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Vacuum infiltration of copper aluminate by liquid aluminium

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Abstract

This paper studies attained microstructures and reactive mechanisms involved in vacuum infiltration of copper aluminate preforms with liquid aluminium. At high temperatures, under vacuum, the inherent alumina film enveloping the metal is overcome, and aluminium is expected to reduce copper aluminate, rendering alumina and copper. Under this approach, copper aluminate toils as a controlled infiltration path for aluminium, resulting in reactive wetting and infiltration of the preforms.

Ceramic preforms containing a mixture of Al_2O_3 and $CuAl_2O_4$ were infiltrated with aluminium under distinct vacuum levels and temperatures, and the resulting reaction and infiltration behaviour is discussed. Copper aluminates stability ranges depend on vacuum level and oxygen partial pressure, which determine both $CuAl_2O_4$ and $CuAlO_2$ ability for liquid aluminium infiltration. At 1100 °C and 0.76 atm vacuum level $CuAl_2O_4$ is stable, indicating pO_2 above 0.11 atm. Reactive infiltration is achieved *via* reaction between aluminium and $CuAl_2O_4$; however, fast formation of an alumina film blocking liquid aluminium wicking results in incipient infiltration. At 1000 °C and 3.8×10^{-7} atm vacuum level, $CuAlO_2$ decomposes to Cu and Al_2O_3 indicating a pO_2 below 6.0×10^{-7} atm; infiltration of the ceramic is hindered by the non-wetting behaviour of the resulting metal alloy. At 1000 °C and 1.9×10^{-6} atm vacuum level $CuAlO_2$ is stable, indicating pO_2 above 6.0×10^{-7} atm. Extensive infiltration is achieved *via* redox reaction between aluminium and $CuAlO_2$, rendering a microstructure characterised by uniform distribution of alumina particles amid an aluminium matrix.

This work evidences that liquid aluminium infiltration upon copper aluminate-rich preforms is a feasible route to produce Al–matrix alumina-reinforced composites. The associated reduction reaction renders alumina, as fine particulate composite reinforcements, and copper, which dissolves in liquid aluminium contributing as a matrix strengthener.

Keywords: B. Composites; B. Microstructure-final; D. Spinels; Reactive aluminium infiltration

1. Introduction

Chemical reactions between liquid aluminium and ceramics are being increasingly studied as a route for synthesising metal/ceramic composites. The reaction front between aluminium and the ceramic surfaces migrates throughout the solid, leaving behind a mixture of solid ceramic reaction products and metallic liquid [1–3]. Reaction thus induces wetting and promotes infiltration.

However, the inherent formation of a stable alumina film enveloping the metal (reaction (1)) is a major issue in aluminium reactive infiltration, because it prevents a true metal/ceramic interface to form and wetting and infiltration to occur.

$$Al(l) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s) \qquad (1)$$

At room temperature the alumina film thickness varies from around 10 nm (STP conditions) to 2 nm (after deep pickling) [4]. Alumina film breakup has been found at temperatures around 1000 °C under high vacuum conditions [4–9], in a process controlled by film reduction in the presence of liquid aluminium (reaction (2)) [3,4,9].

$$4Al(l) + Al_2O_3(s) \rightleftarrows 3Al_2O(g) \qquad (2)$$

Progression of reaction (2) lessens the alumina film, promoting its destabilisation. Al_2O_3 reduction occurs if oxygen

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availability at the surface of the film is lower than the produced oxygen flow, which is proportional to Al_2O partial pressure [10]. Al_2O partial pressure was reported between 10^{-10} atm at 860 °C [4] and 3×10^{-6} atm at 1100 °C [11]. High vacuum is thus a reliable process to effectively destabilize the alumina film enveloping aluminium.

The Al–Cu–O is an interesting system for development of Al–matrix composites through aluminium reactive infiltration involving the system's copper oxides (CuO, Cu_2O) or copper aluminates ($CuAl_2O_4$, $CuAlO_2$). Some studies have been published concerning reaction between liquid aluminium and copper oxide [12–17]. Copper oxide reduction by aluminium renders reinforcement alumina particles and copper, which enters the metal matrix as alloying element. However, the process cannot be carried out under high vacuum, since copper oxides dissociation under low oxygen partial pressure occurs at low temperatures [18,19]. Under atmospheric pressure attained reaction and infiltration are typically small.

Copper aluminates, $CuAl_2O_4$ and $CuAlO_2$, are on their turn less sensitive to oxygen pressure than copper oxides, presenting a broader stability range under vacuum. For example, according to Rogers et al. [20], at 1000 °C $CuAlO_2$ dissociation to alumina, copper and oxygen (reaction (3)) takes place at $pO_2 = 6.0 \times 10^{-7}$ atm, and $CuAl_2O_4$ dissociation to $CuAlO_2$, alumina and oxygen (reaction (4)) takes place at $pO_2 = 4.4 \times 10^{-2}$ atm. According to Gibbs energy calculations by Jacob and Alcock [21], at 1100 °C reaction (4) takes place at oxygen partial pressure bellow 0.11 atm.

$$4CuAlO_2(s) \rightleftarrows Al_2O_3(s) + 4Cu(s) + O_2(g) \tag{3}$$

$$4CuAl_2O_4(s) \rightleftarrows 4CuAlO_2(s) + 2Al_2O_3(s) + O_2(g) \tag{4}$$

In as much, approaching reactive infiltration in the Al–Cu–O system by using copper aluminate as the liquid infiltration path allows the use of high vacuum conditions.

2. Materials and methods

2.1. Preparation of $CuAl_2O_4$-rich preforms

$CuAl_2O_4$ was produced from solid state reaction between Al_2O_3 (CT-1200-SG, ALMATIS; max. 0.34 wt% impurities; $d_{50} = 1.12 \pm 0.02$ μm) and CuO (MERCK; max. 0.4 wt% impurities; $d_{50} = 1.85 \pm 0.01$ μm). A 55 mol%-Al_2O_3/45 mol%-CuO mixture was homogenized, heated in air at 5 °C/min up to 1100 °C with 15 min holding, and cooled inside the furnace. XRD (PW 3020, PHILIPS) showed that CuO is completely eliminated under those conditions, and that $CuAl_2O_4$ and residual Al_2O_3 are the only crystalline phases identified within the equipment's detection limit (Fig. 1). The resulting material was communited by planetary ball milling (PM100, RETSCH). Attained powders ($d_{50} = 1.29 \pm 0.13$ μm) were mixed with 1.5 wt% binder (Duramax B1000, RHOM & HAAS) and used to produce discs (approx. 2 g, Ø 13 mm) by uniaxial dry pressing. Discs were heated up to 300 °C at 5 °C/min, with 30 min holding for debinding.

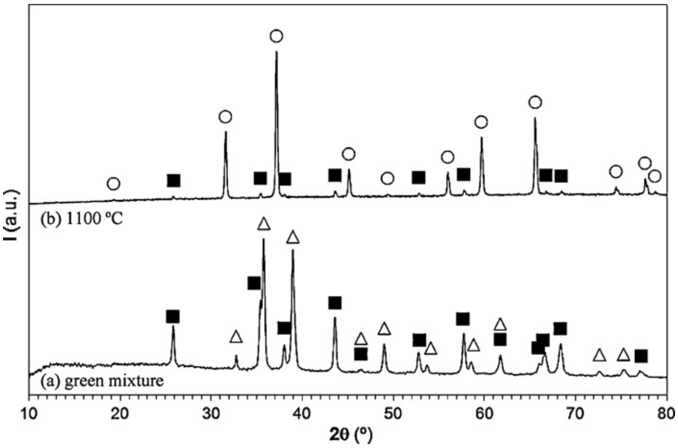

Fig. 1. XRD results concerning Al_2O_3/CuO mixture (a) green; (b) after 15 min holding time at 1100 °C (in air) and slow cooling. ■ alumina; ○ $CuAl_2O_4$, △ CuO.

2.2. Infiltration

Ceramic discs were fitted inside a hollow aluminium part (MOZAL, 99.85%), placed in an alumina crucible and heated at 5 °C/min up to the infiltration temperature (1000 °C or 1100 °C), followed by 1 h holding. Three distinct vacuum levels were studied (Table 1). Aluminium parts were thoroughly cleaned by sonication in NaOH 1 M solution at 80 °C for 10 min, rinsed with distilled water and dried, immediately before infiltration.

The inherent alumina film enveloping liquid Al is susceptible to cracking under small applied stresses [22]. This approach was used through the application of a 3 kPa gravity load on top of the samples. The load forced the formed liquid aluminium drop to deform, promoting destabilisation of the enveloping alumina film and effective Al/ceramic contact.

Samples cooled inside the furnace, and the resulting microstructures were investigated by FEG-SEM (JSM-7001F,

Table 1
Vacuum systems and infiltration conditions used.

Infiltration conditions		Apparatus	
T_{inf} (°C)	p (atm)	Furnace	Vacuum pump
1100	0.76	Carbolite furnace (STF)	Diaphragm (KNF N035.1.2ANI)
1000	1.9×10^{-6}	Prototype vertical vacuum furnace	Turbomolecular (ALCATEL 5081)
1000	3.8×10^{-7}	Vacuum industries (GCA)	Diffusion (GCA)

T_{inf}: infiltration temperature; p: vacuum level.

JEOL) and EDS (Inca pentaFETx3, OXFORD INSTRUMENTS).

3. Results and discussion

As previously discussed, copper oxidation state (0, +1 or +2) depends on temperature and oxygen partial pressure, conditioning copper aluminate stability.

Under a vacuum level of 0.76 atm and 1100 °C, $CuAl_2O_4$ is the copper aluminate present in the preform. Fig. 2 renders general microstructural features of a sample infiltrated under these conditions. Reaction front does not progress significantly into the ceramic preform, and liquid aluminium infiltration is irregular and limited. The maximum observed penetration depth is in the order of 350 μm.

Two regions can be assigned next to the aluminium source: an intermediate dense infiltrated region, and unreacted, partially densified, ceramic preform. The infiltrated region is composed by an alumina irregular film, surrounded in all its extension by a mixture of two phases (Fig. 3). EDS analysis assigned the presence of Cu and O to one of the phases, thus identified as copper oxide. The attained Cu:Al ratio ≈1 in the other phase suggests the presence of $CuAlO_2$. Small formations of the same phases are also distributed throughout the alumina film.

These results suggest a reactive infiltration mechanism where liquid aluminium leaving the metal source reacts with $CuAl_2O_4$ through the CuO groups in the spinel phase, according to reaction (5):

$$2Al(l) + 3CuAl_2O_4(s) \rightarrow 4Al_2O_3(s) + 3[Cu]_{Al} \qquad (5)$$

This reaction leads to rapid formation of fresh alumina between the starting alumina particles, with copper being released into the liquid. Also, at the used vacuum level, oxygen permeating through the ceramic preform reacts at the infiltrating liquid aluminium free surface forming more alumina. When these alumina formations becomes continuous infiltration stops, hindering further Al access to the preform. Infiltrated regions are much denser than the un-infiltrated partially densified preform. It is thus apparent that sintering kinetics in the presence of liquid aluminium is much faster. Due to the infiltration reaction mechanism and direct alumina formation, the Cu-rich aluminium liquid between the alumina formations and the ceramic preform quickly wears out of Al through reaction (5). The remaining entrapped copper liquid is further oxidised due to atmospheric oxygen permeation, rendering Cu_2O that transforms to CuO on cooling. Oxygen saturated liquid copper also reacts with alumina to form $CuAlO_2$ according to reaction (6). Oxygen permeating though the pore structure plays an important role in this reaction [14,23].

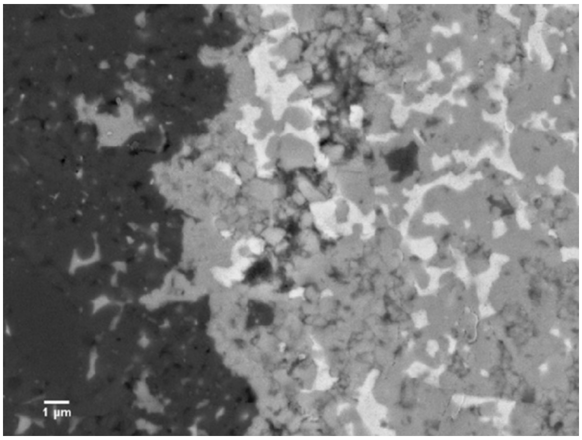

Fig. 3. Backscattered electron image (BEI) of sample infiltrated at 1100 °C under 0.76 atm vacuum level: detail of the interface between infiltration film and starting preform.

$$2Cu(l) + [O]_{Cu(l)} + Al_2O_3(s) \rightleftarrows 2CuAlO_2(s) \qquad (6)$$

In as much, under 0.76 atm and 1100 °C, incipient infiltration is achieved *via* reaction between aluminium and $CuAl_2O_4$; nevertheless fast formation of an alumina film blocks liquid aluminium wicking, hindering infiltration.

Under 3.8×10^{-7} vacuum level and 1000 °C metal/powder mingling appears to have occurred in few locations at the metal/ceramic borders (Fig. 4), which attests that the alumina film

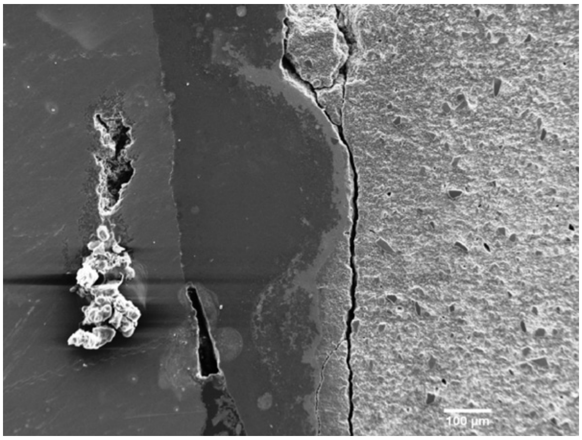

Fig. 2. Low magnification secondary electron image (SEI) of sample infiltrated at 1100 °C under 0.76 atm vacuum level.

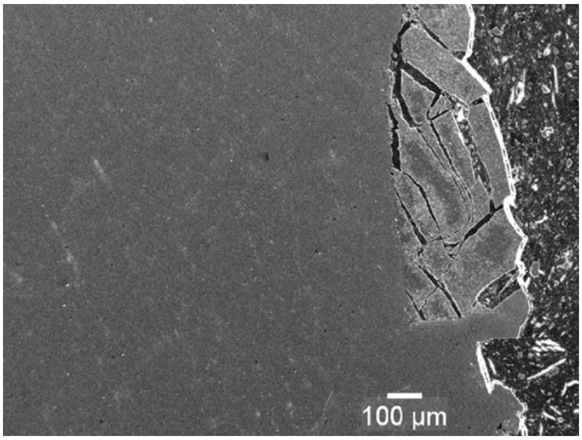

Fig. 4. Low magnification SEI of sample infiltrated under 3.8×10^{-7} atm vacuum level at 1000 °C (rectangle: incipient metal/ceramic reaction).

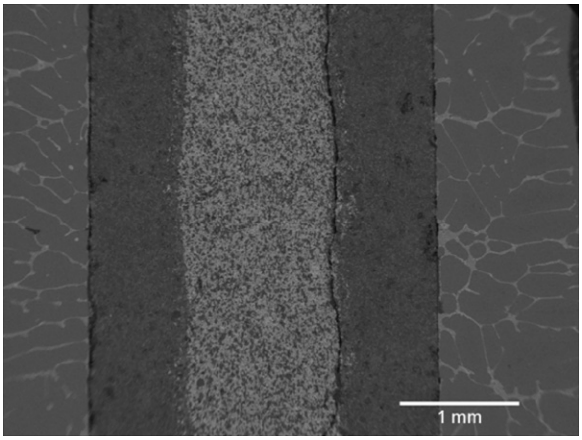

Fig. 5. Low magnification BEI of infiltrated sample (1000 °C, 1.9×10^{-6} atm vacuum level).

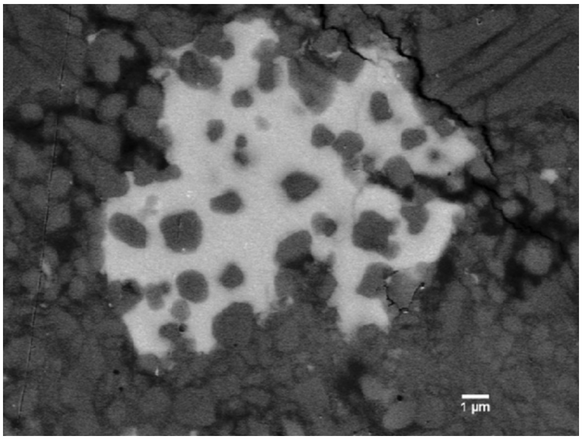

Fig. 7. BEI of infiltrated sample (1000 °C, 1.9×10^{-6} atm vacuum level): detail of the infiltration film.

enveloping liquid aluminium is destabilized. However, infiltration does not take place under these conditions. Instead, $CuAl_2O_4$ transforms to $CuAlO_2$ at low temperatures and further decomposes to alumina, copper and molecular oxygen (reaction (3)). This indicates that $pO_2 < 6.0 \times 10^{-7}$ atm is reached [20]. As follows, released oxygen locally strengthens the alumina envelope film hindering liquid metal/preform contact. Besides, the reactive infiltration mechanism is no longer available because neither copper aluminate nor copper oxide is present. Capillary infiltration is also not possible because the contact angle between the resulting liquid Al–Cu alloy and the ceramic is not sufficiently low to drive capillary rise.

Under 1.9×10^{-6} atm vacuum level and 1000 °C, $CuAlO_2$ is the copper aluminate present in the starting preform, indicating an oxygen partial pressure above 6.0×10^{-7} atm [20]. Fig. 5 renders a general view of the sample, showing extensive infiltration and reaction. The corresponding microstructure presents three distinct regions: the aluminium source; a dense infiltrated region approximately 900 μm thick; and unreacted, partially densified, ceramic preform in the sample centre.

The metal film is composed by primary (Al) phase and (Al)/θ eutectic, distributed throughout. Fig. 6 shows a general view of the metal/infiltration film interface. Unreacted starting alumina particles are visible, merged in a background containing three phases (Fig. 7). EDS analysis assigned the presence of aluminium and oxygen to the abundant round-shaped particles, thus identified as alumina. The intergranular phase was assigned to aluminium. The light regions contain copper and aluminium in a 0.53 atomic ratio, and where assigned to solidified Al–Cu alloy (θ phase).

These results suggest a reactive mechanism where liquid aluminium leaving the metal source reacts with $CuAlO_2$ through the Cu_2O groups in the aluminate phase, according to reaction (7).

$$Al(l) + 3CuAlO_2(s) \rightarrow 2Al_2O_3(s) + 3[Cu]_{Al} \tag{7}$$

As a result, fresh alumina forms between the starting alumina particles, and copper is released into the liquid. The process is similar to reaction (5), but with lower alumina delivery. Also, no oxygen is released at the infiltration reaction front in the preceding case, and the vacuum level is high enough to avoid stabilisation of the alumina envelope film by permeating oxygen. Thus, the alumina formation kinetics is now sufficiently slow to allow extensive infiltration of liquid aluminium, and considerable amounts of copper reach the

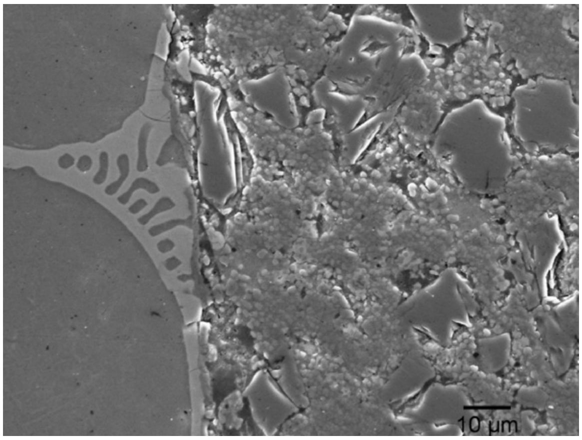

Fig. 6. SEI of infiltrated sample (1000 °C, 1.9×10^{-6} atm vacuum level): transition between metal source and infiltration film.

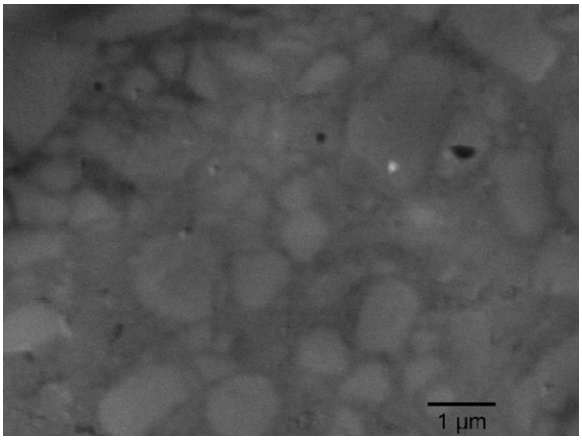

Fig. 8. BEI of infiltrated sample (1000 °C, 1.9×10^{-6} atm vacuum level): detail of formed alumina particles dispersed in Al matrix.

metal source, rendering θ phase on cooling. Formed Al_2O_3 particles are approximately round (Fig. 8) and mostly of the micron order (much smaller than the size of the starting alumina particles). Apparently all $CuAlO_2$ in the reaction film was consumed in the course of reaction (7), toiling as a controlled infiltration path for liquid Al.

It can be concluded that liquid aluminium infiltration of $Al_2O_3/CuAlO_2$ green bodies is possible at 1000 °C under 1.9×10^{-6} atm, with $pO_2 > 6.0 \times 10^{-7}$ atm. Under these conditions $CuAlO_2$ does not decomposes. The use of high vacuum promotes destabilisation of the inherent alumina film enveloping liquid aluminium, creating conditions for enhanced contact between aluminium and the ceramic. Reactive infiltration is achieved *via* redox reaction between aluminium and $CuAlO_2$, rendering a microstructure characterised by alumina particles distributed amid an aluminium matrix.

4. Conclusions

Ceramic preforms containing Al_2O_3 and $CuAl_2O_4$ where infiltrated with liquid aluminium under vacuum and the resulting wetting and infiltration mechanisms were studied. Depending on the infiltration temperature and vacuum level, the stable copper aluminate in the preform is either $CuAl_2O_4$ or $CuAlO_2$.

Under 0.76 atm and 1100 °C, infiltration is achieved *via* reaction between aluminium and $CuAl_2O_4$ in the preform. Nevertheless, fast formation of an alumina film blocks liquid aluminium wicking and results in irregular and hindered infiltration.

Under 3.8×10^{-7} atm and 1100 °C, with $pO_2 < 6 \times 10^{-7}$ atm $CuAl_2O_4$ transforms to $CuAlO_2$ and further decomposes to Cu and Al_2O_3. Infiltration is hindered because no reactive infiltration mechanism is available.

Under 1.9×10^{-6} atm and 1000 °C, with $pO_2 > 6 \times 10^{-7}$ atm $CuAlO_2$ is the aluminate present in the starting preform and does not decomposes. Extensive metal infiltration is achieved *via* reaction between liquid aluminium and the Cu_2O groups in the copper aluminate. Attained microstructure is characterized by uniform distribution of Al_2O_3 particles amid an aluminium matrix.

This work demonstrates that liquid aluminium infiltration of copper aluminate green bodies is a practicable route to produce Al–matrix alumina-reinforced composites. The preliminary results reported show that at 1000 °C extensive infiltration takes place under a vacuum level that destabilises the alumina enveloping film while avoiding decomposition of the aluminates. Infiltration is promoted by the redox reaction between Al and copper aluminate, with full consumption of the latter. The reaction renders alumina precipitates and metallic copper (which dissolves in liquid aluminium) as reaction products, thus combining *in situ* particle reinforcement with *in situ* alloying.

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References

[1] W.B. Hillig, H.C. Mcguigan, An exploratory study of producing non-silicate all-oxide composites by melt infiltration, Mater. Sci. Eng. A 196 (1995) 183–190.

[2] P. Kumar, N.A. Travitzky, P. Beyer, K.H. Sandhage, R. Janssen, N. Claussen, Reactive casting of ceramic composites (r-3C), Scr. Mater. 44 (2001) 751–757.

[3] S.M. Naga, A. El-Maghraby, A.M. El-Rafei, Properties of ceramic-metal composites formed by reactive metal penetration, Am. Ceram. Soc. Bull. 86 (2007) U9301–U9319.

[4] N. Eustathopoulos, J.C. Joud, P. Desre, J.M. Hicter, The wetting of carbon by aluminium and aluminium alloys, J. Mater. Sci. 9 (1974) 1233–1242.

[5] A.J. Klinter, C.A. Leon-Patiño, R.A.L. Drew, Wetting phenomena of Al–Cu alloys on sapphire below 800 °C, Acta Mater. 58 (2010) 1350–1360.

[6] K. Landry, S. Kalogeropoulou, N. Eustathopoulos, Wettability of carbon by aluminum and aluminum alloys, Mater. Sci. Eng. A 254 (1998) 99–111.

[7] V. Laurent, V. Chatain, N. Eustathopoulos, Wettability of SiC by aluminum and Al–Si alloys, J. Mater. Sci. 22 (1987) 244–250.

[8] E. Saiz, A.P. Tomsia, K. Suganuma, Wetting and strength issues at Al/α-alumina interfaces, J. Eur. Ceram. Soc. 23 (2003) 2787–2796.

[9] A.C. Ferro, B. Derby, Wetting behaviour in the Al–Si/SiC system: interface reactions and solubility effects, Acta Metall. Mater. 43 (1995) 3061–3073.

[10] K. Landry, S. Kalogeropoulou, N. Eustathopoulos, Y. Naidich, V. Krasovsky, Characteristic contact angles in the aluminium/vitreous carbon system, Scr. Mater. 34 (1996) 841–846.

[11] L. Coudurier, J. Adorian, D. Pique, N. Eustathopoulos, Study of wettability by liquid aluminum of alumina and alumina covered with a layer of a metal or a refractory compound, Rev. Int. Hautes Tempér. Refract. 21 (1984) 81–93.

[12] M. Guedes, J.M.F Ferreira, A.C. Ferro, Reaction mechanisms in Al_2O_3–CuO preforms infiltration by liquid aluminium, submitted for publication.

[13] Z.J. Huang, B. Yang, H. Cui, X.J. Duan, J.S. Zhang, Microstructure of designed Al matrix composites reinforced by combining *in situ* alloying elements and Al_2O_3(p), J. Mater. Sci. Lett. 20 (2001) 1749–1751.

[14] J.-Z. Huang, B. Yang, H. Cui, J.S. Zhang, Study on the fabrication of Al matrix composites strengthened by combined in-situ alumina particle and in-situ alloying elements, Mater. Sci. Eng. A 351 (2003) 15–22.

[15] G. Chen, G.-X. Sun, Z.-G. Zhu, Study on reaction-processed Al–Cu/α-Al_2O_3(p) composites, Mater. Sci. Eng. A 265 (1999) 197–201.

[16] G. Chen, G.-X. Sun, Z. Zhu, On the chemical reactions to process particle reinforced Al–Cu alloy matrix composites, Mater. Sci. Eng. A 251 (1998) 226–231.

[17] M. Kobashi, T. Choh, Fabrication of particulate composite by in situ oxidation process, Light Met. 42 (1992) 138–142.

[18] R.E. Johnson, F.N. Rhines, Cu–O, in: T. Lyman (Ed.), Metals Handbook, 8th ed., Metallography, Structures and Phase Diagrams, vol. 8, ASM International, Ohio, 1973, pp. 298–357.

[19] B. Hallstedt, D. Risold, L.J. Gauckler, Thermodynamic assessment of the copper–oxygen system, J. Phase Equilib. 15 (1994) 483–498.

[20] K.A. Rogers, K.P. Trumble, B.J. Dalgleish, I.E. Reimanis, Role of oxygen in microstructure development at solid-state diffusion-bonded Cu/alpha-Al_2O_3 interfaces, J. Am. Ceram. Soc. 77 (1994) 2036–2042.

[21] K.T. Jacob, C.B. Alcock, Thermodynamics of $CuAlO_2$ and $CuAl_2O_4$ and phase-equilibria in system Cu_2O–CuO–Al_2O_3, J. Am. Chem. Soc. 58 (1975) 192–195.

[22] R. Prescott, M.J. Graham, The formation of aluminum oxide scales on high-temperature alloys, Oxid. Met. 38 (1992) 233–254.

[23] B.S. Rao, V. Jayaram, Pressureless infiltration of Al–Mg based alloys into Al_2O_3 preforms: mechanisms and phenomenology, Acta Mater. 49 (2001) 2373–2385.