Preparation and properties of Al₂O₃/Al in-situ composites by reactive melt penetration

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Al₂O₃/Al ceramic matrix in-situ composites were prepared by reacting vitreous silica, mullite, or fireclay preforms with molten aluminium. Microstructure of the composites was found to consist of a network of aluminium channels embedded in the ceramic matrix. Properties of the composites like density, hardness, and fracture toughness were determined. Composites made from vitreous silica exhibited low hardness, relatively easy machinability and improved fracture toughness. The process is suitable for producing net-shape or near net-shape composites.

Ceramic matrix composites consisting of WC particles and cobalt have long been in vogue. Addition of the metallic phase greatly improves the toughness, and the composites are produced by consolidation of blended powders. In-situ processes involving a chemical reaction to produce one of the phases of the composite offer several benefits like thermodynamic compatibility of the phases, uncontaminated interfaces, control of particle size and their uniform distribution. Recently, Al₂O₃/Al composites were produced by the directed metal oxidation (DIMOX) process. This involves oxidation of molten aluminium or its alloys at high temperature, > 900°C. At such high temperatures, a layer of Al₂O₃ grows continuously on the surface of molten metal, and channels of aluminium are embedded in it. Another new and promising process for in-situ preparation of Al₂O₃/Al composites involves the use of the well-known reaction between molten Al and several oxides. On account of the very high stability of Al₂O₃, most of the other oxides are reduced to their respective elements by aluminium when heated to the appropriate temperature. Though these reactions are well-known, their exploitation to develop near net-shape composites is of recent origin. Silica, SiO₂, on account of its great abundance and low cost, is eminently suited for producing the composites. Brondyk investigated reaction between molten aluminium and fireclay refractory of the melting furnace, as far back as 1953. Later, Gani et al., studied the reaction of aluminium coated on the surface of silica fibers in order to understand the brittleness induced on heating. They determined the activation energy for the reaction to be about 42 kcal/mole. Standage and Gani investigated the reaction of amorphous silica with molten aluminium and some aluminium alloys and observed an incubation period before the start of the reaction. Praboriputalaoong et al. carried out the reaction in vacuum and observed a drastic increase in the rate of the reaction. Reaction synthesis of Al₂O₃/Al composites from amorphous silica was first reported by Matsuo and Inaba, and then by Breslin et al. The latter proposed that, due to differences in the molar volumes of silica and aluminium, cracks form in the product oxide through which molten aluminium would flow to the reaction front continuously. Loehman et al. proposed the use of mullite preforms for preparing the composites and Gao et al., based on TEM studies concluded that the reaction between mullite preforms and molten aluminium starts at the grain boundaries. The effect of different partial pressures of oxygen, p(O₂), was investigated by Saiz et al., and the reaction rate was found to be independent of p(O₂) values in the range 10⁻¹⁰ to 10⁻²⁰ atm. They also found that the rate of reaction was controlled by silicon diffusion out of the preform. Fahrenholtz et al., reacted mullite with molten aluminium in air, p(O₂) = 0.21 atm., and noted that the rate of reaction increased in the temperature range 900 - 1150°C, and decreased beyond that. In the case of SiO₂, Saiz et al., found a continuous increase in the reaction rate up to 1200°C. They also studied the effect of porosity of the preform and concluded that a higher temperature would be required for infiltration than for reaction. In this paper, the preparation and properties of near net-shape in-situ Al₂O₃/Al composites using vitreous silica, mullite, and fireclay preforms are presented.

Experimental Procedure

The preforms used in this investigation consisted of (i) fireclay brick samples (indegenous), (52.6% SiO₂-41.4% Al₂O₃-1.3% Fe₂O₃-1.5% CaO-3.2% others)
(ii) commercial vitreous silica rods (Vitrosil, England), (iii) mullite tube (Morgon, England). Aluminium of commercial purity containing about 0.2% of iron and silicon as impurity was used. The reaction was carried out in a resistance furnace maintained at 900°C, in ambient atmosphere. Both alumina and Al₂O₃/Al composite crucibles made by the in-situ process from mullite or fireclay preforms were used. When the molten metal was at the required temperature, the samples of 0.6 cm diameter and 5.0 cm long silica rods, or 2.3 cm o.d. 2.0 cm i.d., and 3.0 cm long mullite tube, or 2.0 × 1.0 × 0.5 cm porous fireclay brick samples, as the case may be, were preheated to the temperature of the melt and immersed into it with the help of a graphite rod. The furnace was kept covered, and after a reaction time of 16 to 24 h, the samples were taken out, cooled to room temperature, and any excess aluminium sticking to the surface was removed by careful grinding on an emery belt. A large excess of aluminium was taken in the reaction crucible to ensure that all the Si produced in the reaction would remain dissolved in molten Al. (Preforms weighing 3 to 5 g were immersed in 350 g of molten Al). Samples of the composites were polished in the conventional manner for microscopic examination. Densities of the samples were determined by the Archimedean principle. Hardness of the samples was determined with the help of a Vicker's hardness tester and fracture toughness was determined by the indentation method. The values reported are the average of three tests. Phases present in the composites were determined by means of XRD using filtered Co radiation.

Results and Discussion

Samples of the composites were dark gray in colour. XRD patterns of the composites made from the three different preform materials were similar and only α-Al₂O₃ and Al could be detected. A representative XRD pattern of the composite made from amorphous silica rod is shown in Fig. 1. The near net-shape composites prepared from the preform materials are shown in Fig. 2. No apparent change in the size or shape of the composites, from the preform could be detected. However, from volume measurements of the samples a contraction of 2% was detected in the case of composites made from silica. A small volume expansion of 0.5% was observed in the case of the composites made from mullite. These values are similar to those reported in the literature.

\[ 3 \text{SiO}_2 + 4 \text{Al} = 2 \text{Al}_2\text{O}_3 + 3 \text{Si} \]  
...(1)

\[ \text{Si} + \text{Al} = \text{Al}_2\text{Si} \]  
...(2)

When a preform containing silica is immersed in molten aluminium the formation of the composite is governed by the following reactions:

\[ 3 \text{SiO}_2 + 4 \text{Al} = 2 \text{Al}_2\text{O}_3 + 3 \text{Si} \]  
...(1)

\[ \text{Si} + \text{Al} = \text{Al}_2\text{Si} \]  
...(2)
The second reaction takes place when an excess of aluminium is used in the reaction vessel and represents the dissolution of silicon in molten aluminium to form the alloy. The free energy change accompanying the above two reactions is negative and is of the order of about \(-500\) kJ/mol and \(-25\) kJ/mol respectively, at 900°C. So, when a silica rod is dipped in molten aluminium at 900°C, the surface. Now for further progress of the reaction, a fresh supply of molten Al has to be maintained at the reaction front and silicon produced has to be removed from there. Unhindered progress of the reaction is made possible by the porous nature of the alumina formed. Breslin et al\(^6\), suggested that, on account of the large difference in the molar volumes of the two oxides, SiO\(_2\) and Al\(_2\)O\(_3\), cracks form in the latter through which molten Al is transported to the reaction front continuously. Further, Si produced in the reaction readily dissolves in molten Al on account of its high solubility and diffuses away from the reaction front into the bulk of the metal bath due to the large concentration gradient. The average rate of reaction, as determined by the thickness of the Al\(_2\)O\(_3\) layer formed per hour, was found to be 0.2 mm/h and 0.3 mm/h for the silica and mullite preforms respectively. The values are comparable to the penetration rate of 0.53 mm/h reported by Fahrenholz et al\(^9\), for mullite, at 1000°C, and under ultra-high purity argon atmosphere. During the course of the study it was found that the start of the reaction was preceded by an incubation period, as also noted by Standage et al\(^7\). And resulted in a lower value of the penetration rate. The reaction times for the experimental preforms were the highest, 24 h for fireclay and the lowest, 16 h for silica. It may be noted that when different preform materials like fireclay, silica and mullite are used, even though their actual compositions are different, the basic reactions and the principles of composite formation are the same.

The general features of the microstructure of the composites produced from the different preform materials were the same, and consisted of a uniform distribution of Al in the ceramic matrix, as shown in Fig. 3a. Gao et al\(^11\), reported that the composites contain about 1.0 wt % Si dissolved in the aluminium phase. In the experimental composites Si particles could not be detected, by optical microscopy or XRD. The solid solubility of Si in Al is 1.65 wt% at 577°C and 0.01 wt % at 277°C\(^17\). A large excess of Al was taken in the reaction crucible so that, at the end of the experiment the composition of the molten metal would not exceed about 1 wt % Si. In the case of composites made from fireclay preforms some microstructural in homogeneity was observed, as shown in Fig. 3b. By XRD, the fireclay was found to consist of free silica, \(\alpha\)-Al\(_2\)O\(_3\) and Mullite. Therefore, the Al-free regions can be attributed to the presence of Al\(_2\)O\(_3\) in the fireclay, which does not participate in the chemical reaction. Though such in-homogeneity will not be desirable for some critical applications, crucibles of Al\(_2\)O\(_3\)/Al composites prepared from fireclay preforms have been used in experiments lasting up to 1000 h, at high temperature, about 900°C, and involving several heating/cooling cycles.

The amount of aluminium incorporated in the composite can be determined from the densities of the phases, Al\(_2\)O\(_3\) and Al. From Eq. (1) representing the chemical reaction controlling the formation of the composite, it can be deduced that 1.0 g of silica on reacting with molten Al will form 1.131 g of Al\(_2\)O\(_3\). So, by considering the weights of the preform and composite the weight of Al and hence its volume fraction can be determined. For the composite made from silica, the value so obtained was 0.31. The volume fraction of Al in the composite can also be calculated by considering the molar volumes of the phases involved in the reaction. Assuming no change in size occurs (net-size product), from Eq. (3),

$$3V_{\text{SiO}_2}^m = (2V_{\text{Al}_2\text{O}_3}^m + XV_{\text{Al}}^m)$$

On this basis the volume fraction of Al in the composite was found to be 0.38. Further, applying simple rule of mixtures the density of the composite was calculated to be 3.49 g/cc and compares well with the value of 3.36 g/cc reported by Ewsuk et al\(^5\), for a composite containing 30 vol% Al. Properties of the experimental composites are given in Table 1.

Addition of a soft phase, Al, to alumina will reduce

![Figure 3](image-url)
Table I—Properties of experimental Al2O3/Al in-situ composites

<table>
<thead>
<tr>
<th>Property</th>
<th>A*</th>
<th>B*</th>
<th>Ref. (15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. %, Al</td>
<td>31</td>
<td>25 - 35</td>
<td>30</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>3.38</td>
<td>2.98</td>
<td>3.36</td>
</tr>
<tr>
<td>Hardness, VHN GPa.</td>
<td>2.9 ± 0.5</td>
<td>4.6 ± 1.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>8 - 10</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>VPN, GPa.</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A* - made from vitreous silica preforms.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B* - made from fireclay preforms.</td>
<td></td>
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<td></td>
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<tr>
<td>* - some porosity was observed in the samples.</td>
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the latter's mechanical properties like Young's modulus, hardness, bend strength, etc. but will increase its toughness. In the present investigation Vicker's hardness \( H_v = 1.854 \frac{P}{d^2} \), where \( P \) is the applied load and \( d \) is the diagonal of the indentation was used to assess the effect of Al in the composite. The hardness of the experimental composites made from silica preforms was found to be 2.9 ± 0.5 GPa, compared to the value of about 15.7 GPa for pure Al2O3. The low value of hardness and consequent high machinability of composites was realized from the ease of grinding and polishing during specimen preparation for microscopy. The experimental value is much lower than that reported by Ewsuk et al.\(^6\), for a composite containing 30 vol. % Al, viz., 7.5 GPa. The reason for the low value of hardness of the experimental composite is not clear. The microstructural in-homogeneity of the composites made from fireclay preforma was reflected in their mechanical properties. The hardness values exhibited large variations, from about 2.7 GPa to about 7 GPa, the average value being 4.7 ± 1.7 GPa. Vicker's hardness testing was also employed for determining the fracture toughness of the composites using the relationship proposed by Shetty et al.\(^1,8,15\) and was found to be 8 to 10 MPam\(^{1/2}\). In the case of the composites made from mullite preforms, the mechanical properties were not determined as the samples were in the form of tubes.

Conclusion

The present investigation has shown that near-net-shape Al2O3/Al composites can be easily prepared by using fireclay, vitreous silica, and mullite, preforms and molten aluminium of commercial purity, in air. Among the three different preform materials used vitreous silica gave best results. Composites made from fireclay bricks exhibited non-uniform microstructure and properties. In-situ composite made from vitreous silica exhibit low hardness and good machinability and toughness.

References