J Mater Sci (2006) 41:5081–5087
DOI 10.1007/s10853-006-0443-7

Wettability and spreading kinetics of molten aluminum on copper-coated ceramics

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Received: 30 September 2005 / Accepted: 1 February 2006 / Published online: 18 July 2006

Abstract The purpose of this study was to investigate the influence of Cu-coating on the spreading kinetics and equilibrium contact angles of aluminum on ceramics using a sessile drop technique. Al_2O_3 and SiC plates were coated by electroless plating. The copper film overcomes the low wetting of the uncoated samples by dissolution in the drop at 800 °C in argon, showing an intrinsically favorable effect on the adhesion energy. Just after 2 min, the contact angle decreased to 12.6° and 26°for Al/Cu–Al_2O_3 and Al/Cu–SiC, respectively. However, a de-wetting behavior was observed, reaching equilibrium contact angles of 58.3° and 45.5° for the couples. The dissolution reaction rate at the triple junction was so high that the spreading process was controlled by local diffusion rather than chemical reaction kinetics.

Introduction

Some of the methods used to improve interfacial properties during liquid fabrication of metal-ceramic composites are the modification of the matrix composition, coating or specific treatments to the reinforcements and control of process parameters. Among these, coating of the reinforcement is a successful technique adopted to prevent the interfacial reaction and promote wetting of the ceramics by metals through increasing the overall surface energy of the solid [1]. However few attempts have been made to overcome the non-wettability and lack of adhesion of reinforcement with metal matrices by using metal-coated reinforcements [2–7].

Metal deposition on ceramics generates new interfaces between dissimilar materials, involving considerations of adhesion through physical, chemical, and/or mechanical bonding that act across the coating–substrate interface, and also spreading and interface evolution when in contact with liquid metals. Because wettability governs the reinforcement-matrix compatibility, an understanding of interfacial phenomena in the processing of MMCs using metal coated-ceramics can be significantly assisted by interaction studies on controlled systems; however, only the wetting and spreading kinetics of aluminum on Ni-coated flat ceramics using a sessile drop technique has been reported [8].

The present work discusses and summarizes the results on the wetting behavior of plain and copper-coated alumina and silicon carbide plates by liquid aluminum. This study permits the evaluation of the influence of the deposited interlayer on the wetting of the ceramics in a controlled system using a sessile drop technique; in addition, the interfacial phenomena and work of adhesion related to the metal/ceramic couples are investigated. The wetting data are of crucial importance for understanding the processing of dense materials from coated reinforcements.

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Experimental procedure

Wetting studies were carried out on plain and Cu-coated ceramics using a sessile drop technique at 800 °C. High purity polycrystalline α-Al_2O_3 and SiC plates were coated from an electroless copper sulfate based solution using a technique described elsewhere [9]. The flat ceramic substrates were coated for 30 min; leading to a continuous film of 8.5 μm in thickness irrespective of the ceramic used. Measurement was performed by scanning electron microscopy according to ASTM B748-90 [10]. The continuous film comprised of coherent packing of individual particles showed a great degree of conformity to the ceramic surface and no detachment of the coating from the plates was observed, confirming good coating/substrate adhesion.

The wetting studies were performed in ultra high purity (99.999%) argon atmosphere after repeated evacuation in an experimental set-up consisting of a quartz chamber designed specifically for that purpose [11]. Before reaching 800 °C, the chamber was pumped down to 10^{-3} Pa; a piece of titanium sponge getter was placed in the hot zone to remove residual oxygen in the chamber. Under such experimental conditions, a residual partial pressure of oxygen < 1 Pa is expected. The 0.6 g aluminum sample resting on the substrate was cleaned in acetone and then in hydrofluoric acid prior to testing. Changes in the contact with time were recorded and accurately measured directly from the image of the drop section using computer aided image analysis for kinetic studies. Polished cross-section specimens were examined by field emission scanning electron microscopy (FEGSEM) and EDS analysis.

Results and discussion

Wettability of Plain and Copper-coated SiC and Al_2O_3 Substrates by Al

The sessile drop technique provided a simple method to generate comparative information for the wetting behavior between the as-received and the coated ceramic substrates with molten aluminum. As illustrated in Fig. 1, the measured contact angles for the non-coated Al/SiC and Al/Al_2O_3 systems were advancing angles (a decrease in θ is observed while the spreading radius R increases and the height h decreases); the major changes in θ were observed within the first 60 min, reaching a nearly steady state after ~90 min with final contact angle values of 87.3° for SiC and 115.2° for Al_2O_3 after 2 h holding time. The wetting behavior observed in the Al/SiC couple followed the general form proposed by Laurent et al. [12]. The initial decrease of the contact angle within ~10 min, at a rate of decrease of ~0.18°/s is explained by deoxidation of the drop; the intermediate kinetics is controlled by dissolution of SiC into the liquid metal to form Al_4C_3. Microstructure examination revealed that Al_4C_3 was present at the interface either as a continuous layer or as isolated precipitates (Fig. 2). In the case of the Al/Al_2O_3 system, the plot of the contact angle with time showed two main stages; one where a rapid decrease of θ with time occurred and the other corresponding to a ‘‘steady-state’’ with a very slow decrease of θ at a rate ~0.001°/s. The reactivity of this couple is almost negligible below 1000 °C.

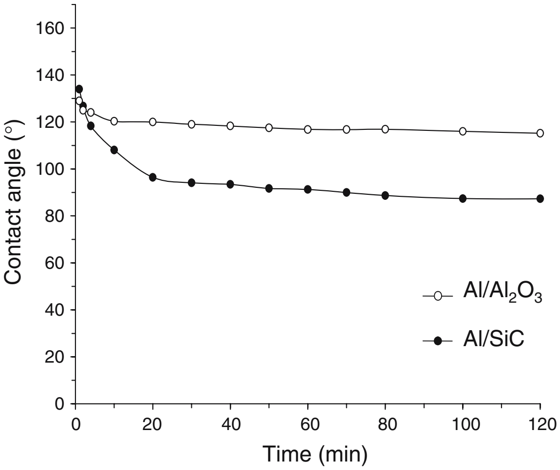

Fig. 1 Contact angle of molten aluminum on plain SiC and Al_2O_3 substrates at 800 °C

Figure 3 shows two images of drops formed in-situ at 800 °C on coated and uncoated alumina plates where the favorable effect of the copper interlayer is clearly observed. The improved wetting is in part attributed to dissolution of the copper coating applied

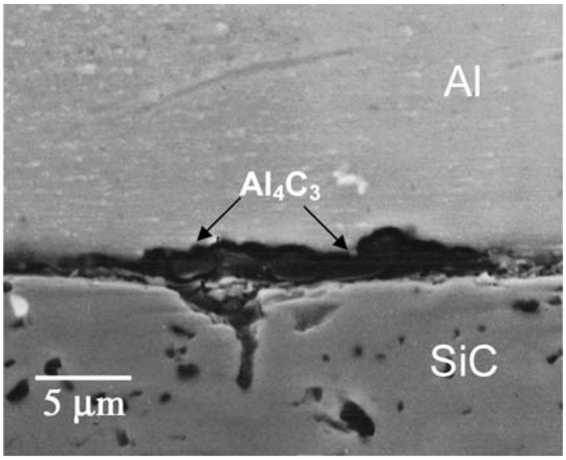

Fig. 2 Microstructure of the aluminum–SiC interface showing the presence of Al_4C_3

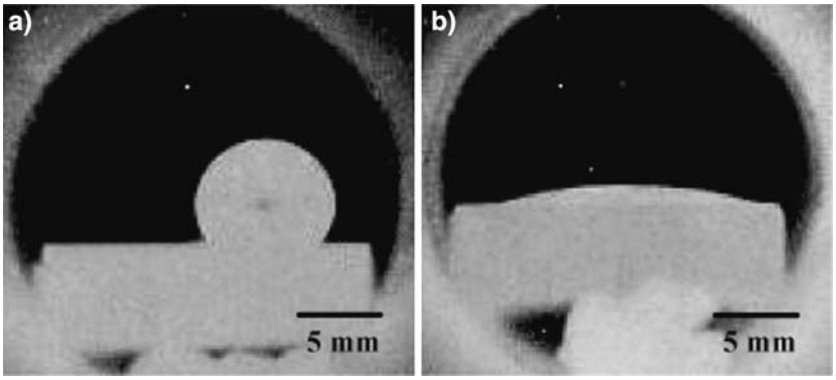

Fig. 3 Wetting behavior of aluminum on (**a**) alumina, 120 min; and (**b**) Cu-coated alumina, 2 min

to the substrates when in contact with the liquid aluminum drop, as discussed later. A non-wetting behavior is evident in the pure Al/Al_2O_3 system (Fig. 3a), as indicated by the spherical drop formed after equilibrium is established at 120 min; whereas the Cu-coated alumina sample revealed improved wetting kinetics for a drop-substrate arrangement corresponding to only 2 min holding time (Fig. 3b).

The wetting behavior of the Al/Cu-coated ceramic substrates is complex. If the measured θ-values are plotted as a function of time (Fig. 4), a complex shape of the $\theta(t)$ curves is observed. Once complete fusion of the aluminum was achieved, the contact angles immediately decreased in two minutes to 12.6° for Al/Cu–Al_2O_3 and 26° for Al/Cu–SiC. Between the instantaneous process of sharp stabilization of θ, there was an intermediate stage characterized by an increase of the contact angle to ~38° in less than 60 s, implying a dewetting period of the liquid from the ceramic surface with a simultaneous reduction of the spreading radius, R, and an increase of the drop height, h. The corresponding variation of θ with time ($d\theta/dt$) during the fast dewetting period (starting from ~3 min) was estimated to be ~0.2°/s and ~0.4°/s for SiC and Al_2O_3, respectively.

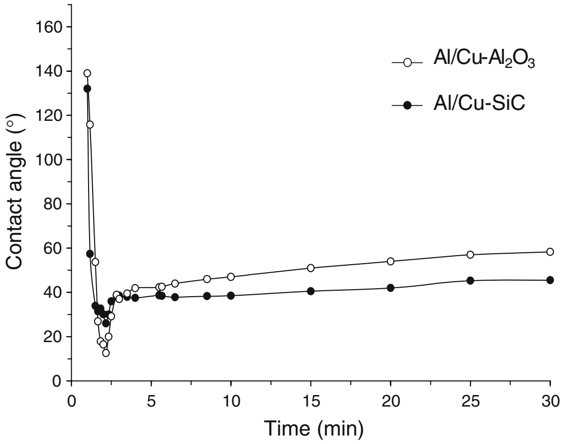

Fig. 4 Wetting behavior of aluminum on Cu-coated Al_2O_3 and SiC substrates

There is a dearth of information on the wetting of metal-coated substrates that might be used to assist in elucidating the dewetting behavior of the Al/Cu-coated ceramic systems. At the time prior to dewetting, metal drops were typically 18 to 20 mm in diameter and 3–5 mm depth at their centers (see Fig. 5). The diffusion constant, D, for a solute in a liquid metal is typically 10^{-8} m^2/s, so that diffusion distances, $\sqrt{(Dt)}$, of 0.1 mm in 1 s are possible. Hence the entire droplet should be affected rapidly by changes in composition. Considering 10 mm, which is the maximum spreading radius of aluminum on the copper coated substrates, and solute diffusion distances of the order of 0.1 mm/s, approximately 100 s are required for copper solute diffusion from the triple line to the centre of the drop. This time matches approximately with the time required by the drop to start dewetting from the ceramic surface. At that point, the composition of the drop has changed; the liquid is no longer pure aluminum and the solid surface should be free of the copper film. Eustathopoulos [13] reported a compilation of experimental results obtained by Li and Labrousse on the variation of the contact angle with the Al molar fraction for the Cu–Al/Al_2O_3 system at 1150 °C in high

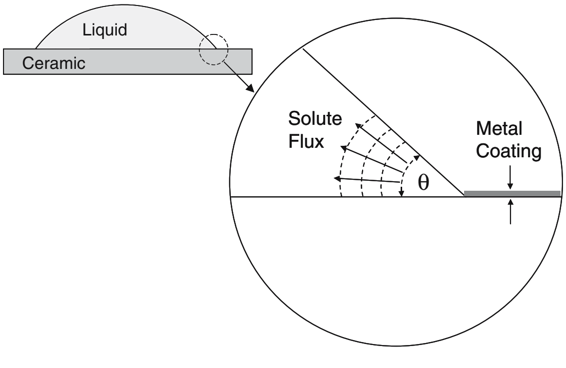

Fig. 5 Schematic of the interaction of the coating with the drop at the triple point

vacuum. The results showed that binary alloys containing copper in the range $0 < X_{Cu} < 0.3$ presented contact angles higher than 70°. In general, the wetting of Al_2O_3 was enhanced by the addition of Al to Cu. In the present work, the maximum copper content in the bulk aluminum after complete dissolution was less than 1%, leading to equilibrium contact angles after 1 h holding time of 58.3° and 45.5° for Al/Cu–Al_2O_3 and Al/Cu–SiC couples, respectively. Hence they are substantially lower values than those quoted in the literature for Al–Cu, and those obtained for pure Al on the uncoated ceramics in the present study (115.2° for Al_2O_3 and 87.3° for SiC).

Spreading kinetics

Figure 6 shows the variation in drop base radius observed in the Al/SiC and Al/Al_2O_3 systems at 800 °C. The *R(t)* curve of the Al/SiC system (Fig. 6a) exhibits the three kinetic stages observed in the $\theta(t)$ curves. Initially the velocity of the triple line decreases progressively; the increase in the spreading radius corresponds to the transition from the unreacted to the reacted interface. Thereafter, a steady configuration is established at the triple line and, as a result, the reaction rate and the triple line velocity are constant with time. Hence, the spreading rate *dR/dt* in the portion of the curve corresponding to $t_2 < t < t_F$ is about 0.07 μm/s. Finally, at times $>t_F$, *R* remains stable. On the contrary, in the non-reactive Al/Al_2O_3 system (Fig. 6b), the spreading rate is controlled by viscous flow. In fact, the second kinetic stage shown in the Al/SiC system does not appear in the Al/Al_2O_3 couple, a stage characteristic of the interfacial reaction between SiC and Al.

When the spread radius of the drop is plotted against the time elapsed for the copper-coated substrates, a different behavior is observed (Fig. 7). In the case of the Al/Cu–Al_2O_3 arrangement (Fig. 7a), initially an abrupt change in the slope of the *R(t)* curves took place, as the velocity of the triple line increased significantly. Experimentally determined instantaneous rates after a few seconds were in the order of 0.12 mm/s. Once the maximum spreading radius was reached, corresponding to the minimum contact angle attained in the system, the drop showed an abrupt reduction in the base spread diameter at a rate ~20 μm/s in a period of 90 s. After this time, the drop radius changed less

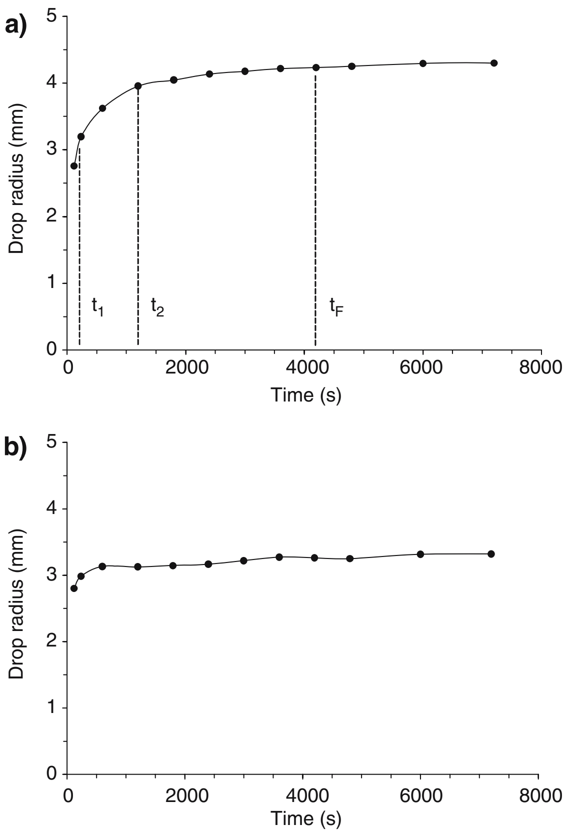

Fig. 6 Drop base radius vs. time in the (**a**) Al/SiC and (**b**) Al/Al_2O_3 systems

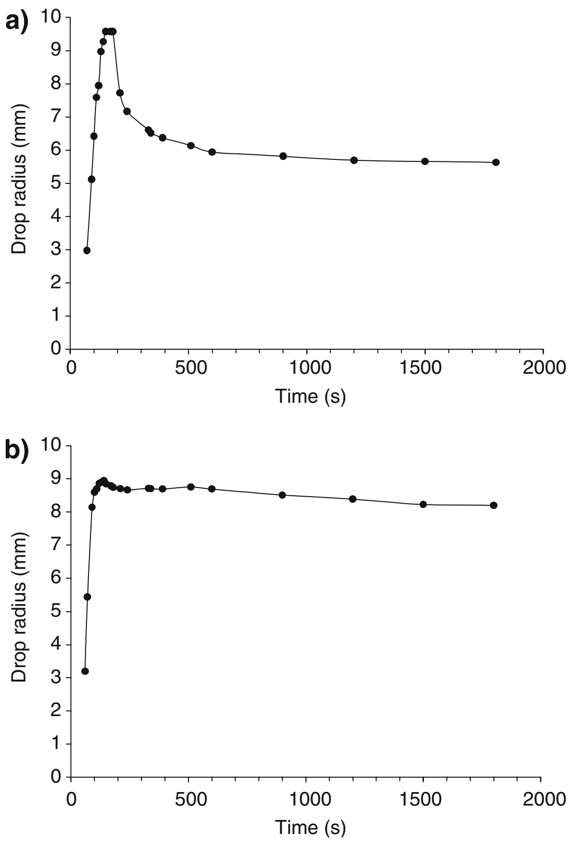

Fig. 7 Drop base radius vs. time in the (**a**) Al/Cu–Al_2O_3 and (**b**) Al/Cu–SiC systems

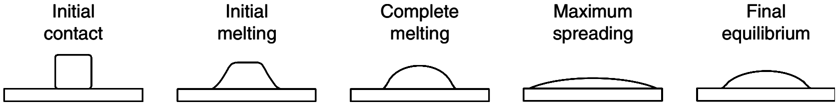

Fig. 8 Schematic of the melting and spreading process of aluminum on the Cu-coated ceramics

quickly until a stationary angle was reached. Figure 8 illustrates a schematic representation of the changes observed in the drop shape in the wetting of aluminum on the metal-coated ceramic plates. A similar dewetting effect and the consequent reduction in spreading diameter was also present, but was less distinguishable in the Al/Cu–SiC couple (Fig. 6b).

The favorable effect of the metallic coatings on the wetting kinetics is somewhat attributed to the significant partial enthalpy of mixing of the Al–Cu liquid system, $\Delta H = -28$ kJ/mol [12], which could lead to the formation of the low melting eutectic composition (548 °C) in the neighborhood of the interface, increasing the fluidity of the aluminum drop by locally reducing the melting point of the alloy. The local dissolution reaction rate is actually so high that the spreading process is presumably controlled by local diffusion rather than chemical reaction kinetics (Fig. 5). Diffusion is basically unsteady, since the metal coating is continuously dissolved from the ceramic surface until the point that it is completely consumed in the surrounding area of the triple line. It is assumed that the reaction proceeds at an appreciable rate only at the contact line, where the liquid has direct access to the metallic film. The advancing front is locally saturated with copper, retarding the dissolution process.

During high temperature wetting experiments, it has been found that alumina, although very chemically stable, may undergo significant morphological changes when in contact with liquid metals like Al and Cu. Saiz et al [14] performed wetting experiments of liquid Cu on sapphire using advancing and receding drops. A contact angle of 114° was reached after 20–30 min at a temperature of 1150 °C in gettered Ar leading to the formation of 10–40 nm ridges on the substrate at the triple points due to local diffusion rather than solution precipitation. Levi and Kaplan [15] investigated the morphology and thermodynamics of the interface made by micron-sized Al particles on the basal plane of sapphire at 900 °C. The morphological inspection showed that evaporation of the sapphire substrate constituents (Al and Al_xO/oxygen) diffusing at the interface did play an important role in the evolution of the Al–Al_2O_3 interface morphology.

Comparing the present results with a previous investigation made on the spreading kinetics of aluminum on Ni-coated ceramics [8], the copper coating led to slightly faster wetting kinetics, decreasing at a rate of 1.8°/s within the first two minutes compared with the rate of 1.5°/s for the nickel coating. This is related to the slower solubility of nickel in the molten aluminum, since the diffusion coefficient of copper in aluminum at 800 °C is reported to be 11.0×10^{-8} compared to 3.9×10^{-8} m^2/s for nickel [16]. However, contrary to the copper-coated ceramics, wetting couples of aluminum on nickel-coated samples maintained their equilibrium contact angle reached without showing any dewetting phenomenon. Since wetting is initially occurring on the copper coating, this is what drives the early spreading due to its dissolution in the molten drop. Once all the copper has dissolved in the aluminum, the wetting front retreats to reach a new but higher equilibrium contact angle. The maximum spreading occurs within the first 2 min therefore there is insufficient time for any grooving to occur that might pin the drop as observed in the experiments of Saiz et al. [14].

Work of adhesion

The work of adhesion W_a was calculated for the uncoated and copper-coated ceramics using the Young-Dupré equation:

$$W_a = \gamma_{LV}(1 + \cos\theta) \qquad (1)$$

The experimental contact angles used for the calculation were those obtained at the end of the wetting curves and provided in Table 1. For pure aluminum, a value of 844 mJ/m^2 was taken for γ_{LV}^{Al}. In the case of the coated samples, the metal drop resulting after dissolution was considered to behave as a dilute alloy with a maximum copper content proportional to the maximum spreading area of the drop. Thus, using the experimental spreading radius and a coating thickness of ≤10 μm, the volume of copper removed from the ceramic surface was estimated (Table 1). Elements like silver, copper, zinc, iron, manganese and silicon have

Table 1 Work of adhesion obtained at 800 °C for plain and coated ceramics

Sample	x_{Al} (at. %)	γ_{LV} (mJ/m^2)	θ (°)	W_a (mJ/m^2)
Al/SiC	1.0000	844.0	87.3	883.8
Al/Cu–SiC	0.9899	848.6	45.5	1443.4
Al/Al_2O_3	1.0000	844.0	115.2	484.6
Al/Cu–Al_2O_3	0.9878	849.6	58.3	1296.0

little effect on surface tension of dilute solutions in the temperature range 700–740 °C under argon atmosphere [17]. Although the surface tension of most binary liquid mixtures exhibits negative deviations from the proportional mathematical addition of the surface tensions for pure components, the latter method was used as a good approximation to determine the surface tension of the Al–Cu liquid drops (γ_{LV}^{Cu} = 1300 mJ/m), values shown in Table 1.

Microstructure examination

The Al/Al_2O_3 couples demonstrate a clean interface (Fig. 9), with the Al/Cu–Al_2O_3 showing the presence of $CuAl_2$ close to the interface that results from precipitation of dissolved Cu after solidification of the drop and cooling to room temperature. The absence of the Cu layer on the alumina surface confirms that wetting of Al_2O_3 is achieved through interaction between Al and the Cu-coating that then, subsequently, dissolved as described above. $CuAl_2$ precipitates illustrated in Fig. 9 were rarely found at the interface but distributed homogeneously throughout the microstructure.

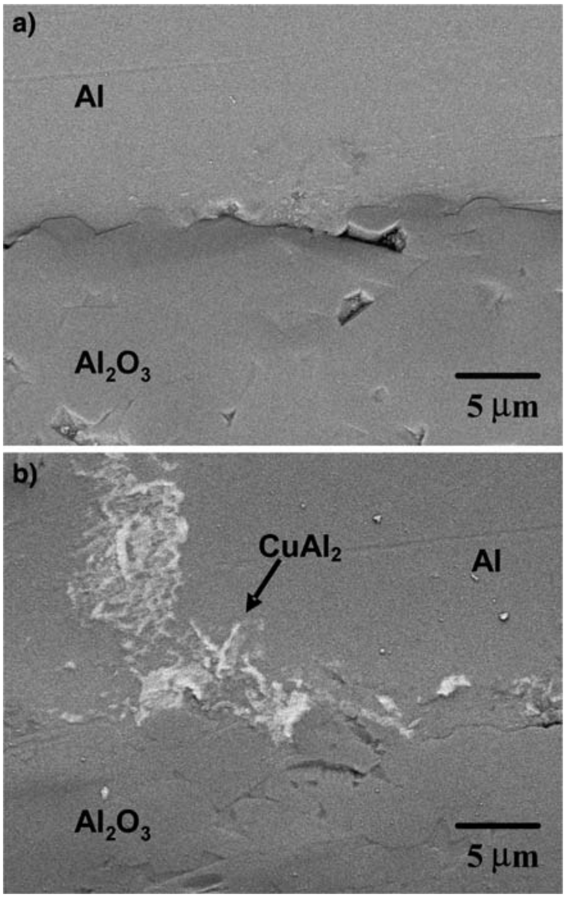

Fig. 9 Microstructures of interfaces after 30 min. holding time at 800 °C (**a**) Al/Al_2O_3, (**b**) Al/Cu–Al_2O_3

The interfacial microstructure observed in the Al/Cu–SiC samples was similar to that for Al/Cu–Al_2O_3 with no formation of Al_4C_3.With the application of a copper coating to SiC, there was no dissolution of this phase in the alloy and no interfacial reaction products were detected, as confirmed by the clean interface of Fig. 10 and associated EDS analysis. Conversely, as shown in Fig. 2 for the simple Al/SiC couple, Al_4C_3 was present either as a continuous layer or as isolated precipitates. Thus, when SiC is coated, the activity of Al at the interface decreases due to the copper layer either eliminating or retarding the formation of Al_4C_3. Important to recall, however, is the fact that the Al/SiC samples examined correspond to solidified drops obtained after reaching the final contact angle after 120 min, whereas for the Al/Cu–SiC sections the final angle was attained after only 30 min.

Conclusions

Significant improvements in wetting of aluminum can be achieved by applying an electroless coating of copper on Al_2O_3 and SiC ceramics. The coatings improved wetting irrespective of the ceramic substrate used. The wetting behavior proved to be very complex, showing a dewetting period at a rate of 0.12 mm/s after reaching a minimum contact angle of 12.6° for Al/Cu–Al_2O_3 and 26° for Al/Cu–SiC within just 2 min. Once the copper is completely removed from the ceramic surface and dissolved into the drop, final contact angles were achieved of 58.3° and 45.5° for the alumina and silicon carbide coated plates, respectively. Moreover, a dewetting phenomenon is observed. These values are substantially lower than those observed for pure aluminum on uncoated ceramics (115.2° and 87.3°). The

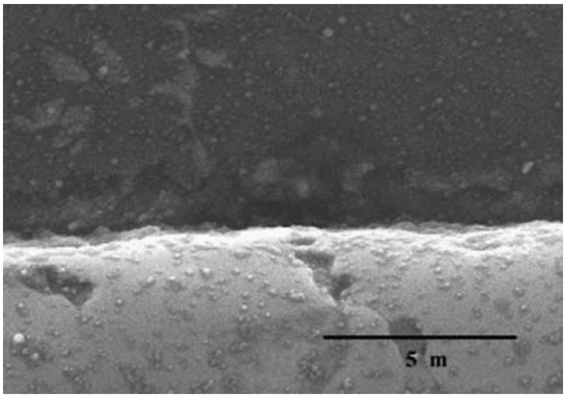

Fig. 10 Micrograph of the Al/Cu–SiC interface showing the absence of Al_4C_3

presence of the copper coating at the interface delayed the reactivity of SiC with Al resulting in a clean interface. On the contrary, Al_4C_3 was formed as a continuous layer or isolated precipitates at the interface of the pure Al/SiC couple.

Acknowledgments The authors would like to thank NSERC (Canada) and CONACYT (Mexico) for financially supporting this research through various grants and scholarships.

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