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Wetting behaviour of silicon nitride ceramics by Ti–Cu alloys

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Abstract

The wetting of Ti–Cu alloys on Si_3N_4 was analyzed by the sessile drop method, using an imaging system with a CCD camera during the heating under argon flow. The contact angle was measured as a function of temperature and time. The samples were cut transversally and characterized by scanning electron microscopy and energy dispersive spectrometry (SEM/EDS). Wettability of the Ti–Cu alloy on Si_3N_4 is influenced by the reaction between the Ti and the ceramic. The TC1 and TC2 alloys presented low final contact angle values around 2° and 26°, respectively, indicating good wetting on Si_3N_4.

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Keywords: Wettability; Silicon nitride; Ti–Cu alloys; Contact angle

1. Introduction

The wetting of solid ceramics by liquid metals is of great importance in many technological application processes such as fabrication of metal–ceramic composite materials, metal–ceramic joining as well as high-temperature ceramic coatings on metal substrates [1–3]. From a theoretical point of view, the study of metal–ceramic interfaces is also very attractive, because it deals with the problems of bonding between two materials which are very different in physical and chemical properties as well as electronic structures.

Based on the nature of the attractive forces, wetting can be classified as physical or chemical. The wetting of ceramics by molten metals usually involves interfacial reactions [4–8]. And when a reaction occurs at the interface, the free energy change per unit area per unit time also enhances wetting [9,10].

When joining metal to ceramic, two main problems have to be overcome. The first is the poor wettability of ceramics by most metals and alloys. The second is the difference in the physical properties between ceramics and metals which is manifested by extreme differences in the thermal expansion coefficients (α) and Young's modulus, which can lead to high residual stresses when cooling from the joining temperature, resulting in reduced strength of the joined components. To overcome the first problem an activator in the alloy such as titanium (Ti) is often used to aid wetting of the ceramic [11–13]. Nevertheless, the reactive metal may also alter the composition of the metal–ceramic interface. The formation of hypostoichiometric TiN_x and titanium silicides as Ti_5Si_3 phases has been reported in the Si–Ti–N system [4,13–16].

The aim of this work was to study the wetting behaviour of Ti–Cu alloys on Si_3N_4 as a function of temperature and time. The wettability between ceramic and metals was studied by the sessile drop method under argon flow.

2. Experimental

The materials used for the wettability study were Si_3N_4 plates (20.0 mm × 15.0 mm × 6.0 mm) with 99.5% density. These plates were prepared from Si_3N_4 powders (LC12-Sx, H.C. Starck, Germany), Y_2O_3 (grade C, H.C. Starck) and Al_2O_3 (CR6, AS 250 KC supplied by Baikalox). It was chosen a composition with a lower quantity of additives (94.4 vol.% Si_3N_4, 3.9 vol.% Y_2O_3 and 1.7 vol.% Al_2O_3), so they would not influence wetting behaviour. The liquid phase sintered plates were ground and polished until 1 μm diamond suspension.

The metals used were Ti (purity ≥ 99.999%) and Cu (purity ≥ 99.99%). Ti–Cu alloys were chosen for their good interaction with Si_3N_4 [4,12–14]. The alloys compositions are reported in Table 1 and Fig. 1.

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Table 1
Ti–Cu alloys compositions and melting point

Code	Compositions (at.%)		Melting temperature (°C)
	Ti	Cu	
TC1	43	57	961
TC2	21	79	905

Alloys spheres of 0.5 g were produced in an arc-melting furnace. After solidification, the spheres were turned and re-melted to ensure chemical and microstructural homogeneity. Arc-melting cycle was repeated four times. The melting points of the alloys were determined in accordance with the DIN 51730 standard and compared with the values found in the phase diagram. The metal and the ceramic plate were cleaned with acetone in an ultrasonic bath.

A metal sphere was put on the Si_3N_4 plate and the set placed in a tubular furnace with a heating rate of 10 °C/min, under argon flow. To study the temperature and time influence on wetting behaviour tests were performed at 25, 50 and 75 °C higher than the melting point of the alloys with different soaking times. The results of the sessile drop tests were analyzed using an imaging system with a CCD camera and a QWin Leica software, for contact angle measurements. The samples were then cut transversally and their microstructure characterized by scanning electron microscopy and energy dispersive X-ray analysis (SEM/EDS) (LEO-Zeiss 1450VP microscope).

3. Results and discussion

Fig. 2 shows the evolution of molten metals spreading on Si_3N_4. It can be observed that the molten alloys spread uniformly on the ceramic plate. The experimental data of the contact angle θ as a function of temperature are plotted in Fig. 3 together with the fitting curves for each alloy. Experimental results of θ versus T were fitted for temperatures $T \geq T_0$. T_0 corresponds to the melting point of the alloy. By using the exponential decay equation, $\theta = \theta_{min} + \theta_i \exp[-\alpha_D(T - T_0)]$, to fitting the experimental results, we found the contact angle curves tested to fit exponential rule very well, where θ_{min} is the minimum contact angle ($\theta_{min} + \theta_i$) is the initial contact angle at $T = T_0$ and α_D is the exponential decay factor. Eqs. (1) and (2) are the formulas obtained from mathematical fitting for the TC1 and TC2 alloys.

$$\theta_{TC1} = 3 + 105.21 \exp[-0.1(T - 960)] \quad (1)$$

$$\theta_{TC2} = 25 + 118.33 \exp[-0.05(T - 905)] \quad (2)$$

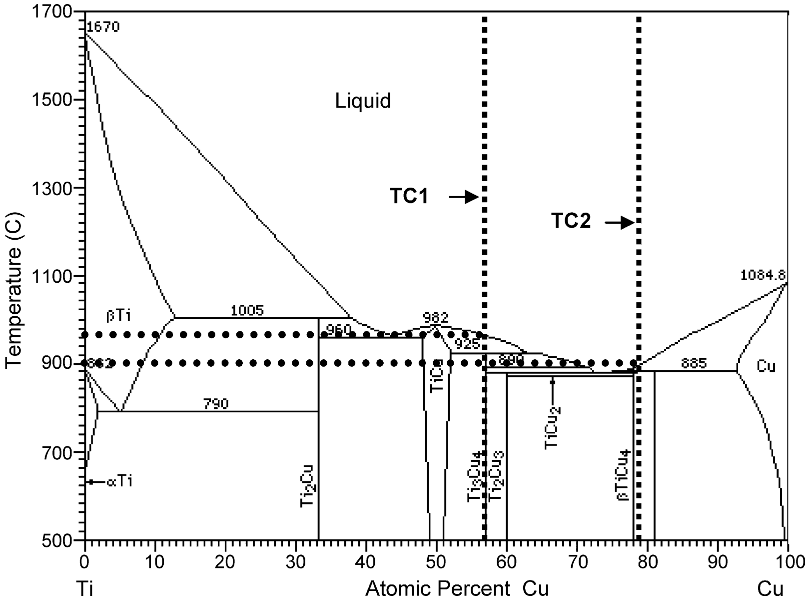

Fig. 1. Phase diagram of Ti–Cu system. Dot lines indicate the composition and melting point of the alloys.

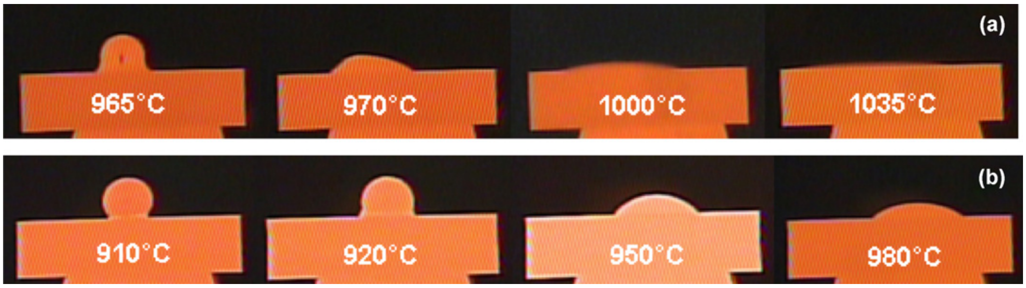

Fig. 2. Sequential images obtained by CCD camera showing the wetting behaviour of: (a) TC1/Si_3N_4 until 1035 °C and (b) TC2/Si_3N_4 until 980 °C.

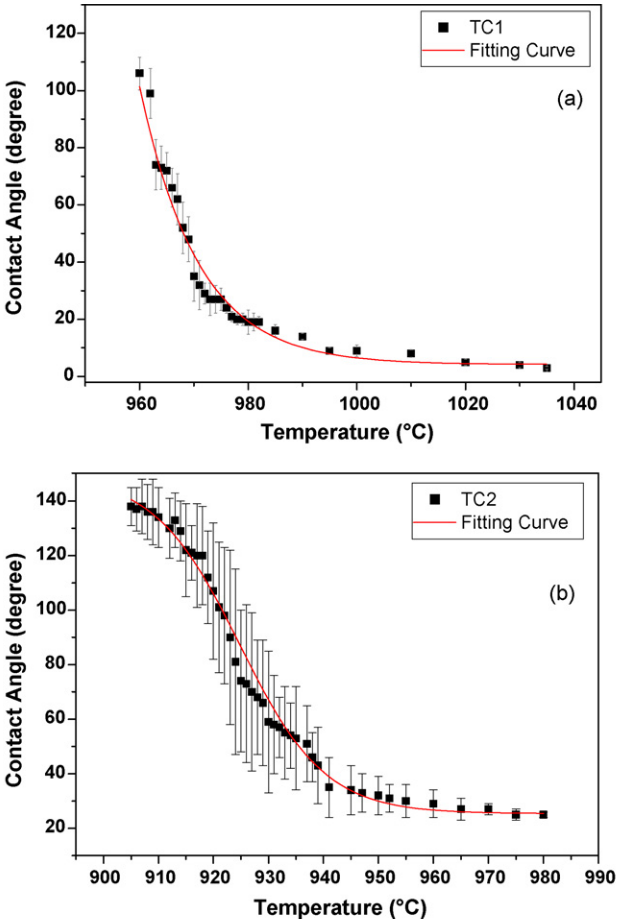

Fig. 3. Temperature influence in the contact angle of: (a) TC1 and (b) TC2.

The θ versus T curves (Fig. 3) have similar behaviour and the contact angle values decreased as the temperature rose and the area of adhesion between the liquid and the plate increased. The alloys showed final contact angle values below 12° for TC1 and 30° for TC2, indicating good wetting. Fig. 3 shows that TC1 alloy, with higher Ti content, wets the ceramic better for the investigated temperatures.

The wetting behaviour depends on the change of the ceramic surface due to reaction between the active component (Ti) in the alloy and the ceramic; the thermodynamics equilibrium offers some important indications on possible reactions [4,12].

$$\mathrm{Si_3N_4 + 4Ti \leftrightarrow 4TiN + 3Si}, \quad \Delta G = -139\,\mathrm{kJ/mol}\ (1100\,\mathrm{K}) \tag{3}$$

$$\mathrm{Si_3N_4 + 5Ti \leftrightarrow Ti_5Si_3 + 2N_2}, \quad \Delta G = -42\,\mathrm{kJ/mol}\ (1100\,\mathrm{K}) \tag{4}$$

Thermodynamic calculations in the Ti–Si–N system at 1300 K as a function of the titanium activity confirm the stability of TiN and Ti_5Si_3 [4]. Figs. 4 and 5 depict the alloys microstructures after the wettability test under argon flow.

The microstructure at the metal–ceramic interface is mainly composed of a bi-layer system of TiN and Ti_5Si_3 containing Cu (Eqs. (3) and (4)). The presence of TiN could not be confirmed experimentally, however, as the EDS system used could not detect nitrogen (which would in any case be dominated by the adjacent Si_3N_4). Based on the Ti–Cu binary alloy phase diagram, a series of invariant reactions upon cooling of the liquid are listed below [12–16]:

$$\mathrm{TiCu + L \leftrightarrow Ti_3Cu_4} \quad (\text{peritectic}, 925\ 10\,^\circ\mathrm{C}) \tag{5}$$

$$\mathrm{Ti_3Cu_4 + L \leftrightarrow TiCu_2} \quad (\text{peritectic}, 890\ 10\,^\circ\mathrm{C}) \tag{6}$$

$$\mathrm{L \leftrightarrow TiCu_2 + \beta TiCu_4} \quad (\text{eutectic}, 875\ 10\,^\circ\mathrm{C}) \tag{7}$$

If the solidification of the molten alloy follows the above Eqs. (5)–(7), the formation of Ti_3Cu_4 occurs by the peritectic reaction between the molten alloy and TiCu. Accordingly, Ti_3Cu_4 subsequently reacts with the residual molten alloy on cooling, and $TiCu_2$ forms via a peritectic reaction. Finally, the residual molten alloy is completely solidified into $TiCu_2$ and $TiCu_4$ via the eutectic reaction as shown in Eq. (7) [15,16]. The

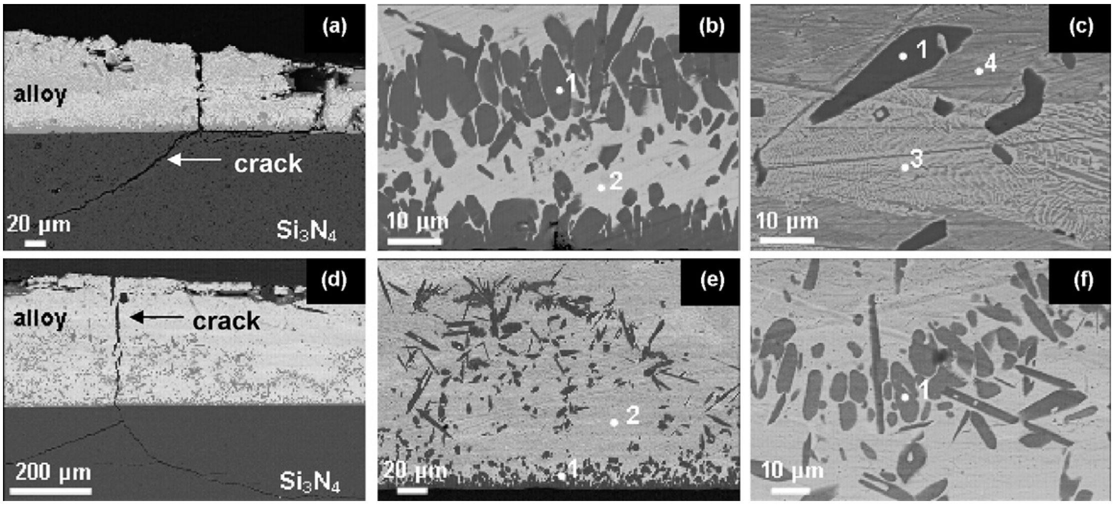

Fig. 4. SEM micrographs of TC1 alloy after the wettability test under argon flow at (a–c) 985 °C/3 min and (d–f) at 1035 °C/6 min.

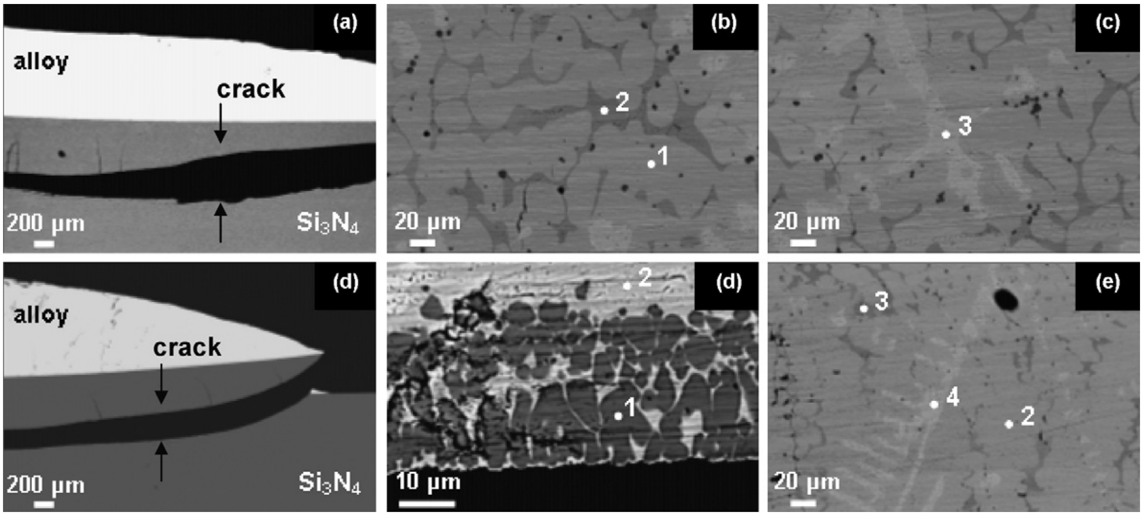

Fig. 5. SEM micrographs of TC2 alloy after the wettability test under argon flow at (a–c) 930 °C/3 min and (d–f) at 980 °C/6 min.

experimental results of Figs. 4 and 5 and Table 2 are consistent with the related phase diagrams.

The specimens showed interfacial cracking inside the ceramic due to a strong bonding between the alloy and the ceramic plate (Figs. 4(a and d) and 5(a and d)), most likely due to the large residual stresses coming from the thermal expansion coefficient (CTE) mismatch.

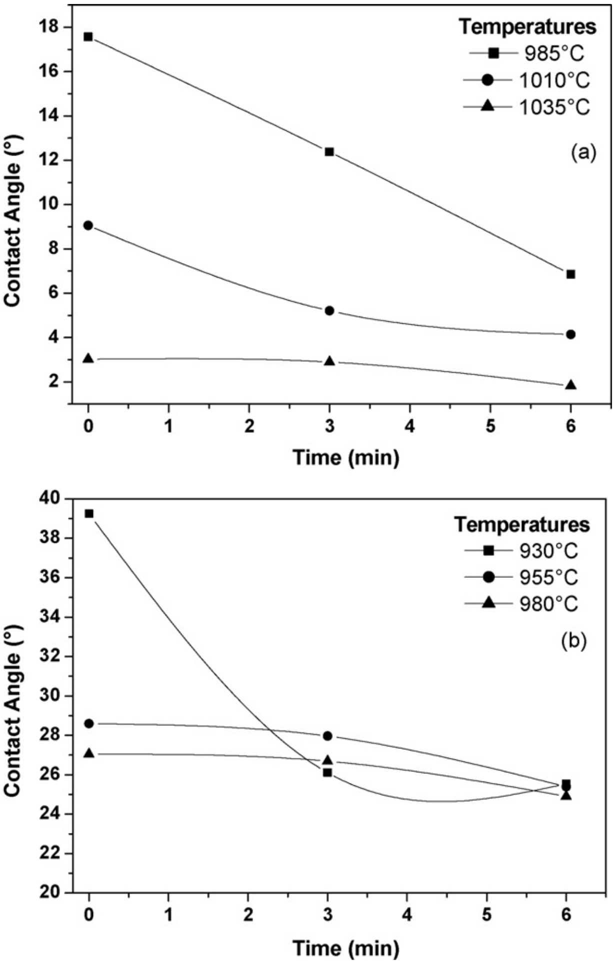

Fig. 6. Time influence on the contact angle of: (a) TC1 and (b) TC2.

The variation of contact angle with time from the sessile drop experiment is presented in Fig. 6. The change of wetting angle with time may be explained in terms of the reaction kinetics in the metal–ceramic system. For a reactive system, the interfacial reactions proceed quickly after physical contact between the ceramic and the molten metal. In such instances, the contact angle drops rapidly in a short time. Further reductions of wetting angle will continue at a slower rate until equilibrium wetting is achieved [4,14].

A rapid reduction of the wetting angle for the Ti–Cu alloy/Si_3N_4 system from 18° to 2° for TC1 and 39° to 26° for TC2 after 6 min results from the high interfacial reactivity due to the presence of Ti which is the reactive metal. Two main cases limiting the rate of spreading must be considered: the rate of chemical reaction at the triple line and the rate of diffusion of an active element (Ti for the present melts) from the bulk to the triple line [16]. According to these mechanisms, responsible for wetting, it would be logical to expect a shorter time to reach the final θ value with an increase in titanium content (TC1) and temperature.

Table 2
EDS analysis and possible phases of samples shown in Figs. 4 and 5

Code/temperature	Elements detected by EDS analysis		Possible phases
	985 °C/3 min	1035 °C/6 min	
TC1	(1) Si, Ti, Cu	(1) Si, Ti, Cu	Ti_5Si_3
	(2) Ti, Cu	(2) Ti, Cu	Ti_3Cu_4
	(3) Ti, Cu		β-$TiCu_4$ and $TiCu_2$
	(4) Ti, Cu		Ti_3Cu_4
	930 °C/3 min	980 °C/6 min	
TC2		(1) Ti, Si, Cu	Ti_5Si_3
	(1) Ti, Cu	(2) Ti, Cu	β-$TiCu_4$
	(2) Ti, Cu	(3) Ti, Cu	$TiCu_2$
	(3) Ti, Cu	(4) Ti, Cu	β-$TiCu_4$ and $TiCu_2$

4. Conclusions

The wettability of Ti–Cu alloys on Si_3N_4 was investigated in function of temperature and time under argon flow using the sessile drop technique. In binary Ti–Cu alloys wetting increases with titanium content and increasing temperature. Ti–Cu alloys react with Si_3N_4 at the interface forming a reaction layer. The variation of contact angle with time results from the high interfacial reactivity due to the presence of Ti which is the reactive metal. However, the results present some negative features like interfacial cracking inside the ceramic due to the thermal expansion coefficient mismatch.

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