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Wetting of HIP AlN-TiB_2 ceramic composites by liquid metals and alloys

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Abstract

A non-oxide ceramic composite family was developed via hot isostatic pressing (HIP) without sintering aids. Fully dense ($\rho_{rel} > 99\%$) aluminum nitride-based samples, with titanium diboride as secondary phase, were designed to be electrical discharge machining (EDM) compatible.

Wetting experiments via the sessile drop method, in vacuum atmosphere, have been performed on three different grades of an AlN-TiB_2 ceramic composite. Contact angle and work of adhesion evolutions with time and temperature were investigated.

In the case of non-reactive wetting, both copper and silver showed a non-wetting behavior, as well as Cu/Ag alloys. A wetting behavior was, instead, observed for Cu/Ag/Ti brazing alloys.

Reactive wetting was observed in the case of nickel. Corrosion was due to Ni diffusion into the ceramic and dissolution of aluminum-based phases in the metal melt.
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1. Introduction

In recent years, the request for ceramics of high thermo-mechanical properties has led to a wide development of non-oxide ceramic composites, mainly for high temperature applications due to their promising mechanical properties and oxidation resistance. One common feature of this wide composite family is a high hardness value which makes traditional diamond-saw machining difficult and costly, whereas electrical discharge machining (EDM) allows the achievement of complex shapes.

Many applications require bonding of these composites materials to metals, such as protective layers for turbine blades. Consequently, in the framework of a wider study on corrosion of non-oxide composite ceramics, the wettability by different metals and alloys of AlN-TiB_2 composites has been analyzed in order to develop brazing techniques.

Aluminum nitride has been intensively investigated by microelectronic industry due to an order of magnitude higher thermal conductivity than currently used alumina.[1] Its electrical resistivity is also tested for possible structural and thermo-mechanical applications.[2] As a result, wetting of aluminum nitride substrates by copper[3,4] and other metals has been extensively studied.[5–8]

Titanium diboride shows some complementary properties with AlN such as good electrical conductivity, high melting point and chemical inertness. Nowadays, it is used for cathode applications in aluminum production, electrical discharge machining, wear resistant components and cutting tools.[9–11] The wetting behavior of this boride by liquid copper and silver was also studied.[12]

Very flew studies have been devoted to the synthesis,[13,14] fracture and impact behavior of aluminum nitride–titanium diboride composite ceramics.[15,16]

To the authors' knowledge, the wetting behavior of this composite has yet not been investigated.

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2. Experimental procedure

Three different AlN-TiB_2 specimens were produced via hot isostatic pressing (HIP) without sintering aids. The composition of the three grades is reported in Table 1. The samples have been prepared by mixing H.C. Starck AlN grade B

Table 1
Powder composition of the AlN-TiB_2 grades

Grades	AlN		TiB_2	
	vol%	mol%	vol%	mol%
A	45	50	55	50
B	65	69	35	31
C	35	40	65	60

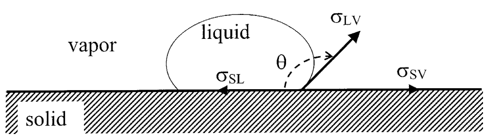

Fig. 1. Young equation scheme.

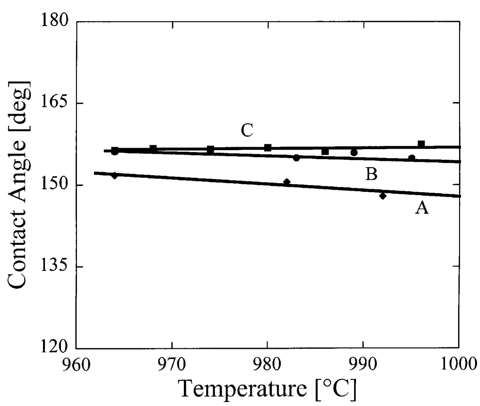

Fig. 2. Temperature dependence of Ag wetting as a function of composites' composition.

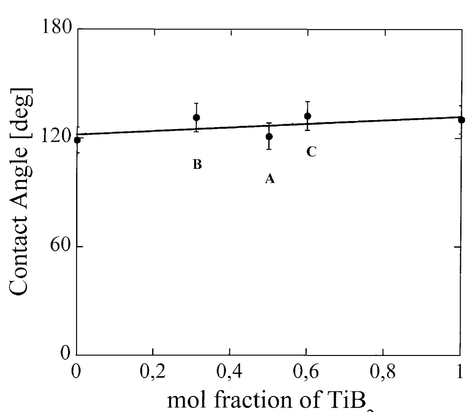

Fig. 3. Contact angle dependence with the composite composition (Cu wetting, 30 min, 1100 °C).

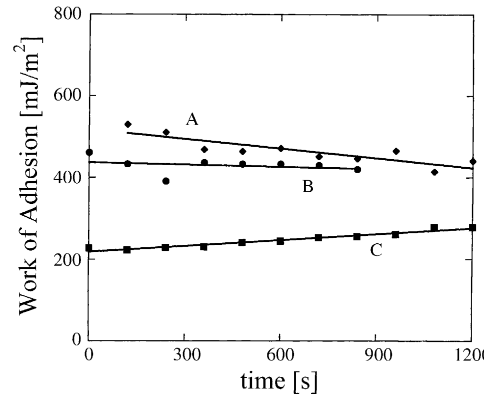

Fig. 4. Work of adhesion vs. temperature for Ag wetting.

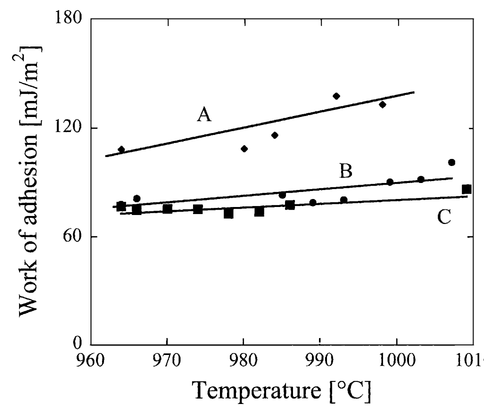

Fig. 5. Work of adhesion vs. time for Cu wetting at 1100 °C.

(mean diameter 2.6 μm) and H.C. Starck TiB_2 grade B (mean diameter 5.2 μm) powders. The starting powders were mixed in anhydrous ether with ultrasonic assistance and then dried up to 100 °C under vacuum. The mixture was then sieved (32 μm) and cold isostatically pressed up to about 60% relative density. The as-obtained cylinder was sealed in a silica container with a BN protective layer and hipped (ACB Alstom Atlantique press) up to 1840 °C and 170 MPa for 1 h dwell time. Using Archimedes principle, a relative density

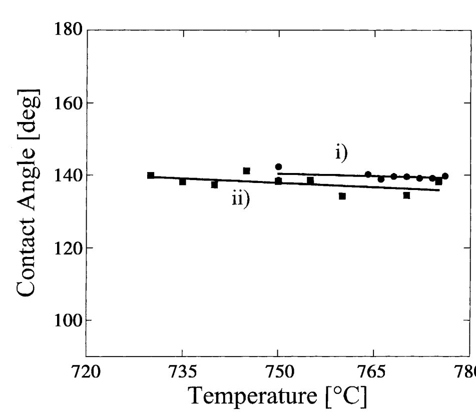

Fig. 6. Contact angle vs. temperature for Ag/Cu alloys: (i) Castolin1086 and (ii) Cast.

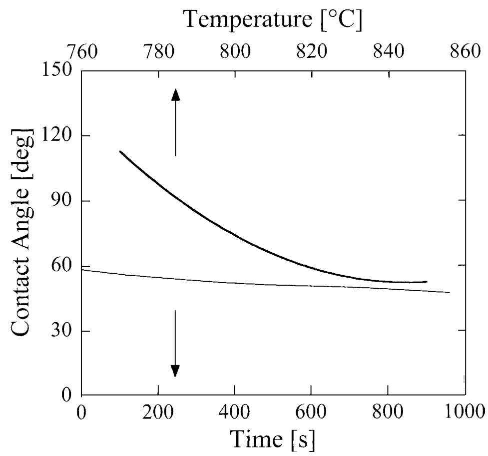

Fig. 7. Contact angle evolution with time and temperature (Ag/Cu eutectic + 3 wt% Ti alloy).

(ρ_{rel}) >99% was measured for all the three grades. Finally, the blocks were cut in the form of disks of 2.0 cm diameter and 0.3 cm height and polished ($Ra < 0.5$ μm). Density measurements on the single disks confirmed the homogeneity of density values across the samples.

Copper (purity > 99.99%), nickel (purity > 99.99%) and silver (purity > 99.95%) came all from Goodfellow, England, in the form of 3.5 mm diameter rods. Castolin1086® is an Ag72%/Cu28% commercial brazing alloy from Castolin, France, (3.5 mm diameter rods). All the metals were machined in 5.0 mm high cylinders maintaining the original diameter. Brazing alloy Cusil ABA® from Wesgo Inc., Belmont, CA, a eutectic Ag/Cu alloy with 1.61 wt% of Ti, received in the form of 0.5 mm wire, was compacted by pressure into the same shape as other metals for comparison. Titanium powder (325 mesh, purity 99.98%) is from Sigma–Aldrich, Germany. Silver/copper (Ag72%/Cu28%) powder is from Goodfellow, England (45 μm maximum grain size). The powders mechanically mixed, were cast into a silica container under vacuum (10^{-4} Pa) in the form of 3.5 mm diameter and 5.0 mm high cylinders. Copper and nickel were cleaned in a nitric acid solution (50.0 vol%) and silver in an ammonia solution (35.0 vol%) in order to remove a possible superficial oxide layer and rinsed with distilled water. Metals and alloys were ultrasonically degreased for 10 min in acetone, along with the ceramic substrates.

Wetting experiments were performed via the sessile drop method in a molybdenum oven working under vacuum up to 1650 °C. A software allows to compute contact angle, drop volume changes and surface tension from real-time digitally acquired images.[17] A scheme of the sessile drop method is shown in Fig. 1.

Young equation (Eq. (1)) and the Young–Dupré equation (Eq. (2)) used to calculate experimental results are shown below:[18]

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV}\cos(\theta) \tag{1}$$

$$W_a = \sigma_{LV}[1 + \cos(\theta)] \tag{2}$$

Rugosity measurements have been performed with a Veeco DEKTAK IIA, XRD analysis with a Siemens D5000 diffractometer (CuK_α) and SEM with a Philips XL30 coupled with an EDAX 9100/60 EDS analyser.

3. Results and discussion

3.1. AlN-TiB_2/copper and silver

A non-wetting behavior was observed for both pure Ag and Cu on all tested grades. No significant temperature dependence of the contact angle values of molten silver was found with respect to the composition of the three substrates (Fig. 2). Results reported in literature for Ag/AlN are slightly

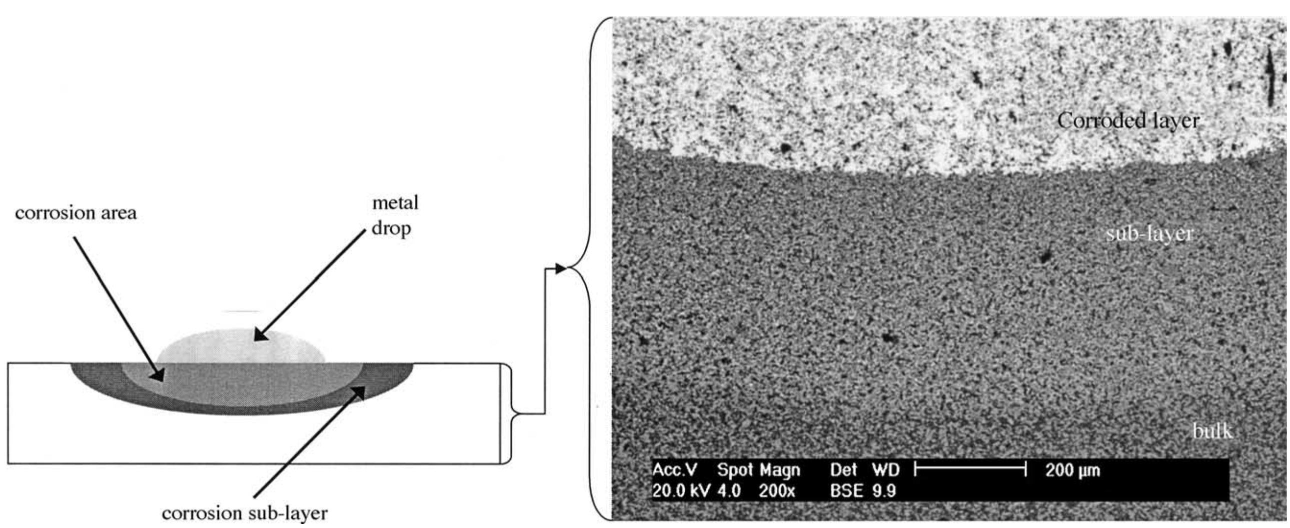

Fig. 8. Scheme for AlN-TiB_2 grade C/Ni system (a) and SEM image of the interfaces (b).

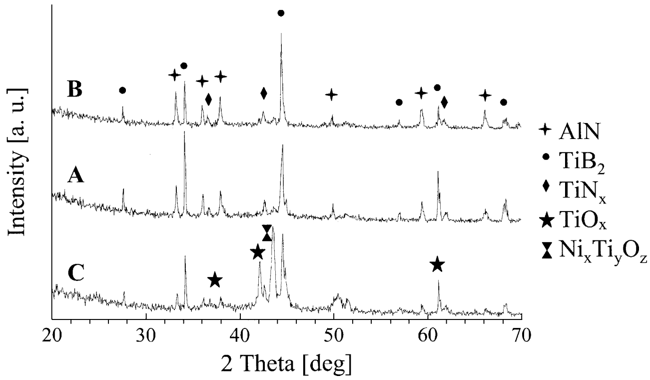

Fig. 9. XRD patterns of AlN-TiB_2/Ni corroded area.

lower but compatible ($\theta \approx 135°$).[19] No reference was found on Ag/TiB_2 wetting.

Similarly, contact angle values for copper melts, over 30 min observations at 1100 °C, showed a very small angle's dependence with the ceramic substrate composition (Fig. 3). These values are almost superposed with previous studies on Cu/AlN interactions ($118° \leq \theta \leq 135°$).[4,19,20] Concerning copper wettability of TiB_2, done in similar experimental conditions, literature values are sensibly lower, from $\theta \approx 58°$[18] to $\theta \approx 91°$.[12]

The work of adhesion (W_a) values are reported for silver as a function of temperature for the three grades (Fig. 4), and for copper as a function of time (Fig. 5). Values for σ_{LV} have been obtained (Eq. (2)) on non-wetting and non-reacting systems from experimental data at the working temperatures.[18]

3.2. AlN-TiB_2/(Ag/Cu)-based alloys

Previous results have shown a substantial independence of the contact angle values with the substrate's composition and a similar behavior may be expected in this case. Hence, results are presented only for the composite of grade C.

Silver and copper (72/28%) form and eutectic which melts at about 770 °C, although, in the literature, wetting experiments denoted a broad range of melting temperatures. Commercial Castolin1086® alloy (i) and the cast cylinder (ii), obtained from the powder mixture, showed a similar wetting behavior and an intermediate value of the contact angle in comparison with the pure metals (Fig. 6). The small amount of impurities present in the commercial brazing alloys seems not to influence the wetting behavior in comparison with the higher purity laboratory powders.

The addition of a 3 wt% of titanium to the Ag/Cu eutectic alloy dramatically decreases the contact angle value (Fig. 7).

The exponential decay is due to the migration of titanium particles from the bulk to the surface and hence to the interface between the ceramic and the molten drop. A light blue titanium oxide scale covering the cooled drop and SEM observations confirm this hypothesis. In the higher temperature range, the quasi-constant value of the contact

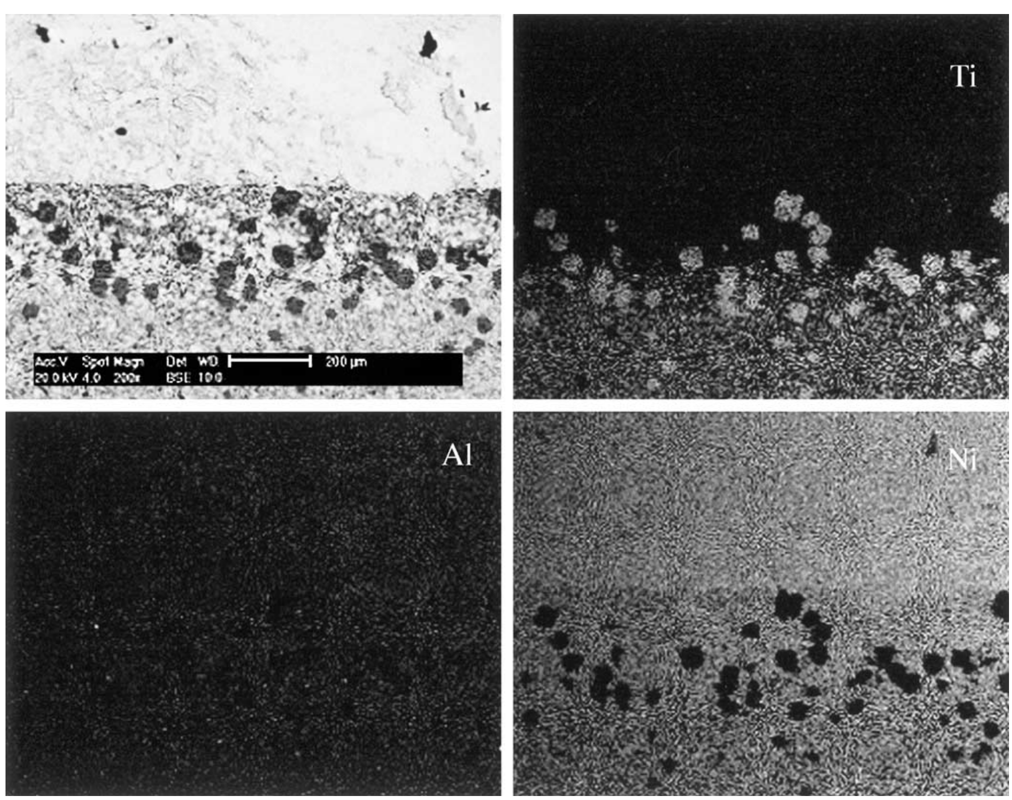

Fig. 10. BSE image and EDS elemental maps of the interface between the molten drop and the corroded area for AlN-TiB_2 grade C/Ni show Ni being continuously present across the interface while Ti being absent in the drop.

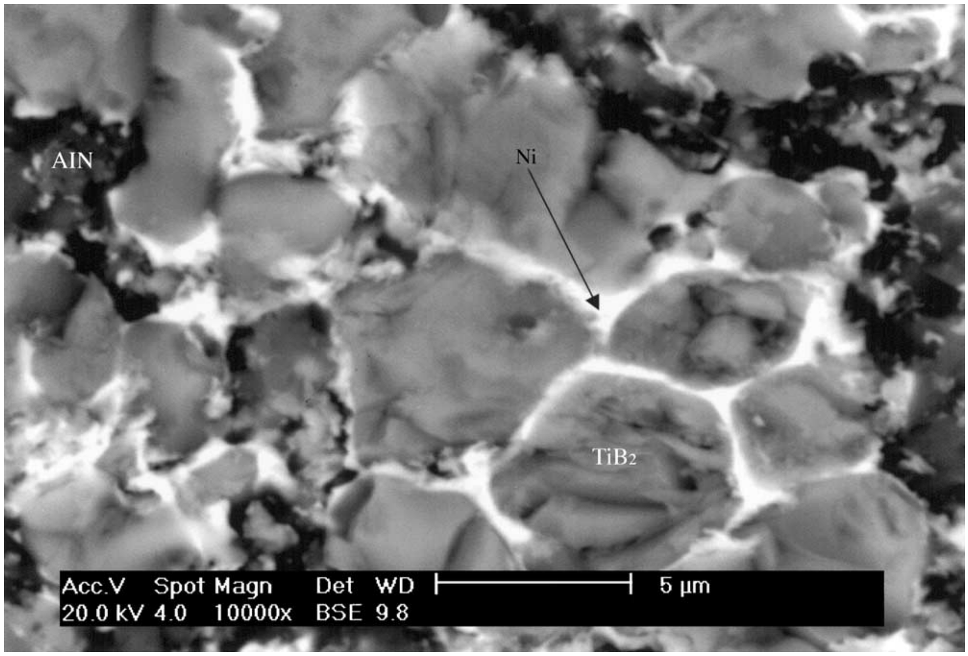

Fig. 11. SEM micrograph of the AlN-TiB_2 grade B/Ni corroded area.

angle suggests that a steady state interface composition is achieved.

Due to a slightly different starting geometry, the wetting behavior of the commercial Cusil ABA® alloy was not possible to be exactly measured but the value is in the same range as the ones already noticed. Though, the alloy well spans over the ceramic substrate. No significant modifications of the contact angle's value with time are noticed, via optical observation, probably due to a finer dispersion of titanium particles in the commercially available alloy.

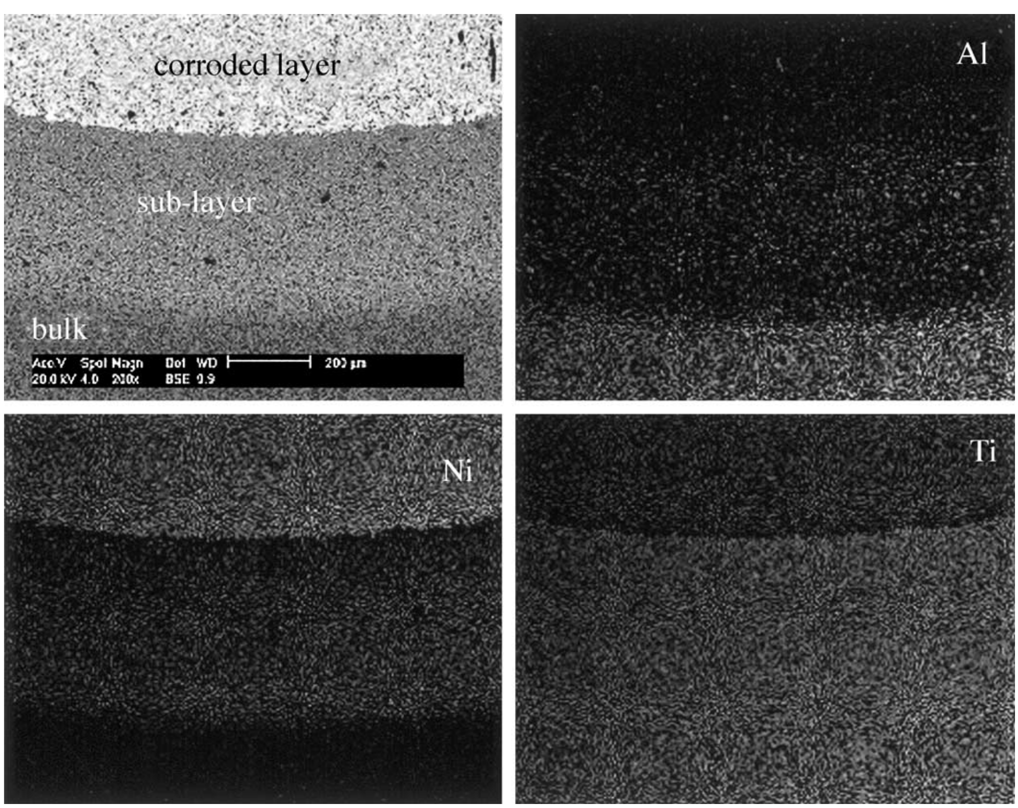

Fig. 12. BSE image and EDS elemental maps of the bulk/sub-layer/corroded layer interfaces for AlN-TiB_2 grade C/Ni (scale 200 μm).

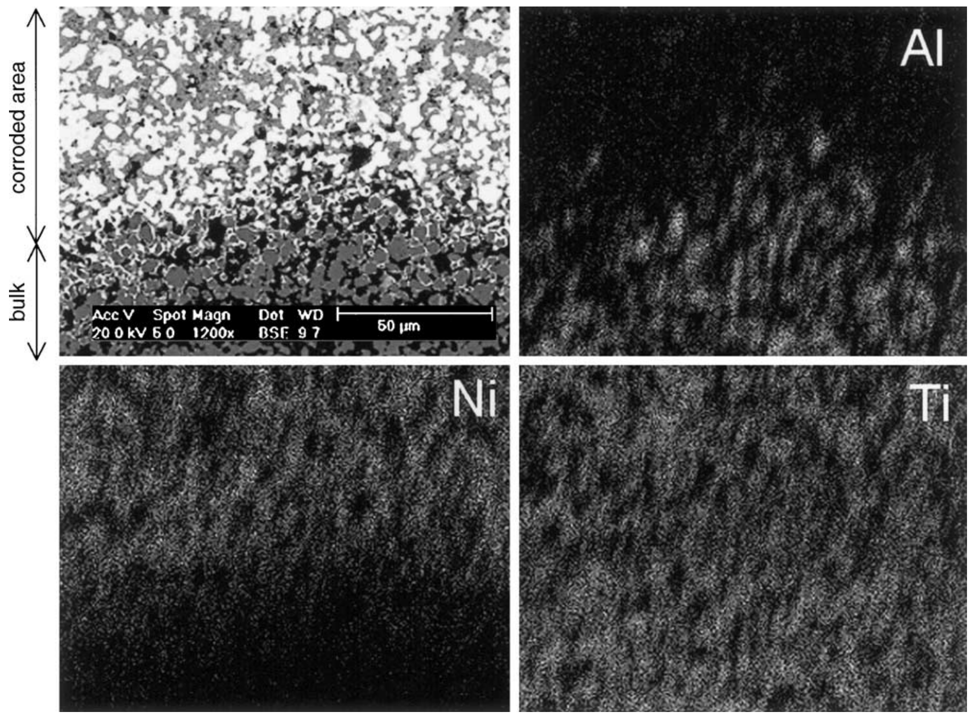

Fig. 13. BSE image and EDS elemental maps of the interfaces between the bulk and the corroded area for AlN-TiB_2 grade A/Ni (scale 50 μm).

3.3. AlN-TiB_2/nickel

Concerning nickel (T_m = 1453 °C), wetting experiments, at 1460 °C for 30 min, showed a deep corrosion of the ceramic area in contact with the liquid metal drop, as schematically shown in Fig. 8a and b. The corroded area appears bigger than the final drop dimensions and may be divided in two parts: a corrosion area at the interface with the metal drop and a sub-layer located between the previous one and the core. The extension and deepness of the corroded layers increase with the percentage of TiB_2 in the ceramic matrix and the composite with the highest TiB_2 content presents the deepest corroded sub-layer.

Nickel is highly reactive with both TiB_2 and AlN and leads to the formation of different phases. Cumulative X-ray diffraction patterns for all ceramic grades show the presence of Al–Ni and Ti–Ni based compounds, their relative quantity and composition varying with the composition of the ceramic composite (Fig. 9). The corroded sub-layer appears to be less uniform in the grade A and B than in the grade C, in relation with the molar percentage of TiB_2. XRD data also shows the presence of a continuous presence of Ti-based elements along the interface in the form of TiB_2 and complex $Ti_xN_y/Ti_xN_yO_z$ phases, which could not be resolved separately (Fig. 9).

EDS elemental maps of the interface between the molten drop and the external corroded layer indicate the absence, from the former, of Ti elements (Fig. 10). A diffusion process inside the ceramics substrate mainly trough an intergranular migration of nickel around the TiB_2 grains is also observed (Fig. 11). Due to the full density of the ceramics, this is made possible only by a partial dissolution of the AlN in the molten metal.

The EDS elemental maps of the bulk/sub-layer/corroded layer interfaces confirm the direct relation between Al dissolution and the Ni diffusion into the ceramic substrate (Figs. 12 and 13).

4. Conclusions

The wetting behavior of different metals and alloys on three AlN-TiB_2 ceramic composite grades was studied. Copper and silver did not wet the ceramics, while an addition of a small quantity of an active metal (Ti in this work) lowered dramatically the contact angle value allowing a good wetting.

On the other hand, contact with molten nickel initiated extensive corrosion phenomena with the formation of various Al–Ni and Ti–Ni secondary phases.

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