

# Wettability of silicon nitride ceramic composites by silver, copper and silver copper titanium alloys

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## Abstract

The sessile drop method under vacuum ( $10^{-2}$  Pa) has been chosen to study the contact behaviour between ceramic composites and liquid metals (silver or copper) or alloys (silver–copper or silver–copper–titanium). With the help of a CCD camera, on-line observations were done and the contact angle evolution was followed as a function of temperature or time. Finally X-Ray diffraction analysis and electron micrographs (SEM, BSE, EDX) were used to analyze the ceramic–metal interfacial zone.

A  $\text{Si}_3\text{N}_4$  powder was mixed with an electro-conductive secondary phase (TiN,  $\text{TiB}_2$ ,  $\text{HfB}_2$ ,  $\text{MoSi}_2$ ) and sintered by either hot isostatic pressing (HIP) or hot pressing (HP). The hiped and hot pressed samples contained at least 27 vol.% of the electroconductive secondary phase to allow electrodischarge machining (EDM). Low amounts of sintering aids were used to reduce the consolidation temperature in order to avoid decomposition of the silicon nitride phase and reactions between the powders. All composites are close to full density (relative density greater than 98%).

Non-wetting was observed with silver, copper and the silver–copper alloy on all ceramic composites but the addition of 3 wt.% titanium to the silver–copper alloy induces wetting.

In the reaction zone, the presence of a high amount of titanium due to the formation of  $\text{TiN}_x$  and  $\text{Ti}_5\text{Si}_3$  is noticed.

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## 1. Introduction

Due to their thermal stability and good corrosion resistance the silicon nitride materials are one of the most important technical ceramics. The machining with conventional techniques as diamond coated cutting saws or grinding wheels are time consuming and unsuitable for complex shape components which can be manufactured by electrical discharge machining (EDM). But this technique requires a low electrical resistivity ( $10^{-2}$ – $10^{-3}$   $\Omega$  cm). In consequence, an electroconductive secondary phase as TiN,  $\text{TiB}_2$ ,  $\text{HfB}_2$  or  $\text{MoSi}_2$  can be added to the  $\text{Si}_3\text{N}_4$  matrix,<sup>1–5</sup> and when the powder grain size is in the range of some microme-

ters, the threshold of the percolation concentration is reached ( $\sim 27$  vol.%).

The main method to manufacture dense silicon nitride ceramics is conventional hot-pressing (HP), where the use of oxide additives as  $\text{Al}_2\text{O}_3$  and/or  $\text{Y}_2\text{O}_3$  play an important role in promoting densification. To reduce reactions between the sintering aids and the main powders ( $\text{Si}_3\text{N}_4$ , TiN,  $\text{TiB}_2$ ,  $\text{HfB}_2$ ) hot isostatic pressing (HIP) was used. With this technique, a lower amount of sintering aids is requested as the high pressure facilitates the densification.

The study of the contact between ceramic materials and liquid metals is of great interest, for the joining of structural ceramics and for the melting or casting of metals. To achieve a successful brazing, the ceramics must be wetted by the alloys or metals. Due to large commercial applications, concerning the  $\text{Si}_3\text{N}_4$ /metal systems, reactive metals as titanium-based

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alloys have been used for active metal brazing. But the reactive metal could be active enough to alter the composition of the ceramic/metal interface. In literature, the formation of hypostoichiometric  $TiN_x$  and titanium silicides as  $Ti_5Si_3$  phases is noticed in the Si–Ti–N system.

The joining of ceramics to metals is difficult due to the differences in physical and mechanical properties. The reaction products formed at the interface influences the mechanical, electrical and thermal properties.

No paper is concerned with wettability of electroconductive ceramic composites by liquid metals. The electroconductive secondary phase may change the wetting behaviour and the nature of reaction products. The bonding between the ceramic composites and the metals was studied by the sessile drop method under vacuum. This work was concerned with the behaviour of silver, copper or a silver–copper–titanium alloy (as an active metal braze) on electroconductive silicon-nitride composites with increasing temperature and time.

## 2. Experimental procedure

The starting commercially powders were obtained from UBE SN10 (silicon-nitride), Cerac-325 mesh (hafnium-diboride), Starck Grade C (titanium-nitride), Starck Grade F (titanium-diboride) and Aldrich ( $MoSi_2$ ). The starting powders and the sintering aids  $Y_2O_3$  and  $Al_2O_3$  were dispersed with ultrasonic assistance in ethanol. Then, the mixture was dried at 100 °C, sieved at 32  $\mu m$  and cold isostatically pressed at 200 MPa (relative density: 60%). The crude cylinder was introduced inside a silica container and sealed. After degassing in vacuum at 400 °C for 10 h, the container was welded under vacuum and hipped (25 mm diameter, 35 mm length billets).

With an increasing melting point of the secondary phase ( $TiN$ :  $2950 \pm 120$  °C,  $TiB_2$ :  $3044 \pm 180$  °C,  $HfB_2$ :  $3377 \pm 60$  °C<sup>6–8</sup>), it is more and more difficult to consolidate the composite to full density. The borides of the transition metals are not stable in presence of the silicon nitride matrix which decomposes above 1700 °C. Consequently, it is necessary to minimize the consolidation temperature at 1710 °C but the quantity of sintering aids must be increased following the increasing melting point of the secondary phase. The composition and the sintering parameters are given in Table 1.

Table 1  
Composition and sintering parameters of all materials

	Powders	HIP/HP cycle	$d_{relative}$ (%)
$Si_3N_4$	$Si_3N_4 + Y_2O_3$ 0.5 wt.%, $Al_2O_3$ 0.25 wt.%	1730 °C 1 h 180 MPa HIP	100
TiN	Without sintering aids	1630 °C 1.5 h 180 MPa HIP	$99.3 \pm 0.1$
$TiB_2$	Without sintering aids	1900 °C 1.5 h 190 MPa HIP	$98.4 \pm 0.2$
$HfB_2$	$HfB_2 + Y_2O_3$ 0.5 wt.%, $SiO_2$ 0.25 wt.%	1850 °C 1 h 180 MPa HIP	$91 \pm 1$
$Si_3N_4$ –TiN	$Si_3N_4 + TiN$ 35 vol.% $Y_2O_3$ 0.26 wt.%, $Al_2O_3$ 0.13 wt.%	1725 °C 1 h 180 MPa HIP	100
$Si_3N_4$ – $TiB_2$	$Si_3N_4 + TiB_2$ 35 vol.% $Y_2O_3$ 0.5 wt.%, $Al_2O_3$ 0.25 wt.%	1710 °C 1 h 180 MPa HIP	98
$Si_3N_4$ – $HfB_2$	$Si_3N_4 + HfB_2$ 27 (vol.%) $Y_2O_3$ 2.0 (wt%), $Al_2O_3$ 1.0 (wt%)	1710 °C 1 h 180 MPa HIP	98
$Si_3N_4$ – $MoSi_2$	$Si_3N_4 + MoSi_2$ 35 (vol.%) $Y_2O_3$ 2.5 (wt.%) $Al_2O_3$ 1.0 (wt.%)	1740 °C 10 min 30 MPa HP	100

Table 2

	Equilibrium contact angles (degree) of silicon nitride based composites				
	$T$ (°C)	SN–TiN	SN– $TiB_2$	SN– $HfB_2$	SN– $MoSi_2$
Ag–28 wt.%Cu	800	149	150	150	148
Ag	980	151	154	152	152
Cu	1100	139	130	125	130

The density of the composites was measured by using Archimede's principle and the phase composition by using a X-ray PHILIPS-CGR Bragg–Brentano diffractometer. SEM, BSE and EDS images of the surfaces and cross sections were carried out with a PHILIPS XL30 scanning electron microscope.

The sessile drop technique was applied to determine the contact angle between the polished ceramic composites (roughness  $< 500$  Å) as a substrate and the liquid metals (Ag, Cu, purity  $\geq 99.99\%$ , Ag–28 wt.%Cu, Ag–28 wt.%Cu–3 wt.%Ti). The commercial Ag–28 wt.%Cu alloy (Castolin 1806) comes from Castolin, France. The Ag–Cu–Ti alloy was prepared by using metal powders from Sigma/Aldrich, Germany (325 mesh, purity 99.98%) for titanium and Goodfellow, England for the copper and silver powders. The powders were mixed mechanically and cast in a cylindrical graphite mould (3.5 mm diameter, 5 mm) at 800 °C under vacuum ( $10^{-4}$  Pa). The silver copper alloy (Ag–28 wt.% Cu) forms an eutectic at 778 °C. To eliminate the oxidation layer of the metal surface, it is necessary to treat the metal in a nitric acid ( $HNO_3$ ) solution for few seconds. Then the metal and the substrate are cleaned with acetone in an ultrasonic bath. The metal specimen was put on the ceramic substrate in a molybdenum furnace and heated up under vacuum ( $10^{-2}$  Pa). Real time images were taken with a CCD camera and the contact angle evolution is followed as a function of temperature and time.

## 3. Results

Non-wetting is observed on all composites (Table 2), either in presence of the pure metal (Ag or Cu) or of the silver–copper braze. The contact angle remained virtually unchanged with time at the quoted temperatures.

Concerning the four ceramic composites, the equilibrium contact angle values of the silver–copper alloy are

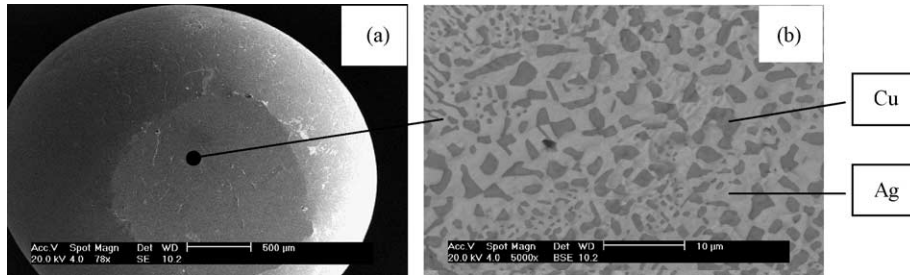


Fig. 1. SEM (a) and BSE (b) contact area images (Ag–28 wt.%Cu alloy on SN–TiB<sub>2</sub> composite material).

closer to the silver ones and the influence of copper is weak.

The back-scattered image on Fig. 1 shows the contact area of a silver copper alloy after the sessile drop experiment. The copper (gray color) is homogeneously distributed inside the silver (white matrix) and is concerned with the immiscibility gap at low temperature.

The bonding of the alloy to the ceramic surface was very weak. SEM micrographs and microprobe analysis through the interface show no penetration of the alloy elements inside the ceramic. No reaction or corrosion zone between the metals (Ag, Cu) or the alloy (Ag–28 wt.%Cu) and the composites (SN–TiN, SN–TiB<sub>2</sub>, SN–HfB<sub>2</sub>, SN–MoSi<sub>2</sub>) was noticed as shown for Si, Ti and Cu through the well defined interface region (composite SN–TiN and copper on Fig. 2). Lower angle values were observed on TiN and TiB<sub>2</sub>. It is known, that TiN can form sub-stoichiometric phases (TiN<sub>x</sub>) as Ti<sub>2</sub>N, Ti<sub>4</sub>N<sub>3–x</sub>. Copper do not wet stoichiometric TiN but wetting can occur with hypostoichiometric TiN products<sup>9</sup> which is not the case here.

The non-wetting behaviour and the contact angles of the four ceramic composites with copper and silver are similar as the values found with monolithic Si<sub>3</sub>N<sub>4</sub> by Sangiorgi et al.<sup>10</sup> (contact angle value of copper on Si<sub>3</sub>N<sub>4</sub>: about 135°), but the equilibrium value obtained between 110 and 130° probably corresponds to the Cu–Si<sub>3</sub>N<sub>4</sub>–Y<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> system.<sup>11</sup> Jungberg and Arren<sup>12</sup> found a contact angle between silver and monolithic Si<sub>3</sub>N<sub>4</sub> of about 155°.

Sangiorgi and al.<sup>10</sup> have shown that the presence of a higher quantity of sintering aids (Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>) in the hot pressed composite has no significant influence on the wet-

ting behaviour. On the contrary, it is known that metallic sintering aids as nickel can change the wetting behaviour dramatically.<sup>13</sup>

It is well known that the addition of a reactive metal as titanium to the Ag–Cu braze improves greatly the wettability by reactions at the interface when they are in presence of solid silicon nitride substrates.<sup>14,15</sup>

To study the wetting influence of titanium, an Ag–Cu–Ti eutectic alloy with 3 wt.% titanium was tested. The contact angle evolution as a function of temperature and time for both the monolithic materials (Si<sub>3</sub>N<sub>4</sub>, TiN, TiB<sub>2</sub>, HfB<sub>2</sub>) and the ceramic composites, with the same Ag–Cu–Ti alloy, are given in Figs. 3 and 4.

These reactive systems are characterized by a variation of the contact angle with temperature and time.

At the melting temperature (778 °C), in a first step, a non-wetting drop of the Ag–Cu–Ti alloy was formed. Then, immediately the braze wetted the silicon nitride based ceramic composite as inside the Ag–Cu–Ti drop, the titanium particles need time to diffuse to the ceramic surface.

Good wetting was observed in all the four cases after few minutes. The contact angle decreased slightly but continuously with temperature and time during the first 30 min and then, stabilized progressively.

The samples put into resin were cut with a slow spin saw. All the composite materials showed a rupture inside the ceramic due to a strong bonding between the alloy and the substrate (Fig. 5).

In the literature, the titanium diffusion into a silicon nitride ceramic has been examined between 600 and 700 °C. The diffusion constant  $D_0$  which has been found for short duration,

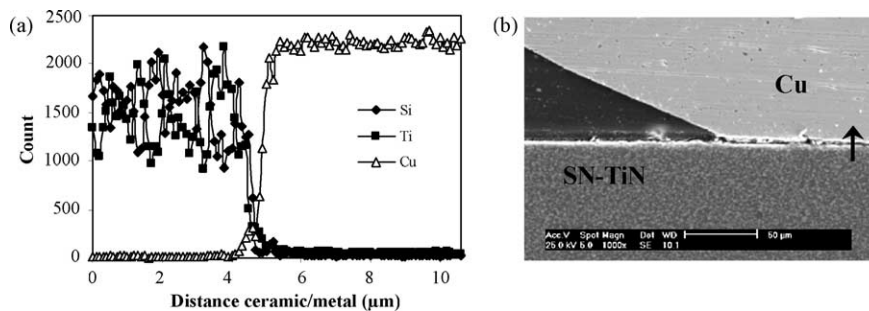


Fig. 2. Microprobe analysis of Si, Ti and Cu content (a) and SEM image of the interfacial region between the SN–TiN ceramic composite and the copper drop (b). The direction of the line scan is shown by an arrow.

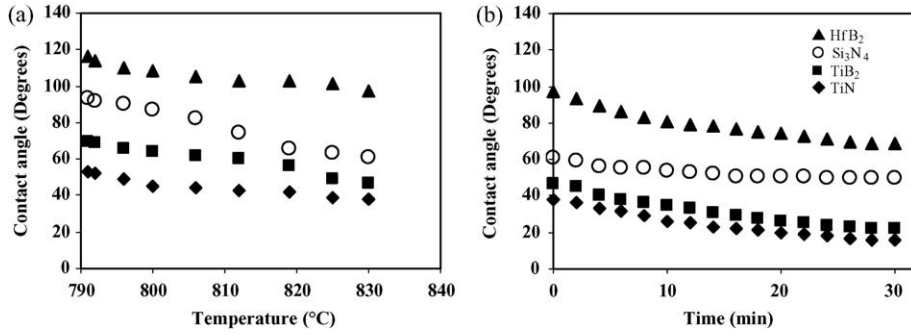


Fig. 3. Contact angle evolution plotted as a function of temperature (a) and time (b) for the four monolithic ceramics (Si<sub>3</sub>N<sub>4</sub>, TiN, TiB<sub>2</sub>, HfB<sub>2</sub>) with the Ag–Cu–Ti alloy.

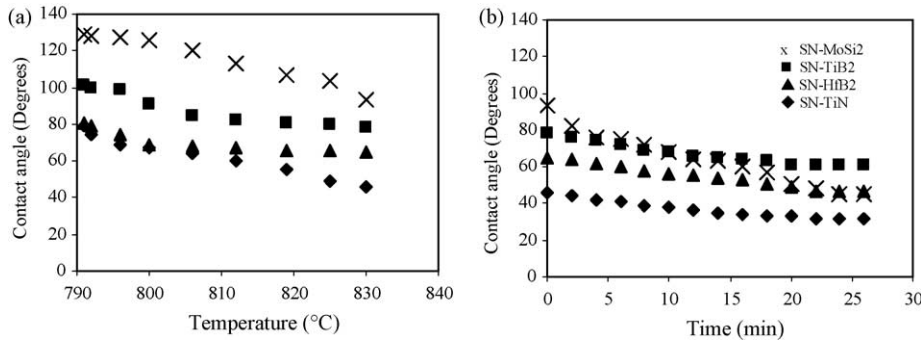


Fig. 4. Contact angle evolution plotted as a function of temperature (a) and time (b) for the four ceramic composites with the Ag–Cu–Ti alloy.

equal to  $3.4 \times 10^{-15} \text{ m}^2/\text{s}$  decreases for longer durations to  $5.7 \times 10^{-20} \text{ m}^2/\text{s}$ . This decrease is explained by the growth of an intermediate layer at the interface mainly consisting of titanium, silicon and oxygen which hampers further titanium diffusion into the ceramic.<sup>16</sup>

In addition, the difference in thermal expansion coefficient of the Ag–Cu–Ti alloy (Ag  $19.1 \times 10^{-6} \text{ K}^{-1}$ ,<sup>17</sup> Cu  $17 \times 10^{-6} \text{ K}^{-1}) and the ceramic composites (Si<sub>3</sub>N<sub>4</sub>  $3.25 \times 10^{-6} \text{ K}^{-1}$ ) may play a role.$

The Fig. 5 shows the SN–TiB<sub>2</sub> and the SN–MoSi<sub>2</sub> composite materials after the sessile drop experiment.

Cross-section images of the interface between all four ceramic composites and the Ag–Cu–Ti alloy showed a reaction zone of some micrometers thickness.

The wettability of the monolithic TiN, TiB<sub>2</sub> and HfB<sub>2</sub> ceramics by the Ag–Cu–Ti alloy has not shown the formation of

an interface layer. Consequently, the secondary phases TiN, TiB<sub>2</sub> and HfB<sub>2</sub> are not involved in the interfacial reaction process.

Conversely, the monolithic Si<sub>3</sub>N<sub>4</sub> ceramic material represents a behaviour similar to the composite materials and the titanium has reacted with the silicon nitride matrix to form TiN or Ti<sub>5</sub>Si<sub>3</sub>.

Thermodynamic calculations of the Gibbs free energy show two possible reactions (Eqs. (1) and (2)) between silicon nitride and titanium at 1000 and 1100 K.

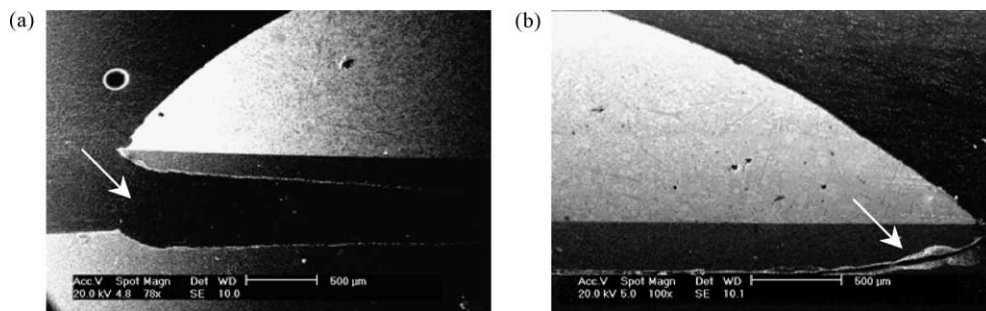
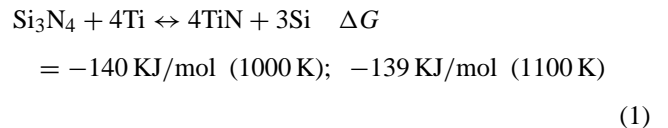


Fig. 5. SEM images of the cross section between SN–TiB<sub>2</sub> (a) and SN–MoSi<sub>2</sub> (b) composite materials and the Ag–Cu–Ti alloy. Arrows indicate cracks inside the composite materials.

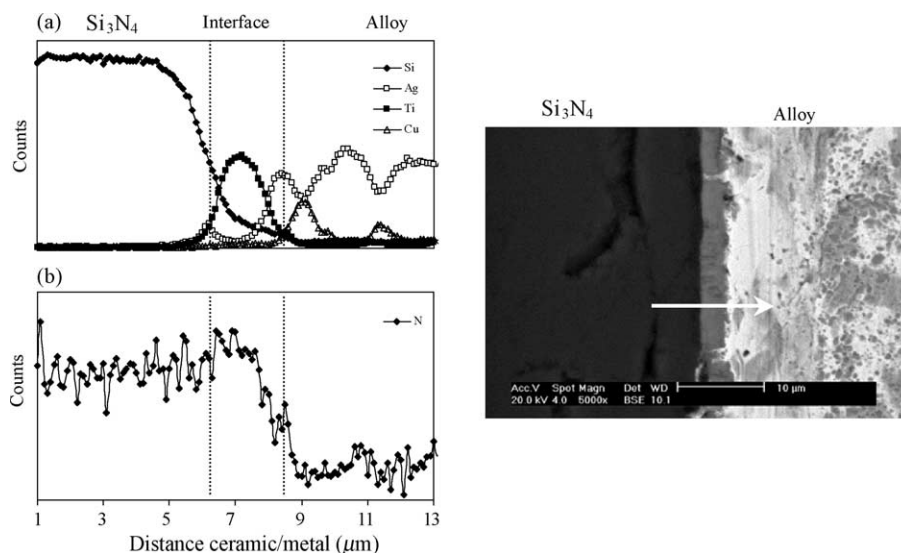
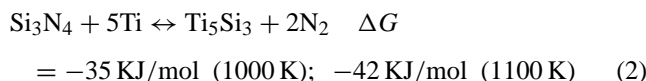


Fig. 6. (a, b) EDS profile and (c) SEM analysis of a cross-section: Al–Cu–Ti alloy on HIP Si<sub>3</sub>N<sub>4</sub> monolithic material.



Thermodynamic calculations from Nomura et al. in the Ti–Si–N system at 1300 K as a function of the titanium activity confirm the stability of TiN and Ti<sub>5</sub>Si<sub>3</sub>.<sup>9</sup> X-ray photoelectron spectroscopy (XPS) has also been used to characterize the interfacial products that form between a commercial Cu–Ag–1.5%Ti brazing alloy and silicon nitride.<sup>18</sup> Ti segregates as TiN<sub>x</sub> and due to thermodynamic incompatibility between Ti and Si<sub>3</sub>N<sub>4</sub>, titanium silicide may be formed.

Fig. 6 shows the SEM images and the EDS analysis of the reaction zone at the interface.

A semi-quantitative analysis of the elements Si, Ag, Ti, Cu and N was made through the interfacial zone from the monolithic Si<sub>3</sub>N<sub>4</sub> material to the Ag–Cu–Ti alloy. The main elements found at the interface are silicon, titanium and nitrogen. No presence of Cu or Ag element could be noticed inside this interface.

The Ag–Cu–Ti alloy shows white areas of silver and gray areas of copper corresponding to the eutectic phase formed at 778 °C. A strong join is noticed between the alloy and the Si<sub>3</sub>N<sub>4</sub> material. Fracture took place inside the Si<sub>3</sub>N<sub>4</sub> material similarly to the previous cases (Fig. 5). The interface thickness of  $3.3 \pm 0.6 \mu\text{m}$  is wide in comparison with some literature values. Nomura et al.<sup>14</sup> found a thickness of around 60 nm which consisted of an inner TiN layer near the ceramic and an outer Ti<sub>5</sub>Si<sub>3</sub> layer near the Ag–Cu–Ti alloy, both with a thickness of around 30 nm. But thicker layers are found by Nicholas et al.<sup>15</sup> with Cu–5 wt.%Ti and Cu–10 wt.%Ti alloys on Si<sub>3</sub>N<sub>4</sub> ceramic materials. The thickness varies between 10 and 30 μm with increasing titanium amount.

The profile analysis of the HIP Si<sub>3</sub>N<sub>4</sub> material proves the presence of a double interface layer. The distribution of nitrogen inside the interface corresponding to TiN has a tendency to be located near the Si<sub>3</sub>N<sub>4</sub> substrate.

Nevertheless, X-ray diffraction analysis of the interface region confirms the presence of titanium-based phases (Table 3).

All the four composite grades show a similar titanium, silicon and nitrogen enriched interfacial zone between the composite material and the Ag–Cu–Ti alloy.

Figs. 7 and 8 show two profile analysis (SN–TiN and SN–MoSi<sub>2</sub> composite materials) of the interface between silicon nitride and the Ag–Cu–Ti alloy.

The semiquantitative evolution of nitrogen (Figs. 7b and 8b) confirms the presence of nitrogen, observed in a higher amount at the ceramic substrate interface. X-Ray diffraction analysis has shown the presence of Mo<sub>5</sub>Si<sub>3</sub>, Ti<sub>5</sub>Si<sub>3</sub> and TiN<sub>0.76</sub> in the interface layer between the SN–MoSi<sub>2</sub> material and the Ag–Cu–Ti alloy.

The titanium and nitrogen rich interface layer was also found between the composites SN–HfB<sub>2</sub>; SN–TiB<sub>2</sub> in contact with the Ag–Cu–Ti alloy. The main reaction products found by X-ray diffraction were also Ti<sub>5</sub>Si<sub>3</sub> and TiN<sub>0.76</sub>. Concerning the SN–HfB<sub>2</sub> material, HfN was also formed by reaction between nitrogen coming from the Si<sub>3</sub>N<sub>4</sub> decomposition and HfB<sub>2</sub>.

Concerning the wetting angles of the composite materials with the Ag–Cu–Ti alloy, the Si<sub>3</sub>N<sub>4</sub>–TiN material presents the lowest equilibrium angle value in accordance

Table 3	
Reaction products at the interface between Si <sub>3</sub> N <sub>4</sub> and Ag–Cu–Ti (XRD)	
	X-ray diffraction analysis
Interface Si <sub>3</sub> N <sub>4</sub> –Ag–Cu–Ti	TiN, Ti <sub>2</sub> N and Ti <sub>5</sub> Si <sub>3</sub>

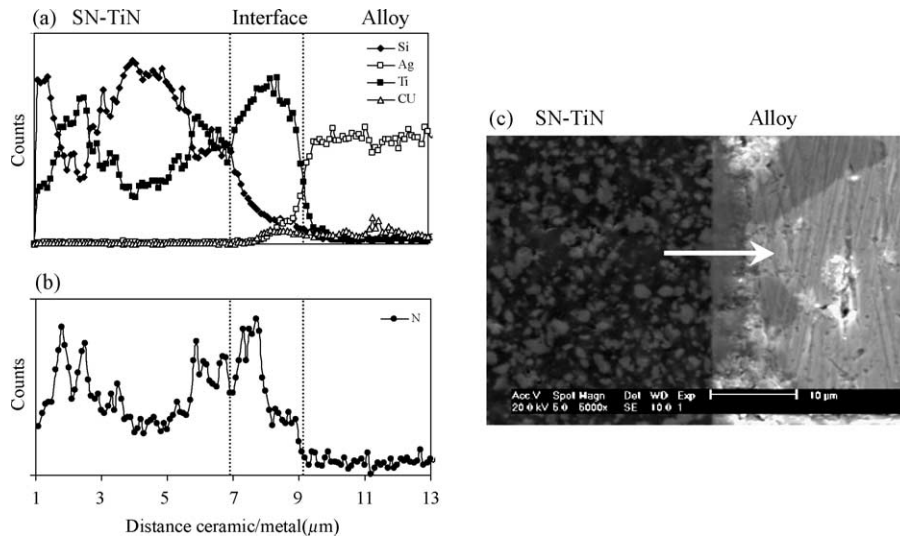


Fig. 7. (a, b) EDS profile analysis and (c) SEM micrograph of a cross section of Al–Cu–Ti on the SN–TiN sample.

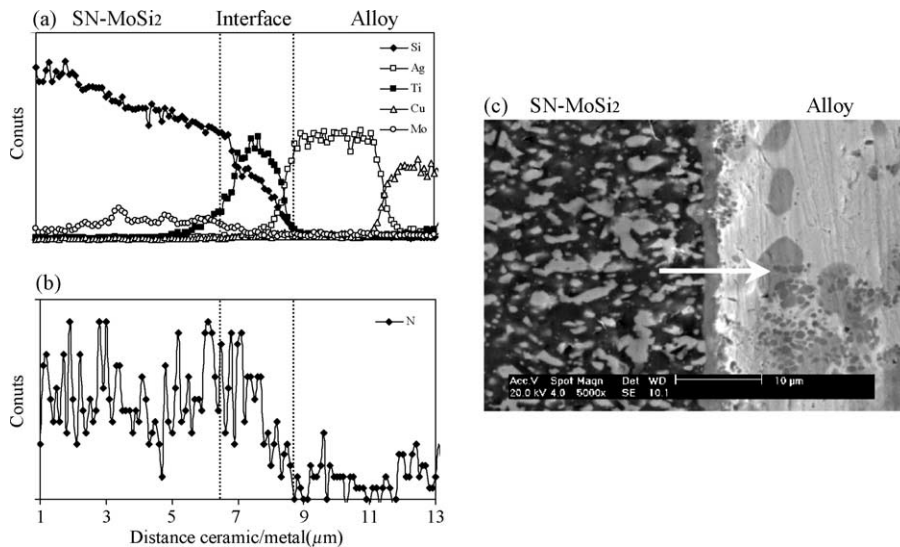


Fig. 8. (a, b) EDS profile analysis and (c) SEM micrograph of a cross section of Al–Cu–Ti on the SN–MoSi<sub>2</sub> sample.

with the same lowest contact angle on the TiN monolithic material.

The Ag–Cu–Ti alloy wets the material with formation of a  $3 \pm 1 \mu\text{m}$  thick Ti enriched interface. The reaction products found in this interface layer are TiN<sub>x</sub> phases as TiN and Ti<sub>2</sub>N and Ti<sub>5</sub>Si<sub>3</sub> coming from the reactions between Si<sub>3</sub>N<sub>4</sub> and titanium.

The double interface layer consisting of a TiN layer near the ceramic composite and a second Ti<sub>5</sub>Si<sub>3</sub> layer near the Ag–Cu–Ti alloy found in all the composite materials is in accordance with the results of Nomura et al.<sup>14</sup> Nomura et al. used 40 mg heavy Ag–Cu–Ti samples which formed about 50 times smaller interface layers than the interface layers found in this work with 450 mg heavy Ag–Cu–Ti cylinders. These observations confirm that higher quantities of Ag–Cu–Ti alloys produce thicker layers.

#### 4. Conclusions

The wettability of electroconductive silicon nitride based ceramic composites by molten metals (Cu, Ag) or alloys (Cu–Ag, Cu–Ag–Ti) was investigated.

The equilibrium contact angle decreases with an increase in temperature and time and then stabilizes after approximately 30 min.

Non-wetting was observed for all the ceramic composites (Si<sub>3</sub>N<sub>4</sub>–TiN, Si<sub>3</sub>N<sub>4</sub>–TiB<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>–HfB<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>–MoSi<sub>2</sub>) with liquid silver, copper and an Ag–Cu alloy. The formation of an interface layer or the presence of reaction products was not noticed between the solid/liquid phases.

The addition of 3 wt.% of titanium to the silver–copper alloy induced reactions at the interface between the braze and the Si<sub>3</sub>N<sub>4</sub> based composites. The wetting observed in all

cases was essentially related to the silicon nitride phase as the  $\text{TiB}_2$  secondary phase is not involved in the reaction process. The  $\text{TiN}$  secondary phase forms hyperstoichiometric phases ( $\text{TiN}_x$ ). The secondary phases  $\text{HfB}_2$  and  $\text{MoSi}_2$  are involved in reaction processes.  $\text{HfB}_2$  reacts with nitrogen coming from  $\text{Si}_3\text{N}_4$  to form  $\text{HfN}$  and  $\text{MoSi}_2$  is involved in the main reaction process to form  $(\text{Mo, Ti})_5\text{Si}_3$ .

The formation by reaction of an interlayer, the thickness and composition of this interface will play a major role in the bonding of these silicon nitride composites.

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