Preparation of functionally graded mullite-zirconia composite using electrophoretic deposition (EPD)

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Abstract: The mechanical properties such as hardness and especially fracture toughness of present structural ceramics are not enough to permit design of high performance products. It is generally believed that further improvement of fracture toughness and hardness is only possible by making composites of ceramics with ceramic fiber. The wide-spread use of mullite–zirconia (MZ) composites is due to the fact that the zirconia dispersion in the mullite matrix improves the thermo-mechanical properties. The preparation process to produce the composite sample using electrophoretic deposition (EPD) which deals with three types of powder: \(\alpha\)-alumina, silica and zirconia, mixed with the suspension based on 2-butanone, n-butylamine and polyvinyl butyral (PVB). Hardness and fracture toughness were measured using indentation methods on cross sections of the sample with applying two loads: 5kg and 10kg. Electron microscopy analysis (SEM) and X-ray diffraction (XRD) tests were used to examine the microstructure, composition and crystallization behavior of the deposits. The results were compared with mullite matrix properties to detect the enhancement in mechanical properties.

Key–Words: Electrophoretic deposition, ceramic matrix composites, mullite, zirconia, functionally graded material, mechanical properties

1 Introduction

During the last 25 years, tremendous progress has been made in the development and advancement of CMCs (ceramic matrix composites) under various research programs. CMCs find applications in advanced aerojet engines, stationary gas turbines for electrical power generation, heat exchangers, hot gas filters, radiant burners, heat treatment and materials growth furnaces, nuclear fusion reactors, automobiles, biological implants [1]. Mullite is one of the basic ceramic materials traditionally used for refractories and is considered an attractive selection for many industrial applications because of its high temperature mechanical properties. For the development of the structural materials, mullite has been delayed since it has a low fracture toughness and relatively low strength at room temperature compared with other engineering ceramics.

The extensive use of mullite/zirconia composites is due to the fact that the zirconia dispersion in the mullite matrix improves the thermo-mechanical properties, leading to toughness by transformation and microcracking[2].

Mullite/zirconia composites can be prepared using various methods: (1) Sintering of mullite powder and zirconia powder (2) Reaction sintering of alumina and zircon powders (3) Reaction sintering of alumina, silica and zirconia powders [2–3].

It has been reported that the optimum content of zirconia is \(\approx 15\) wt%[4].

In this research the third method was used and the fracture toughness and hardness are improved when zirconia reinforced mullite matrix using EPD technique to fabricate the composite sample.

2 Experimental

2.1 Materials

Commercially available (\(\text{SiO}_2\), 99.9% purity, Aldrich Chemical Company Inc., USA) and \(\alpha\)-\(\text{Al}_2\text{O}_3\) (99.95% purity, Alfa Aesar Chemical Company Inc, USA) powders were used as the starting materials representing the composition of mullite (\(3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\)) and \(\text{ZrO}_2\) (99.5% purity, Alidrich chemical company Inc, USA). 2-butanone (96% purity-Ajax), n-butylamine and PVB form the suspension medium.
2.2 Suspension preparation

A total of 50g of mullite (α-Al₂O₃/SiO₂) with 60wt% for α-Al₂O₃, 40wt% for SiO₂ and 10g ZrO₂ were prepared for the sample. These three powders were separately milled for 24h in a planetary ball mill at 200rpm using zircoia balls with 10mm diameter as milling media with a ball to powder ratio of 5:1. Subsequently, the powders were milled horizontally in ethanol for 24h using the same balls to break up hard agglomerates. The ethanol was evaporated in an oven at 90°C for 48h, then the powders were placed in a drying cabinet at 25°C.

The present study used non-aqueous EPD which uses organic solvents which normally are less polar than water. A basic requirement for EPD is that suspended particles must have a high electrophoretic mobility that can be increased by adding dispersants, so n-butylamine was used as dispersant in this suspension, and polyvinylbutyral (PVB) as a binder. The suspension system used technical grade 2-butanone, n-butylamine and PVB as suspension medium. n-butylamine was used to disperse the metal oxide powders in 2-butanone and PVB.

The mixing proportion is 10g of powder per 100mL in the ratio of 60wt% for α-Al₂O₃ and 40wt% for SiO₂. All weight percentages of additives are taken from total powder weight. 2wt% of PVB was added as well as 10vol% of n-butylamine. PVB was first dissolved in 40mL of 2-butanone and then added to the main suspension.

Three suspensions were prepared and mixed with the powders that were prepared previously in a glass container by a magnetic stirrer for 24 hour, and then the pH value was measured by a pH meter for each suspension. The suspensions were then put in glass containers and placed in an ultrasonic cleaning bath with a frequency of about 15kHz to 45kHz for 30min. Table 1 indicates the suspension compositions.

2.3 Electrophoretic deposition and sintering

EPD is one of the colloidal processes that is used in ceramic production with many advantages: short formation time, simple equipment and the process can be applied to any shape depending on the electrode shape such as cylinder, spherical and flat plates.

The parameters affecting EPD, can be classified in two types, firstly those related to the suspension properties such as electrical conductivity, pH, particle size and size distribution, binder and dispersant concentration and ζ-potential, and secondly the parameters that relate to the EPD process, such as deposition time, the applied voltage, size and shape of the electrode and the distance between the electrodes.

The EPD cell in this study was described in [5] and consisted of two stainless steel electrodes with a surface area of 10cm² (5.25cm × 1.923cm) and a thickness of 0.5cm. The surfaces of the deposition electrodes were polished to facilitate the removal of the deposit and to avoid cracking of the deposit during drying. Furthermore, the edges of the deposition electrode were enclosed by tape in order to avoid deposition around the edges of the electrode. The electrodes were cleaned with acetone then vertically placed in a polytetrafluoroethylene (PTFE) vessel. PTFE was used in order to avoid deposition between suspension and vessel as PTFE is a non-conductive polymer. The PTFE container had a volume of 100mL. The distance between the electrodes was fixed at 3cm.

A DC voltage source, Apparatus Corporation, was used to apply the electric field. The source was capable of performing either as a constant current or as a constant voltage source. A voltage of 275V was applied for 30min. The suspensions were pumped through the deposition cell by peristaltic pumps. Peristaltic tubing with a diameter of 4mm was used for the circulation system. The maximum and minimum feed rates were 4.25mLs⁻¹ and 0.12mLs⁻¹, respectively.

The total deposition time for composite material was 30min. A magnetic stirrer was used to mix the suspension during all EPD steps. Initially suspension I, loaded with 100gL⁻¹ mullite (silica and alumina), was poured in the deposition cell and circulating process continued between the deposition cell and the circulating beaker using pump 1 for 600s, and then suspension II with 50gL⁻¹ mullite and 50gL⁻¹ ZrO₂ was added into the beaker of circulating suspension using pump 2 and was pumped through the deposition cell by means of pump 1 at a rate of 2.5mLs⁻¹. The pump rate between deposition cell and circulating suspension was fixed throughout the deposition process.

<table>
<thead>
<tr>
<th>suspension</th>
<th>Mullite (g)</th>
<th>ZrO₂</th>
<th>2-butanone (mL)</th>
<th>n-butylamine (mL)</th>
<th>PVB (g)</th>
<th>pH at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>12</td>
<td>8</td>
<td>0</td>
<td>180</td>
<td>20</td>
<td>0.4</td>
</tr>
<tr>
<td>II</td>
<td>6</td>
<td>4</td>
<td>10</td>
<td>180</td>
<td>20</td>
<td>0.4</td>
</tr>
<tr>
<td>III</td>
<td>12</td>
<td>8</td>
<td>0</td>
<td>180</td>
<td>20</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 1: Compositions for 200mL suspension
After 1200s of deposition, suspension III, with 100 g L\(^{-1}\) mullite was added to the circulating suspension by pump 2 at a rate of 0.4 mL s\(^{-1}\). After 300s of deposition, the addition of the suspension was completed. During the subsequent step, the suspension was circulated for 300s without any future additions, and during all the described steps, EPD was continued in the deposition cell. The powder deposits took place on the anode electrode due to the negative charge of the particles.

After EPD, the green bodies were dried in air for 48h. Afterwards, the powder deposits were removed from the electrode. The green bodies were dried in an oven at 100°C for 12h in order to avoid cracking and preparation for sintering. The two main factors affecting sintering are sintering temperature and time. Pure oxide ceramics require relatively long time and high temperature because the diffusion proceeds in solid state. The green bodies obtained by the EPD were sintered in a chamber furnace, after the sample had dried; the sintering process took place at 1500°C for 2h. Fig. 1 shows the sample after EPD.

![Sample after EPD](image)

Figure 1: The sample after EPD

To provide time for the binder to burn out, the sample was heated at 3°C min\(^{-1}\) to 500°C, held at 500°C for 30min and then heated to the final sintering temperature at a rate of 5°C min\(^{-1}\) and held at 1500°C for 2h and furnace cooled. To avoid and minimize the damage to the samples during sintering, the samples were placed on an alumina crucible. Length and width of sample were measured before and after sintering to determine linear shrinkage.

### 2.4 Preparation of samples

The sintered samples were cross-sectioned on a diamond cutter using sufficient flow of non-oily coolant. The surfaces of the sintered samples were ground with emery paper of 400, 600, 800, 1200 and 1500 grit and polished to a near mirror finish. The ground samples were polished with cotton to reduce scratches on the surface, and to make a mirror surface finish with minimum scratches. After grinding and polishing, the samples were thermally etched at 1350°C for 30min.

Finally, the samples were moulded in epoxy to allow easier handling during the hardness tests.

### 2.5 Hardness and toughness test

The Vickers hardness was determined on a Mitutoyo, AVK-C2. The test force is maintained for 15s and 5kg and 10kg loads were applied by the indenter to the sample’s cross-sectioned surface to obtain a hardness profile.

The indentation fracture toughness, \(K_{\text{IC}}\) was calculated from the length of the cracks induced by the same indent using the Anstis formula, as shown in eq. 1[6].

\[
K_{\text{IC}} = \eta \sqrt{ \frac{E}{H} } \frac{F}{C^2} \tag{1}
\]

Where \(\eta\) is a geometric factor, estimated at 0.016, \(E\) the Young’s modulus, \(H\) is the hardness, \(F\) is the indentation load, and \(C\) is the indentation radial crack half length of the cracks parallel to the layers at the surface. Since the \(E\) value for the composite is not known \(\eta \sqrt{ \frac{E}{H} }\) is estimated to be 0.062 which is a suitable value for mullite ceramics.

### 3 Results and Discussion

#### 3.1 Density and porosity

The sample deposit was smooth and an approximately flat surface was obtained. Exactly how roughness is affected by the suspension stability is unclear but one can assume that the convective motion, powder amounts and applied voltage play important roles. The dimension of the green deposit and shrinkage of the deposit with dimensions after sintering are shown in Table 2.

It is observed that the shrinkage perpendicular to the deposition surface is significantly higher than parallel to the deposition surface.

Density measurements were taken according to the Archimedes method. The result is shown in Table 3. The porosity may be caused by exaggerated grain growth.
Table 2: Dimensions and shrinkage of the deposits before and after sintering

<table>
<thead>
<tr>
<th></th>
<th>Green (mm)</th>
<th>Sintered (mm)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>32.25</td>
<td>30.45</td>
<td>5.6</td>
</tr>
<tr>
<td>width</td>
<td>30.62</td>
<td>29.28</td>
<td>4.4</td>
</tr>
<tr>
<td>thickness</td>
<td>8.18</td>
<td>7.15</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Table 3: Theoretical and sintered density and open porosity of the sample.

<table>
<thead>
<tr>
<th>Theoretical density (g cm(^{-3}))</th>
<th>Sintered density (g cm(^{-3}))</th>
<th>Open porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.50</td>
<td>3.067</td>
<td>12.4</td>
</tr>
</tbody>
</table>

The level of porosity would decrease with increasing sintering temperature, but this might also lead to cracking due to the mismatch in coefficients of thermal expansion between the constituents of the composite. The porosity and the grain size affect hardness and fracture toughness of the product.

3.2 Microstructure

The microstructures of the sample were analysed on SEM. Mullite phase commences to appear in temperature range 1400°C to 1500°C during sintering process[7] when alumina (Al\(_2\)O\(_3\)) and silica (SiO\(_2\)) powders combine in solid state reaction to form mullite phase. The microstructure was observed after thermal etching.

A highly porous microstructure with small pores homogeneously distributed was observed after sintering at 1500°C, due to the diffusion processes in zirconia, silica, and alumina grains. Sintering at 1500°C produced important changes in the microstructure. A dense matrix composed of grey and black areas (mullite and alumina, respectively) in zone (A), white grains (tetragonal zirconia) were observed in zone (B), mullite grains were well developed in the dense matrix and some of grains showed a change from rounded to slightly elongated shape and it was difficult to detect zirconia grain boundaries in zone (C). The SEM images show that some microcracks appear clearly due to the difference in average particles size, 0.3μm, 0.5μm and 0.5μm for alumina, silica and zirconia respectively and the mismatch of the coefficient of thermal expansion. The porosity is observed while two types of grains were noticeable dispersed grains (white) of zirconia, and a mullite matrix (gray) in zone (D) as indicated in Fig. 2.

3.3 XRD

XRD analysis showed that the formation of mullite was essentially complete with only traces of residual alumina or silica detected. Furthermore, due to the presence of yttria as well as the containing effect of the matrix on the submicrometer grains, the zirconia was present in the tetragonal phase, which is beneficial for transformation toughening. The addition of zirconia caused rapid mullite formation in the presence of the Y\(_2\)O\(_3\) that is used to stabilise the zirconia [8].

3.4 Hardness and toughness

The hardness and toughness were measured across the cross section at regular intervals. The results are depicted in Figs. 3 and 4 for hardness and toughness, respectively.

As expected the material close to the surfaces was harder than the core material due traces of alumina due to incomplete reaction between alumina with silica to form mullite phase. The alumina traces affect hardness and other mechanical properties of composite, as alumina is harder than zirconia, (\(H_{\text{Al}_2\text{O}_3} = 18\) GPa > \(H_{\text{mullite}} \approx H_{\text{ZrO}_2} = 10\) GPa to 15 GPa) [9]. Besides this, the coefficient of thermal expansion for zirconia is larger than that of mullite (10.3 × 10\(^{-6}\) vs 5.3 × 10\(^{-6}\)), causing the zirconia-rich inner layer to be under tension and the surface layer to be under compression[5]. Therefore in this case the outer layers are more enduring than the inner layer against
wear and stress.

The lowest hardness was found in the core of the sample and was around 11 GPa for both indentation loads. This is slightly lower than the literature value for mullite, perhaps due to porosity or microcracking. The highest measured hardness was 21.3 GPa.

The indentation load is critical in the measure of hardness and fracture toughness using the indentation method. The amount of load could affect the indentation size and the crack length, being dependent of the sample dimension and the microstructure of the material.

The presence of zirconia promoted the densification through a marked reduction in porosity by filling of interparticle voids which was considered to be the important contributor for the increase in strength and $K_{ic}$. The major improvement in $K_{ic}$ in the mullite/zirconia composite is also due to the presence of microcracking and crack-closure compressive strains as a result of transformation toughening. This is because of thermal contraction mismatch between the phases and volume expansion associated with zirconia transformation and mullite formation.

The fracture toughness for the pure components is $K_{ic, Al_2O_3} = 1.5 \text{MPa} \sqrt{\text{m}}$ to $4.5 \text{MPa} \sqrt{\text{m}}$, $K_{ic,mullite} = 2.6 \text{MPa} \sqrt{\text{m}}$ and $K_{ic,ZrO_2} = 14 \text{MPa} \sqrt{\text{m}}$. The highest measured fracture toughness was $5.5 \text{MPa} \sqrt{\text{m}}$, while the lowest value was $3.4 \text{MPa} \sqrt{\text{m}}$. Both are significantly higher than the toughness of pure mullite.

4 Conclusions

A functionally graded zirconia/mullite composite was prepared from alumina, silica and partially stabilised zirconia by EPD with single phase mullite near the surface and composite containing $\approx 15\%$ zirconia in the core.

The formation of mullite from alumina and zirconia was essentially complete, with traces of unreagent alumina increasing the surface hardness to 21.3 GPa whereas the zirconia in the core increased the fracture toughness to $5.5 \text{MPa} \sqrt{\text{m}}$. However, the hardness in the core layer was lower, perhaps due to the occurrence of micro-cracking.

It was found that the measurement of hardness and toughness depends critically on the applied load during testing.

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References:


