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Transmission electron microscopy observations on phase transformations during aluminium/mullite composites formation by gas pressure infiltration

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ABSTRACT

The porous ceramic preforms were manufactured using the powder metallurgy technique. First, the start-up material (halloysite with the addition of carbon fibres as the pore-forming agent) was slowly heated to 800 °C and then sintered at 1300 °C. Degradation of the carbon fibres enabled the open canals to form. At the end of the sintering process, the porous ceramic material consisting mainly of two phases (mullite and cristobalite) was formed, without any residual carbon content. During infiltration, the liquid metal filled the empty spaces (pores) effectively and formed the three-dimensional network of metal in the ceramic. The cristobalite was almost entirely decomposed. In the areas of its previous occurrence, there are new pores, only in the ceramic grains. The mullite, which was formed from halloysite during annealing, crystallized in the *Pbam* orthorhombic space group, with the ($3Al_2O_3 \cdot 2SiO_2$) stoichiometric composition. The mullite structure does not change during the infiltration. The composite components are tightly connected. A transition zone between the ceramics and the metal, having the thickness of about 200 nm, was formed. The nanocrystalline zone, identified as γ-Al_2O_3, was formed by diffusing the product of the cristobalite decomposition into the aluminium alloy matrix. There is an additional, new phase, identified as $(Mg,Si)Al_2O_4$ in the outer parts of the transition zone.

1. Introduction

Mullite is one of the most important ceramic materials. Because of the formation conditions (high temperature, low pressure), it is rarely formed in natural conditions. Nevertheless, its importance in traditional and advanced ceramics (including electronic, optical, and high-temperature structural applications) is huge and is still increasing [1,2]. Mullite consists of many phases, which differ in aluminium, oxygen and silicon content [3]. The general composition of mullite can be collectively described as $Al_{4+2x}Si_{2-2x}O_{10-x}$ $(0 < x \leq 1)$ [4]. The first of this group is sillimanite Al_2SiO_5, for which $x = 0$. The structure of all mullite phases can be described as modified sillimanite where aluminium atoms are exchanged for silicon atoms while overall charge neutrality is maintained [5]. The charge neutrality condition causes part of the oxygen atoms to be removed, and vacancies appear in these places. The parameter x gives the number of oxygen vacancies per unit cell. Theoretically, all mullite compositions with x between zero and one are possible, but so far only phases with x between 0.2 and 0.9 have been observed [6]. Most frequently described are [7,8]:

a. "Sinter-mullite" with stoichiometric composition ($3Al_2O_3 \cdot 2SiO_2$) obtained as a result of heat treatment, typically via solid-state reactions. In this case $x = 0.25$ corresponding to about 72 wt.% of Al_2O_3,
b. "Chemical-mullite", also obtained as a result of heat treatment but with no stoichiometric composition. Composition of these mullites strongly depends on the starting materials and the temperature treatment,
c. "Fused-mullite" ($2Al_2O_3 \cdot SiO_2$) produced by crystallizing aluminosilicate melts. In this case $x = 0.40$ corresponding to about 78 wt.% Al_2O_3.

The structure and chemical composition change depending on the process formation temperature and velocity. The mechanical properties and electronic structures of mullite can be calculated based on its structural models [9]. Therefore, the knowledge and understanding of mullite are so much important. Nevertheless, the structure and chemical composition change depending on the process formation temperature and velocity. All mullites are crystalline in the orthorhombic space group *Pbam* [10,11] and do not transform to a tetragonal form [12]. If mullites are obtained from homogenous, powdered precursors in low temperatures (below 1200 °C), mullite with high Al_2O_3 (70 mol% Al_2O_3) forms first and without regard to the initial material composition. Mullite crystals formed this way have an *a* lattice close to the *b* lattice ("mullite with pseudo-tetragonal metric") [13,14]. The degree of diversification between *a*

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and *b* can be rated by analysis of the shape of the X-ray diffraction (XRD) reflex that appears at the angle of about $2\theta \approx 26°$ (for CuKα radiation). For $a = b$, it should be a single, symmetrical reflex. The larger the difference between *a* and *b*, the more asymmetric it becomes, and finally it splits into two separate reflections: (120) and (210), corresponding to two interplanar distances ($d_{120} = 0.3428$ nm, $d_{210} = 0.3390$ nm) [15]. Incorporation of SiO_2 into the mullite structure causes differentiation in the lattice sizes and a corresponding structure change.

Mullite can be used in one of the following forms: monolith mullite ceramics, mullite coatings and mullite matrix in composites. In particular, investigations in the field of mullite composites have been intensively conducted in the last two decades. The main aim of this research focused on improving the toughness. Despite previous intense efforts, no significant breakthrough has been achieved. The unresolved problem is the inhomogeneous dispersion of mullite grains in the metal matrix. A new, promising approach is the application of mullite in the form of continuous fibres or three-dimensional skeletons (preforms), which are then filled with molten metal, usually aluminium or its alloys [1,16].

A successful example of that approach is the obtaining of a three-dimensional network of metal in the ceramic [17]. In this case, porous ceramic preforms were manufactured using a powder metallurgy technique. The start-up material, halloysite powder (delivered by NaturalNano) with the addition of 30 wt % carbon fibres (SGL Carbon Group) as a pore-forming agent, was subjected to dry mixing in a Fritsch Pulverisette 6 ball mill for 10 min. The prepared powder mixture was compacted in a steel die with an inside diameter of 30 mm on a LabEcon600 platen press at 100 MPa pressure and then sintered at 1300 °C (heating rate ~2.5 K/min). Thermal degradation of the carbon fibres facilitated the formation of open porosity. Sintering of nanotubular halloysite up to 1300 °C induces the formation of a mullite phase [18]. At the end of the sintering process, porous crystalline mullite was formed without any residual carbon content. In order to fabricate the composite materials reinforced by the previously prepared porous preforms, the gas pressure infiltration technique was used. The infiltration process was performed in a specially designed autoclave [19]. The AlSi12 alloy was heated to 800 °C in silicon carbide crucible. The molten aluminium alloy was infiltrated into the pores of the preform under the influence of nitrogen pressure (3 MPa for 30 s). As a result, the infiltrated composite characterized by a very homogeneous distribution of the mullite phase and the absence of unfilled pores was obtained. A detailed description of the process mentioned above was presented in [17]. The critical significance of the interfacial properties of the composite components on the essential properties of the composite causes their recognition and understanding to be of the paramount importance [20]. The aim of the present paper is to investigate the phase-transformation process during the infiltration of aluminium into porous mullite preforms.

2. Experimental procedure

2.1. Samples preparation

During the investigations, the structures of ceramic (mullite) preform before and after infiltration were compared. The ceramic preform was sintered at a temperature of 1300 °C. Its white colour confirms thermal decomposition of the carbon fibres. The preform hardness was 22 HRF. The bulk density of the preform was 1.32 g/cm^3. The volume fraction of the pores was equal to 55.9%; the volume fraction of mullite 44.1% (accordance with Archimedes' principle). The composite material was obtained as a result of infiltration when liquid AlSi12 aluminium alloy filled the pores in the ceramic preform. After infiltration, the colour of the preform changed to metallic, and its hardness increased five times up to a value of about 111 HRF.

2.2. Characterization

The ceramic preform and composite samples were characterized using the XRD (PANalytical X'Pert Diffractometer PW 3040/60 equipped with Cu-Kα radiation ($\lambda = 0.15406$ nm) in Bragg–Brentano geometry). The preform sample for the transmission electron microscopy (TEM) study was prepared by crushing in an agate mortar and dispersing ethanol suspensions of the obtained powder onto lacy carbon-coated copper grids. The composite sample was prepared by the focused ion-beam milling and in-situ lift-out. TEM investigations were undertaken with a field-emission transmission electron microscope (FEI Titan 80–300 TEM/STEM) with a super twin lens operated at 300 kV and equipped with an annular dark-field detector. The chemical composition was determined in the same apparatus using energy dispersive spectroscopy (EDS). Information about the structure of the investigated materials came from the database maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada [21]. The Eje-Z program, available on the University of Cádiz (Spain) server, http://www2.uca.es/dept/cmat_qinor/catalisis/tem-uca-server.htm, was used for phase identification by nano diffraction, and fast Fourier transform (FFT) obtained for the high-resolution images, [22].

3. Results and discussion

3.1. XRD analysis

Comparison of the X-ray diffractograms of the ceramic preform and composite sample obtained by aluminium infiltration is given in Fig. 1a.

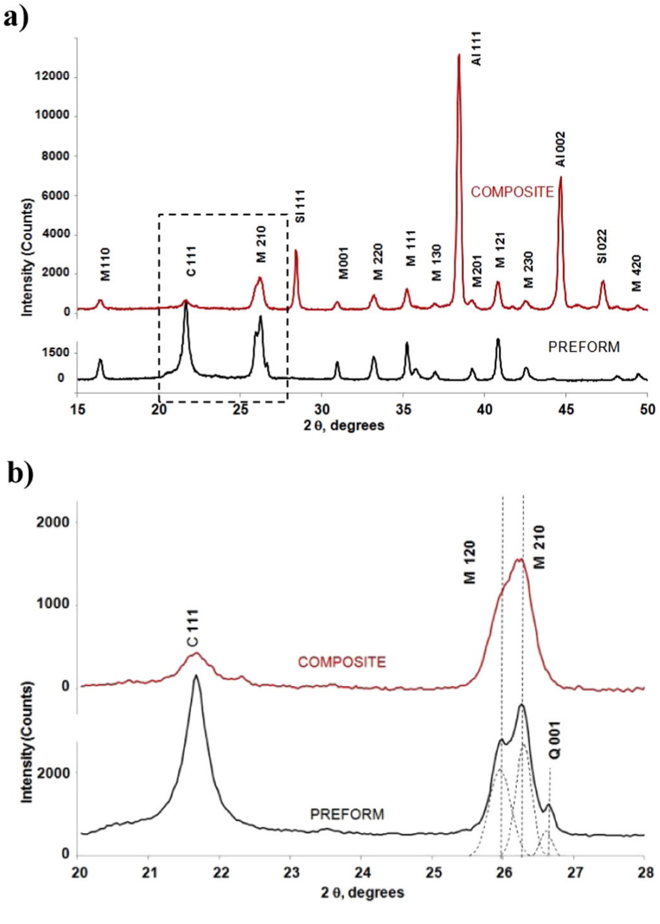

Fig. 1. (a) X-ray patterns of the ceramic preform (PREFORM) and composite sample after infiltration (COMPOSITE). (b) Magnification of part of the image from Figure (a). Description: C — cristobalite high, M — mullite, Al — aluminium, Si — silicon, Q – quartz.