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 oxygen partial pressure; selection of infiltration temperature and vacuum level determines both $CuAl_2O_4$ and $CuAlO_2$ ability for liquid aluminium infiltration. At 1100ºC and pO_2 = 0.16 atm, reactive infiltration is achieved *via* reaction between

aluminium and $CuAl_2O_4$; however, fast formation of an alumina layer blocking liquid aluminium wicking results in incipient infiltration. At 1000 ºC and $pO_2 = 8x10^{-8}$ atm, $CuAlO_2$ decomposes to Cu and Al_2O_3 and infiltration of the ceramic is hindered by the non-wetting behaviour of the resulting metal alloy. At 1000 ºC and $pO_2 = 4x10^{-7}$ 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: Reactive Aluminium Infiltration; B. Composites; B. Microstructure-final; D. Spinels.

1. Introduction

Chemical reactions between liquid aluminium and ceramics are being increasingly studied has 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.

$$Al(l) + 3/2\,O_2(g) \rightarrow Al_2O_3(s) \qquad (1)$$

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 ºC under high vacuum conditions [4-9], in a process controlled by film reduction in the presence of aluminium liquid (reaction 2) [3,4,9].

$$4Al(l) + Al_2O_3(s) \leftrightarrows 3Al_2O(g) \quad (2)$$

Progression of reaction (2) lessens the alumina layer, promoting its destabilisation. Al_2O_3 reduction occurs if oxygen 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 ºC [4] and $3x10^{-6}$ atm at 1100 ºC [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 ºC $CuAlO_2$ dissociation to alumina, copper and oxygen (reaction 3) takes place at pO_2 = $6.0x10^{-7}$ atm, and $CuAl_2O_4$ dissociation to $CuAlO_2$, alumina and oxygen (reaction 4) takes place at pO_2 = $4.4x10^{-2}$ atm. According to Gibbs free energy calculations by Jacob & Alcock [21], at 1100ºC reaction (4) takes place at oxygen partial pressure bellow 0.11 atm.

$$4CuAlO_2(s) \leftrightarrows Al_2O_3(s) + 4Cu(ss) + O_2(g) \quad (3)$$

$$4CuAl_2O_4(s) \leftrightarrows 4CuAlO_2(s) + 2Al_2O_3(s) + O_2(g) \quad (4)$$

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 ± 0.02 μm) and CuO (MERCK; max. 0.4 wt% impurities; d_{50} = 1.85 ± 0.01 μm). A 55 mol%-Al_2O_3/45 mol%-CuO mixture was homogenized, heated in air at 5 ºC/min up to 1100 ºC 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 ± 0.13 μm) were mixed with 1.5 wt% binder (Duramax B1000, RHOM & HAAS) and used to produce discs (approx. 2 g, ∅ 13 mm) by uniaxial dry pressing. Discs were heated up to 300 ºC at 5 ºC/min, with 30 minutes holding for debinding.

2.2. Infiltration

Ceramic discs were fitted inside a hollow aluminium part (MOZAL, 99.85%), placed in an alumina crucible, and heated up at 5 ºC/min followed by 1 h holding (prototype vertical vacuum furnace). A 3 kPa gravity load was applied to enhance Al/ceramic contact. Aluminium parts were thoroughly cleaned by sonication in NaOH 1M solution at 80 ºC for 10 minutes, rinsed with distilled water and dried, immediately before infiltration.

Samples cooled inside the furnace, and the resulting microstructures were investigated by FEG-SEM (JSM-7001F, 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 pO_2 = 0.16 atm and 1100 ºC, $CuAl_2O_4$ 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 (Fig. 3) is composed by an alumina irregular layer, surrounded in all its extension by a mixture of two phases. EDS analysis assigned the presence of Cu and O to one of the phases, thus identified as copper oxide. The attained Cu:Al ratio $\approx$ 1 in the other phase suggests the presence of $CuAlO_2$. Small formations of the same phases are also distributed throughout the alumina layer.

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

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

This reaction leads to rapid formation of fresh alumina between the starting alumina particles, with copper being release into the liquid. When the alumina layer becomes continuous, infiltration stops, hindering Al access to the ceramic preform. The Cu-containing aluminium liquid between the alumina formations and the ceramic preform quickly wears out of Al through reaction (5). Remaining copper liquid entrapped near alumina reacts to form $CuAlO_2$ according to reaction (6). Oxygen permeating though the pore structure plays an important role in this reaction [14,22].

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

In as much, under $pO_2 = 0.16$ atm and 1100ºC, incipient infiltration is achieved *via* reaction between aluminium and $CuAl_2O_4$; nevertheless fast formation of an alumina layer blocks liquid aluminium wicking, hindering infiltration.

Under $pO_2 \approx 8x10^{-8}$ atm and 1000 ºC, $CuAlO_2$ is the copper aluminate present in the starting preform. Metal/powder mingling appears to have occurred in few locations at the metal/ceramic borders (Fig. 4), which attests that the alumina layer enveloping liquid aluminium is destabilized. But under these conditions, infiltration does not take place. Instead, the aluminate decomposition (reaction 3) is triggered [20], and copper dissolves into aluminium liquid. As follows, neither reactive infiltration nor spontaneous infiltration are possible, respectively because the reactive infiltration mechanism is no longer available,

and because the contact angle between the resulting Al-Cu alloy and the ceramic is not sufficiently low to drive capillary rise.

Under $pO_2 = 4x10^{-7}$ atm and 1000 ºC, $CuAlO_2$ is the copper aluminate present in the starting preform [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 layer is composed by primary (Al) phase and (Al)/θ eutectic, distributed throughout. Fig. 6 shows a general view of the metal/infiltration layer 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).

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

As a result, fresh alumina forms between the starting alumina particles, and copper is release into the liquid. The process is similar to reaction (5), but with lower alumina delivery. Apparently, the alumina formation kinetics is now sufficiently slow to allow extensive infiltration of liquid aluminium, and considerable amounts of copper reach the 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 layer 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 1000ºC under $pO_2 = 4x10^{-7}$ 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 oxygen partial pressure, the stable copper aluminate in the preform is either $CuAl_2O_4$ or $CuAlO_2$.

Under pO_2 = 0.16 atm and 1100 ºC, infiltration is achieved *via* reaction between aluminium and $CuAl_2O_4$ in the preform. Nevertheless, fast formation of an alumina layer blocks liquid aluminium wicking and results in irregular and hindered infiltration.

Under $pO_2 = 8x10^{-8}$ atm and 1100 ºC, $CuAlO_2$ is the copper aluminate present in the starting preform. $CuAlO_2$ decomposes to Cu and Al_2O_3, and infiltration is hindered because no reactive infiltration mechanism is available.

Under $pO_2 = 4x10^{-7}$ atm and 1000 ºC, $CuAlO_2$ is the aluminate present in the starting preform. Under these conditions $CuAlO_2$ does not decomposes. Extensive metal infiltration is achieved *via* reaction between liquid aluminium and 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 ºC extensive infiltration takes place under a vacuum level that destabilises the alumina enveloping film while avoiding decomposition of the aluminates. Reactive 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 alumina) as reaction products, thus combining *in situ* particle reinforcement with *in situ* alloying.

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Figure Captions

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

Figure 2. Low magnification secondary electron image (SEI) of sample infiltrated at 1100 ºC under pO_2 = 0.16 atm.

Figure 3. Backscattered electron image (BEI) of sample infiltrated at 1100 ºC under pO_2 = 0.16 atm: detail of the interface between infiltration layer and starting preform.

Figure 4. Low magnification SEI of sample infiltrated under $pO_2 = 8x10^{-8}$ atm at 1000 ºC (rectangle: incipient metal/ceramic reaction).

Figure 5. Low magnification BEI of infiltrated sample (1000 ºC, $pO_2 = 4x10^{-7}$ atm).

Figure 6. SEI of infiltrated sample (1000 ºC, $pO_2 = 4x10^{-7}$ atm): transition between metal source and infiltration layer.

Figure 7. BEI of infiltrated sample (1000 ºC, $pO_2 = 4x10^{-7}$ atm): detail of the infiltration layer.

Figure 8. BEI of infiltrated sample (1000 ºC, $pO_2 = 4x10^{-7}$ atm): detail of formed alumina particles dispersed in Al matrix.

Figure

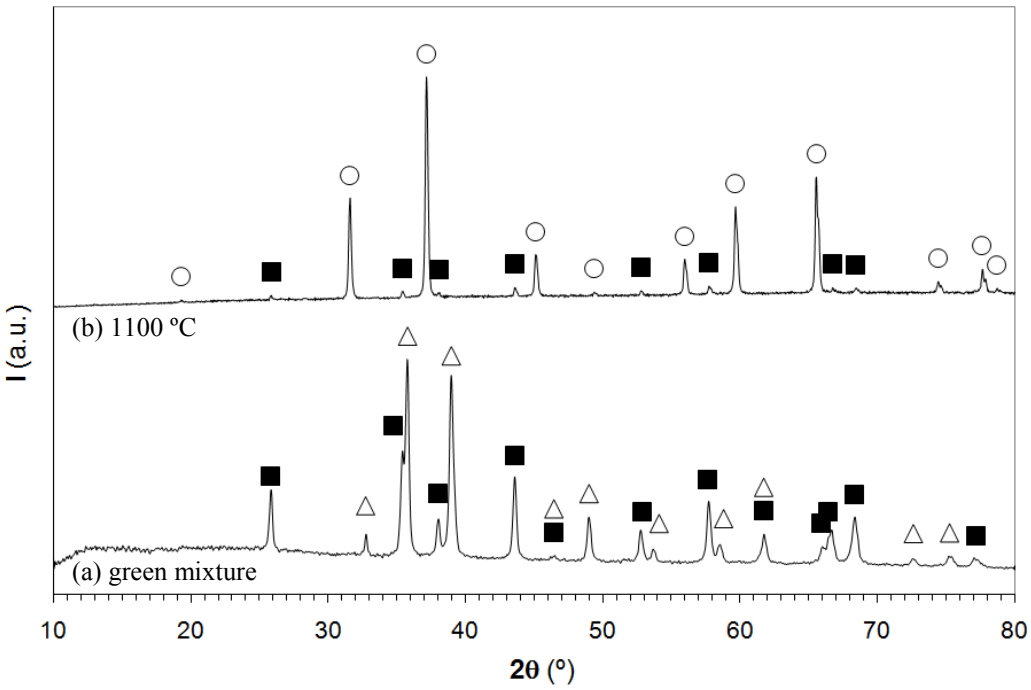

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Figure

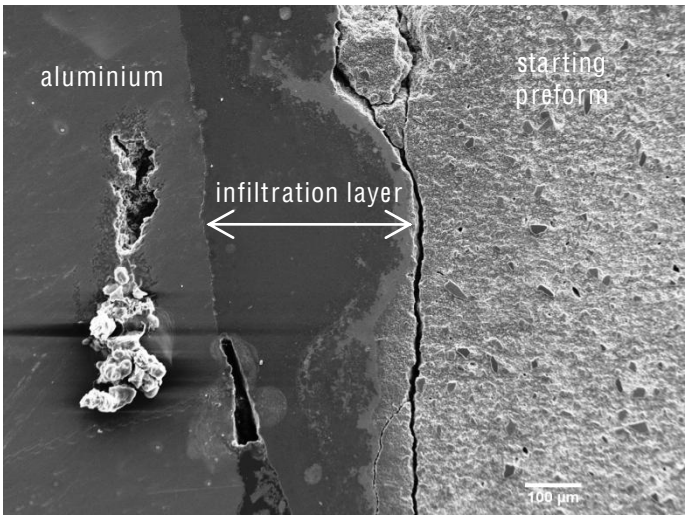

Figure 2. Low magnification secondary electron image (SEI) of sample infiltrated at 1100 ºC under pO_2 = 0.16 atm.

Figure

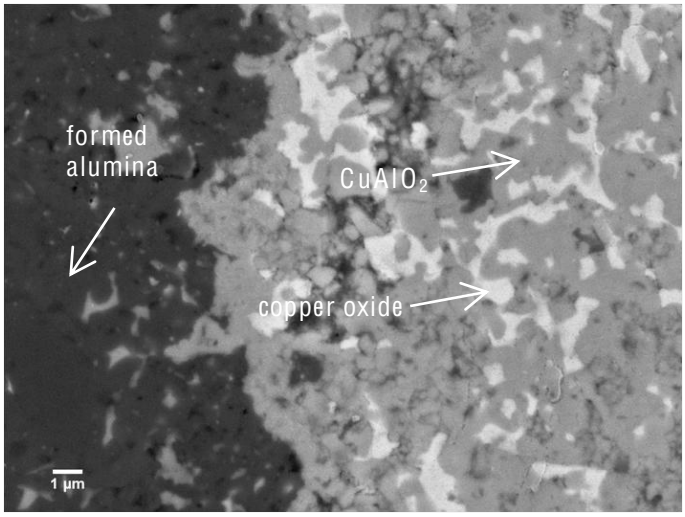

Figure 3. Backscattered electron image (BEI) of sample infiltrated at 1100 ºC under pO_2 = 0.16 atm: detail of the interface between infiltration layer and starting preform.

Figure

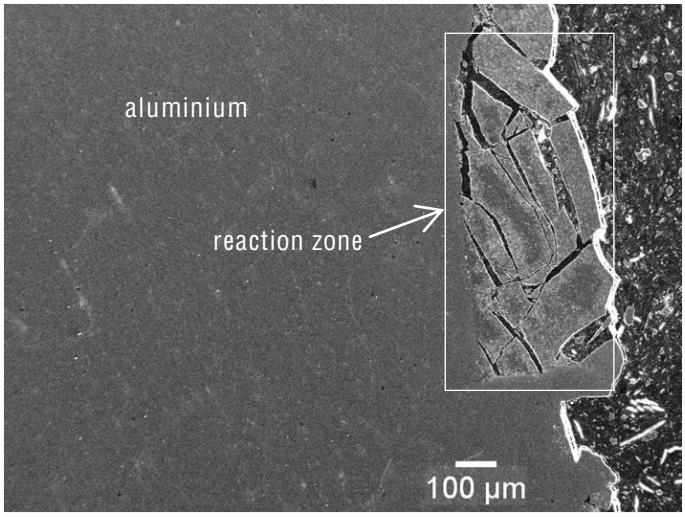

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Figure

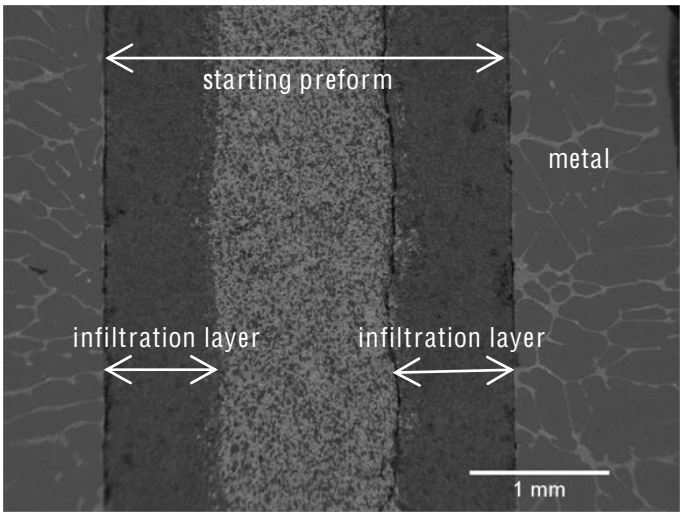
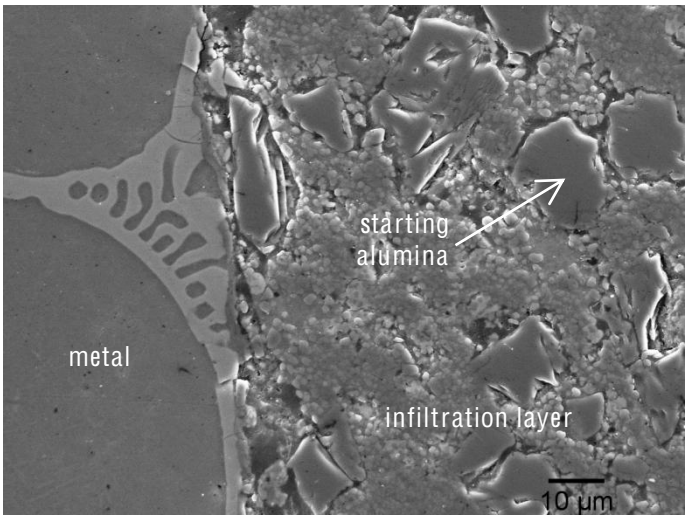


Figure 5. Low magnification BEI of infiltrated sample (1000 ºC, $pO_2 = 4x10^{-7}$ atm).

Figure



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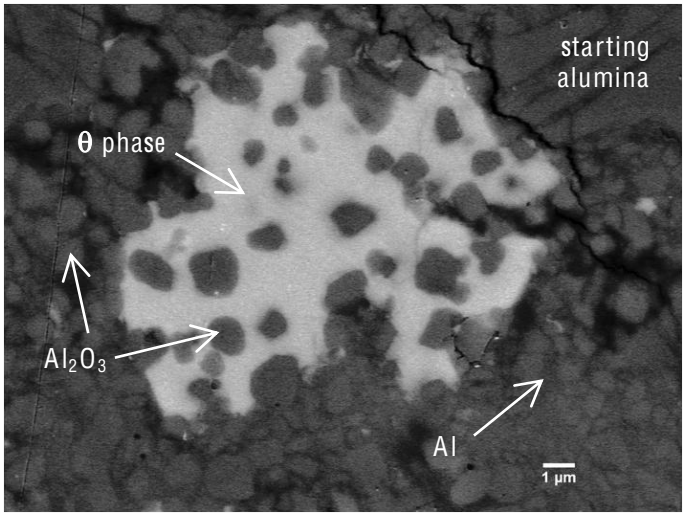

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Figure

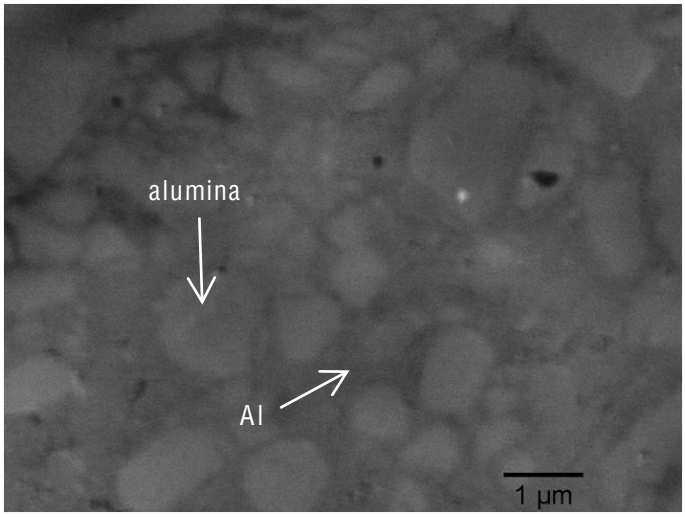

Figure 8. BEI of infiltrated sample (1000 ºC, $pO_2 = 4x10^{-7}$ atm): detail of formed alumina particles dispersed in Al matrix.