SiC substrate. There also seems to be a tendency towards slightly poorer wetting conditions as the amount of Ti contained in the alloy is increased.

The table also includes the contact angle measured for the Cu 4.42 wt%Zr under vacuum but using a

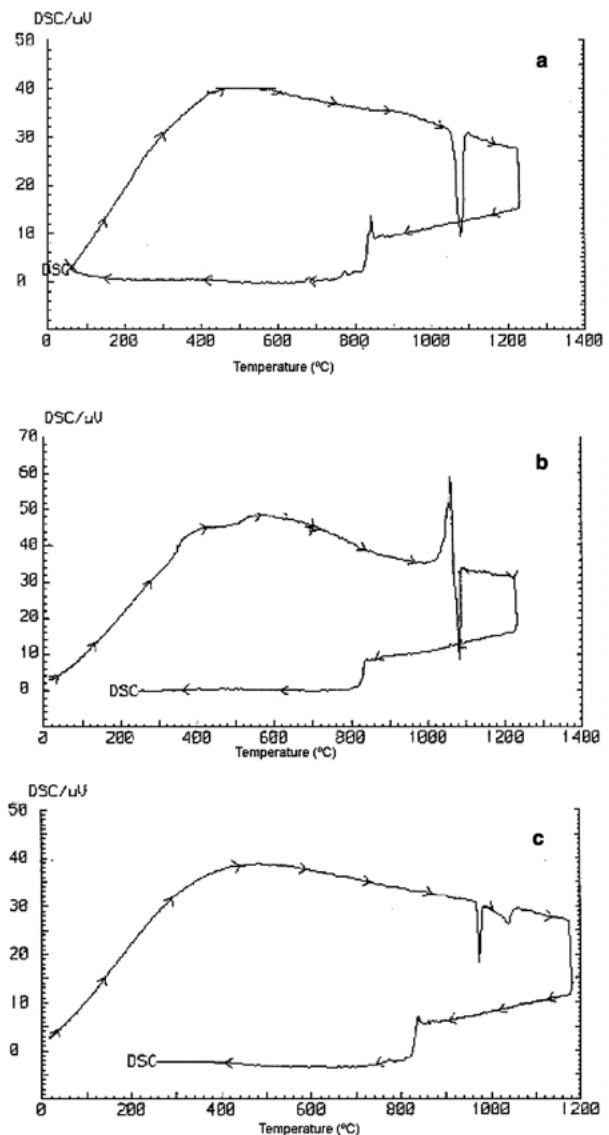


Figure 3 DSC traces corresponding to mixtures of SiC powder with metal alloy filings: (a) Cu 2.7 wt%Ti, (b) Cu 4.13 wt%Ti, and (c) Cu 4.42 wt%Zr.

Si-infiltrated SiC substrate. Under this conditions the measured angle indicates that wetting by this copper alloy is at least as good as that obtained with the Ti-containing alloys on the polycrystalline SiC substrate.

### 3.3. DSC analysis

As mentioned before a complex interaction between the liquid copper alloys and SiC takes place at the

reaction interface. In order to analyze the behavior of these alloys during heating and cooling and to investigate the reactivity of these metal-ceramic systems in more detail a set of DSC experiments were performed, up to 1400°C in an argon atmosphere. For the experiments the samples were prepared by mixing controlled amounts of the SiC powder with metal alloy fillings and subsequently heated in alumina crucibles. The results obtained are shown in Fig. 3 including the heating and

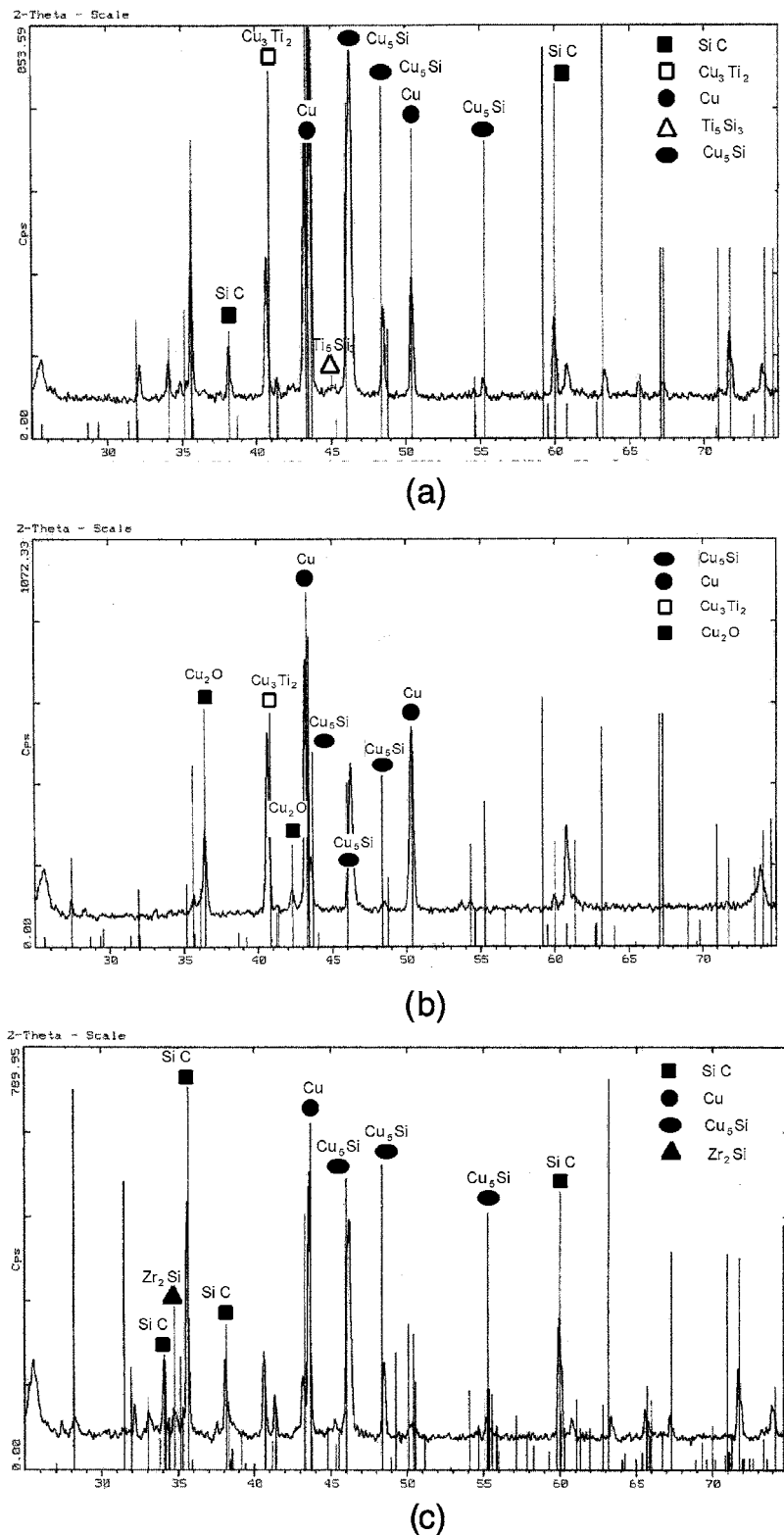


Figure 4 XRD traces corresponding to mixtures of SiC powders with metal alloy fillings after DSC experiments for (a) Cu-2.7 wt%Ti, (b) Cu-4.13 wt%Ti, and (c) Cu-4.42 wt%Zr.

cooling segments of the DSC cycles as indicated by the arrows. As observed in Fig. 3a for the combination Cu 2.7%Ti/SiC, the first significant reaction, as evidenced by the endothermic peak taking place between 1030 and 1090°C approximately, is the melting of the metallic alloy. This observation is in reasonably good agreement with the range of temperatures indicated by the Cu/Ti phase diagram for the melting of this alloy. It is also apparent that no solid state reactions are detected during the heating period. In contrast, as cooling of the metallic-ceramic system takes place three exothermic peaks are detected, the first at about 850°C and another two of minor importance at about 780°C and 680°C respectively. The Cu/Ti equilibrium phase diagram, these peaks may be associated to the precipitation of Cu<sub>4</sub>Ti, the formation of Cu<sub>5</sub>Si as a reaction product and minor amounts of Cu<sub>3</sub>Ti<sub>2</sub> respectively. This seems to indicate that some of the Cu<sub>4</sub>Ti precipitates may react with SiC to produce Cu<sub>5</sub>Si, Cu<sub>3</sub>Ti<sub>2</sub> (a product with a lower Cu:Ti atomic ratio than Cu<sub>4</sub>Ti) and possibly some small amounts of Ti<sub>5</sub>Si<sub>3</sub> (whose main XRD reflections overlap with those of Cu<sub>3</sub>Ti<sub>2</sub>), as well as TiC.

As observed in Fig. 3b, the picture is basically the same as before for the endothermic peak at 1090°C during heating and for the main exothermic peak at 850°C during cooling. On the other hand, the DSC trace in this case shows a main difference due to the exothermic peak, preceding that at 1090°C, which might be related to the formation of titanium silicide (Ti<sub>5</sub>Si<sub>3</sub>) as reported before [9].

For the Cu-4.42 wt%Zr in contact with the polycrystalline SiC (Fig. 3c) shows two endothermic peaks during heating at 974°C and another of less intensity at

1038°C. According to the Cu-Zr phase diagram, these temperatures are in reasonable agreement with melting of the Cu-Zr eutectic, on the Cu-rich side of the diagram, and melting of a Cu solid-solution respectively. During cooling the exothermic peak at about 837°C most likely correspond to the formation of Cu<sub>5</sub>Zr. The sudden change, at approximately 850°C, in the base level of the signals shown in Fig. 3 are due to a change in cooling rate from 2 to 5°C/min. It must also be pointed out, as noticed in Fig. 4a–c, that although Cu or a Cu-rich solid solution, is present in all cases, its solidification was not detected by the DSC traces due to the slow cooling rate (2°C/min from 1200 to 850°C) used in these experiments.

### 3.4. Analysis of the ceramic-metal interfaces

As shown by the wettability tests these copper alloys exhibit an attractive wetting behaviour in contact with SiC, but the chemical interaction of these liquid metals with this ceramic may be expected to be complex, since several compounds may potentially be formed, including carbides, silicides and ternary compounds. In order to have a closer appreciation of the reactions taking place, and complementarily to the DSC experiments, a microscopical analysis of the generated interfaces was carried out. To this purpose the sessile drop specimens were sectioned and observed under the SEM after polishing. The corresponding micrographs are presented in Fig. 5.

As observed in Fig. 5a a reaction film of approximately 25 μm in average thickness was formed at the ceramic-metal interface. As obtained by the EDS, a

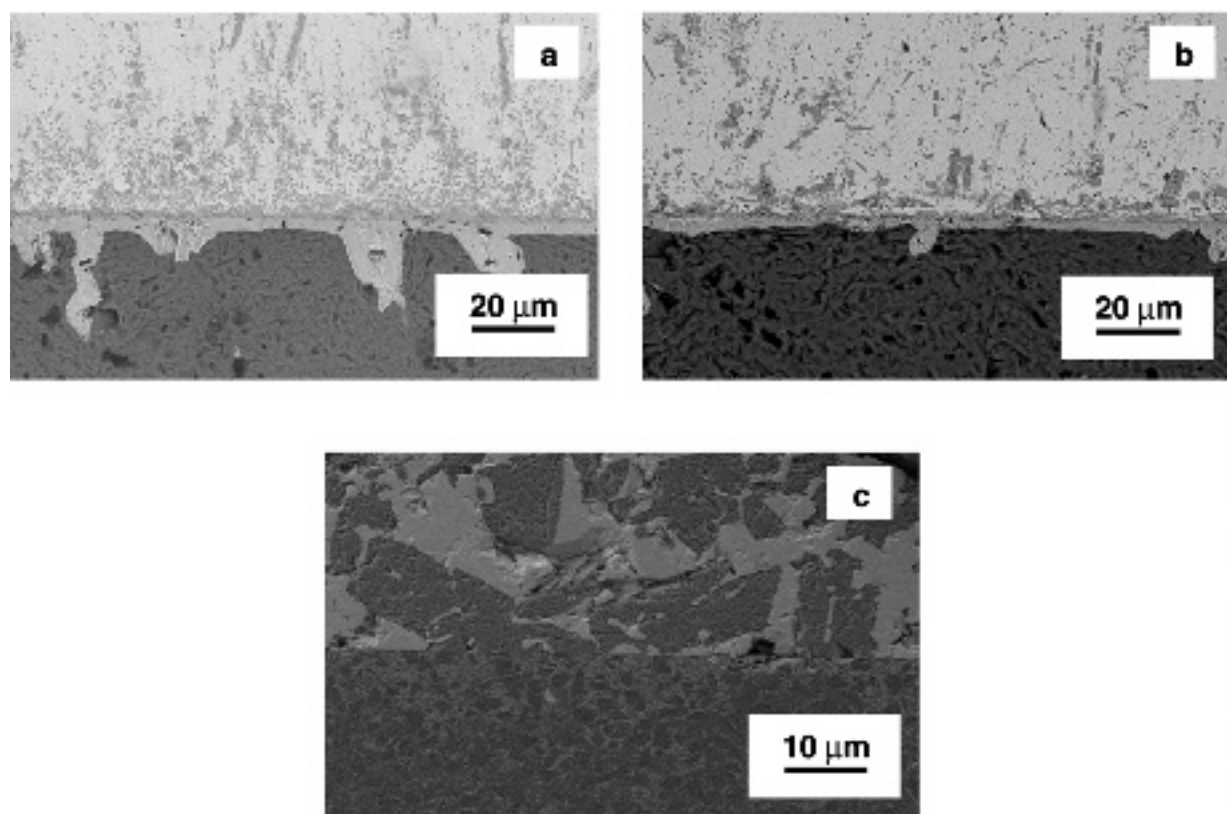
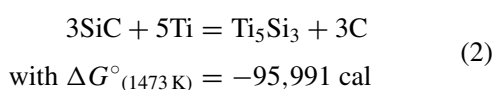


Figure 5 SEM micrograph for the ceramic-metal alloy interfaces for the systems: (a) Cu 2.7 wt%Ti/SiC, (b) Cu 4.13 wt%Ti/SiC, and (c) Cu 4.42 wt%Zr/Si infiltrated SiC.

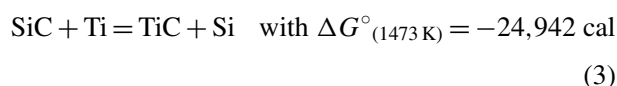
continuous metallic Cu/Ti alloy and a set of cuboid crystals whose chemical composition confirmed their identification as  $Ti_5Si_3$  constituted the reaction zone. Although some differences may have been expected, the general appearance of the reaction zone (Fig. 5b) and the microstructure of the interface generated using a higher Ti content in the copper alloy, were very similar to the previous case. In both cases, it was also observed that the  $Ti_5Si_3$  crystals exhibited a tendency to float in the liquid Cu/Ti alloys, which on the other hand may not be surprising considering that their density of  $4.3 \text{ g/cm}^3$  is much lower than  $8.7 \text{ g/cm}^3$  corresponding to the metallic alloys. It could therefore be concluded that as far as the microstructure and constitution of the reaction interface is concerned the amount of Ti contained in the copper alloy (at least up to the concentration used in the present work) did not produce any significant changes.

The formation of  $Ti_5Si_3$  crystals as a reaction product may be understood by considering the following chemical reaction:

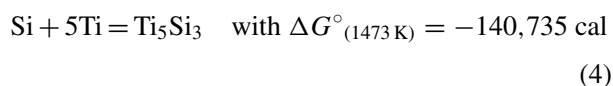


which indicates that the formation of such product is thermodynamically possible. It could also be argued that the liberation of carbon through reaction (2) may be accompanied by the subsequent formation of TiC.

As an alternative mechanism  $Ti_5Si_3$  may also be formed by considering the direct formation of TiC by:



followed by reaction of the liberated silicon with additional titanium through:



As seen by these reactions the formation of titanium silicide, by either mechanism, should be apparently accompanied by the formation of TiC, however, these carbides may be very small so they are undetected under the SEM thus requiring further analysis by TEM to verify their presence.

An additional effect caused by the formation of  $Ti_5Si_3$ , was the creation of a compositional gradient, as observed through the EDS analyses (Fig. 6a–c) carried out from the upper surface of the drop to the reaction interface and well into the SiC substrate. According to the analysis shown in Fig. 6a the outer zone of the drop is depleted of titanium, containing instead a certain amount of silicon and traces of oxygen and carbon, apart from copper which is the dominant element. In contrast, the analysis illustrated in Fig. 6b clearly indicates the presence of titanium at the reaction interface along with the rest of elements mentioned above. These results seem to indicate that the diffusion of titanium towards the reaction interface is continuously promoted

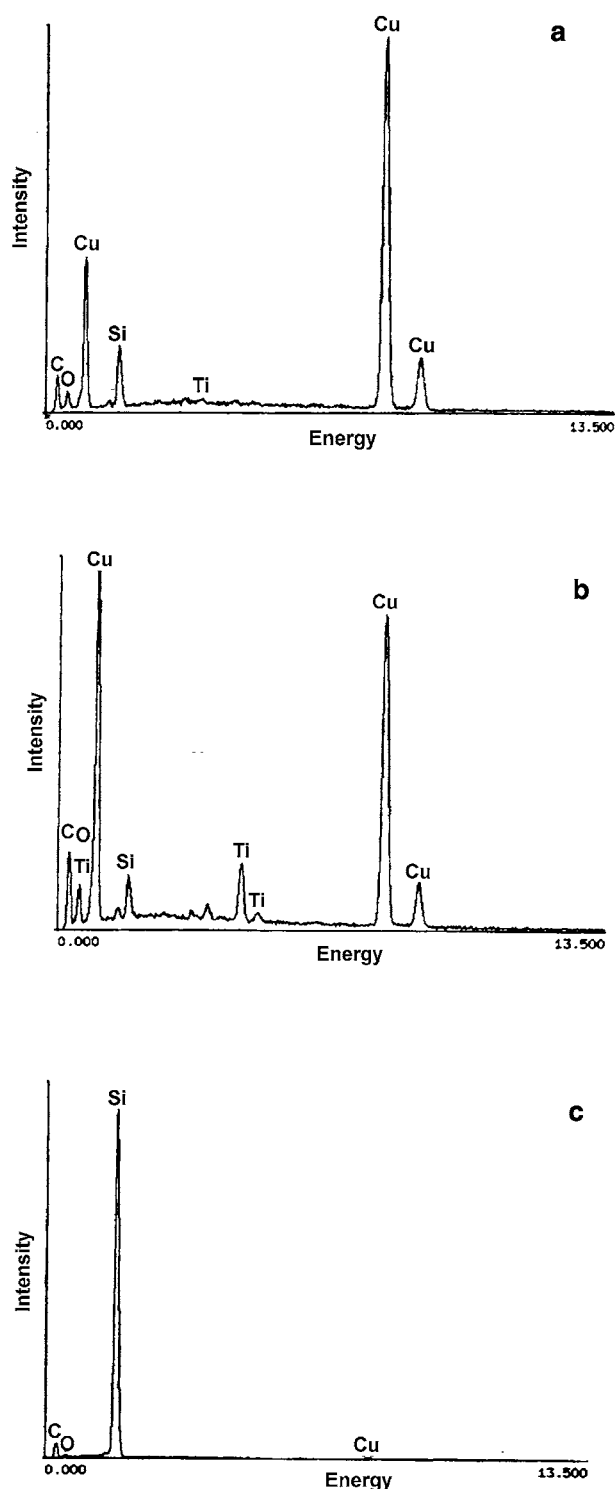
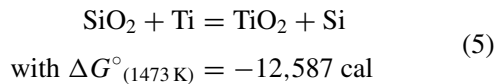


Figure 6 EDS analyses corresponding to the system Cu 4.13 wt%Ti on SiC obtained from the (a) outer part of the drop, (b) ceramic-metal interface, and (c) inner part of the ceramic substrate.

as the titanium silicide is being formed. In addition, the detection of silicon in the outer part of the drop may be associated with the formation of a Cu-Si solid solution or, alternatively it may be the result of some SiC grains being detached from the substrate and floated in the liquid. Of course the oxygen detected must be associated to the existence of some sort of oxides. The analysis shown in Fig. 6c only indicates SiC far away from the reaction interface.

At the reaction interface carbon and oxygen were also detected and may be associated in the case of

carbon to either SiC or TiC, whereas oxygen may come from the silica layer initially covering the surface of the ceramic substrate. In fact, it may also be pointed out, complementarily to the aforementioned reactions, that the reduction of the silica layer by Ti, which is also thermodynamically favourable, may be another source of silicon for the formation of titanium silicide, for instance, through the reaction:



and subsequently followed by reaction (4). For the sake of completion the formation of some ternary oxides or certain oxycarbides should also be contemplated.

For the CuZr alloy in contact with Si-infiltrated SiC the micrograph in Fig. 4c shows a planar contact surface between the metallic alloy and the silicon carbide substrate without evident creation of any reaction products as it is the case of the Cu-Ti/SiC system. Instead, an important diffusion of Si from the substrate to the liquid metallic alloy and consequently an advance of the liquid front into the substrate is observed. This event, upon solidification during cooling, leads to the formation of a microstructure composed by a proeutectic Cu-Si solid solution (white areas) and a eutectic mixture of Cu-Si + (Cu-Si)<sub>5</sub>Zr in dark contrast. This microstructure is therefore common to, both, the metallic drop and the intergranular areas in the substrate.

#### 4. Conclusions

The preparation of Cu-Ti and Cu-Zr alloys by vacuum melting leads to binary alloys without significant oxidation, but with a slight loss of Ti or Zr, probably due to the formation of volatile Ti oxides. The microstructures obtained in both cases are the result of a eutectic reaction upon cooling, thus being constituted by a Cu-rich proeutectic and an eutectic mixture.

The wettability test carried out in vacuum using these copper alloys, exhibit and attractive wetting behavior in contact with SiC resulting in contact angles smaller than 45° in all cases

The microstructure of the metal-ceramic interfaces created show a set of distinct characteristics depending on the chemical composition of the alloy and substrate used. On the one hand, a strong chemical reaction

leading to the formation of a titanium silicide is characteristic on the interaction between liquid Cu-Ti and SiC. Besides, a Ti compositional gradient is generated causing, a Ti depleted zone in the outer part of the liquid drop as a result of the formation of Ti<sub>5</sub>Si<sub>3</sub> cuboids crystals which tend to float in the liquid. Some mechanism, base on the identification of possible chemical reactions, resulting in the formation of such silicide have been proposed.

In contrast, the interaction between liquid Cu-Zr and silicon infiltrated SiC is characterized by the dissolution of free silicon into the liquid and the formation of an eutectic microstructure upon cooling.

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