Short communication

Effect of V$_2$O$_5$ on the properties of mullite ceramics synthesized from high-aluminum fly ash and bauxite

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1. Introduction

Mullite is a unique family of oxides belonging to the aluminium silicate family. It has an orthorhombic structure, consisting of a three-dimensional framework, with alternate corner-sharing among the [AlO$_4$] octahedra and the [SiO$_4$] (or [AlO$_4$]) tetrahedra [1]. Because of their excellent mechanical properties, high melting points (1830°C), low coefficients of thermal expansion (4.5 × 10$^{-6}$ K$^{-1}$), excellent creep resistance, good chemical stability, and high strength at high temperatures, mullite and mullite ceramics have been widely used in many fields [2,3]. To reduce their cost, many studies have been carried out in their preparation, characterization, and sintering, including their synthesis from various cheaper natural mineral materials, such as kaolinite [4–6], the sillimanite group (sillimanite, andalusite, kyantite) [7–9], staurolite, and topaz [10]. Fly ash is a by-product of coal combustion in thermal power plants and the huge amount of the recovery is a most important economic concern as well as environmental problem, requiring urgent attention [11,12]. Because high-aluminum fly ash contains appreciable amounts of silica and alumina [13], it may be useful in manufacturing mullite ceramics. Until now, there have only been a few reports of the preparation of mullite from fly ash. Huang et al. reported the preparation of mullite using a fly ash and alumina mixture [14]. Jung et al. synthesized yttria-stabilized zirconia (3YSZ)-doped mullite from waste fly ash, Al$_2$O$_3$ powder, and 3YSZ [15]. Dong et al. reported the preparation of low-cost mullite ceramics from natural bauxite and industrial waste fly ash [16]. Park et al. manufactured mullite whiskers by firing compacts of coal fly ash and NH$_4$Al(SO$_4$)$_2$$\cdot$12H$_2$O powder with a small quantity of NaH$_2$PO$_4$$\cdot$2H$_2$O [17]. However, new methods are still being explored with an aim of reducing the sintering temperature and densifying the final mullite products. It has been reported that the addition of V$_2$O$_5$ reduces the temperature of the mullite phase formation in a mixture of Al$_2$O$_3$ and SiO$_2$, whereas Nb$_2$O$_5$ and Ta$_2$O$_5$ inhibit mullitization [18]. A further study indicated that the rare earth element oxides (Y$_2$O$_3$, La$_2$O$_3$, and CeO$_2$) had a positive effect on mullitization behavior and lowered the mullite formation temperature by about 100°C [19]. In this study, we synthesized mullite ceramics from a high-aluminum fly ash and bauxite, and linked the physical properties of the final mullite to the doping content of V$_2$O$_5$.

2. Experimental

Bauxite (no. CB-1) (Al$_2$O$_3$ 88.60, SiO$_2$ 4.91, TiO$_2$ 3.55, other 2.94 [wt%]) and fly ash (no. BF-1) (SiO$_2$ 48.13, TiO$_2$ 1.66, Al$_2$O$_3$ 39.03, Fe$_2$O$_3$ 2.94, FeO 0.77, MgO 1.05, CaO 3.30, Na$_2$O 0.21, K$_2$O 0.69, MnO 0.017, P$_2$O$_5$ 0.63, and loss on ignition 0.90 [wt%]) from Beijing Thermal Power Plant were used as received. A series of 29.9 wt% bauxite was added to 70.1 wt% fly ash to dope it with V$_2$O$_5$ (Beijing Chemical Reagent Ltd., Beijing, China) in a molar ratio of 5 mol% (2.18 wt%), 10 mol% (4.50 wt%), or 20 mol% (9.59 wt%). The mixed powders were ball milled for 2 h. The particle size distribution of the mixture is shown in Fig. 1. The specific surface area of the milled mixture was...
3.73 m² g⁻¹, which is approximately twofold higher than that of the original fly ash. The treated mixture was dried at 105 °C for 12 h, and then pressed into bar compacts (40 mm × 6 mm × 6 mm) with an isostatic pressure of 136 MPa. The compacts were heated to the designated temperatures (1100 °C, 1200 °C, 1300 °C, 1400 °C, and 1500 °C) at a rate of 10 °C/min, and kept at these temperatures for 4 h. All the samples were cooled down naturally.

A procedure defined by the American Society for Testing and Materials (ASTM) C373, based on Archimedes’ principle, was used to calculate the bulk density and apparent porosity of the final mullite specimens [20]. The particle size distribution was determined using a laser particle-size analyzer (Mastersizer 2000, Malvern Corporation, Britain). Water absorption was measured from the percentage increase in weight of “surface dry” samples after they had been submerged in water for 24 h. The bending strength of the rectangular specimens was determined by the three-point bending technique at room temperature on a Reger Universal Testing Machine (Shenzhen, China). The lower span for the bending test was 20 mm and the loading rate was 0.5 mm/min.

3. Results and discussions

Table 1 summarizes the physico-mechanical parameters of the prepared specimens with different content of the V₂O₅ and the sintering temperatures. As expected, an increase in temperature accelerates the bulk densification process. The apparent porosity, and water absorption decreases with the increase of sintering temperatures from 1100 °C to 1500 °C (runs 1–5). At 1500 °C, the apparent porosity, and water absorption decreases with the doping content of V₂O₅ (runs 5–7). It seems that bulk density is not influenced by V₂O₅ at the temperature of 1500 °C and the bulk density remains at 2.7 g cm⁻³ in the content of V₂O₅ 5~20 mol%. According to the formula $D = D_0 \exp(-Q/RT)$ [21], the sintering process is dominated by surface diffusion at low temperatures, and by body diffusion at high temperatures. Only body diffusion influences the densification of the final products. Therefore, temperature is the major element in densifying the final product in this process, however the porosity decreases greatly with V₂O₅ doping at 1500 °C. This indicates V₂O₅ favors the formation of the liquid phase and promotes the sintering process and densification at high firing temperatures.

![Fig. 1. Particle size distribution of the ground mixture of fly ash and bauxite with V₂O₅.](image1)

![Fig. 2. Plot of the mullite content (a) and bending strength (b) versus sintering temperature and V₂O₅ doping content.](image2)

The plot of mullite content versus sintering temperature and V₂O₅ doping content is illustrated in Fig. 2a. The mullite content increases with an increase in the sintering temperature from 1100 °C to 1500 °C. At a same temperature in 1100–1300 °C, the content of mullite increases with the doped V₂O₅, i.e. the highest content of mullite appears in the case of 20 mol% V₂O₅. However, at the sintering temperature of 1400–1500 °C the highest percentage of mullite was found in the product that was prepared with

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>V₂O₅ (mol%)</th>
<th>Bulk density (g cm⁻³)</th>
<th>Apparent porosity (%)</th>
<th>Water absorption (%)</th>
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<td>2</td>
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<td>2.04</td>
<td>32.7</td>
<td>16.0</td>
</tr>
<tr>
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<td>1400</td>
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<td>2.15</td>
<td>28.6</td>
<td>13.3</td>
</tr>
<tr>
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<td>1500</td>
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<td>2.70</td>
<td>4.15</td>
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<td>20</td>
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5 mol% V₂O₅. Fig. 2b illustrates the bending strength at various temperatures and V₂O₅ contents. With a content of 5 mol% V₂O₅, the bending strength increased significantly from 1100 ºC to 1500 ºC, and a reverse of trend in porosity was found in this region. This can be explained by the disappearance of the gas pores, and the stress surrounding the pores was removed at a certain V₂O₅ doping content [22]. The highest bending strength (108 MPa) was achieved at 10 mol% V₂O₅ content. This effect is attributable to the low melting point of V₂O₅ (690 ºC), which enhances the formation of the liquid phase, thus facilitating sintering, although it does not enhance the mechanical strength of the products [23]. However, the anisotropic grain growth of the mullite phase increases its strength as the temperature increases. This effect is similar to that reported by Mechnich et al., whereby microstructural homogeneity was improved and the mechanical properties could be tuned by changing the amounts of doped yttria and ceria [24]. Therefore, the mechanical properties depend on a compromise between these two factors. Here, V₂O₅ accelerated mullite formation through transient and metastable melting, yielding homogeneous and relatively dense ceramics at 1400–1500 ºC.

The microstructures of the samples were recorded by scanning electron microscopy (SEM; JEOL JSM-4300F), and are shown in Fig. 3. In the product sintered at 1100 ºC with 5 mol% V₂O₅, some puncheon-shaped mullites appear among glassy spheres that is attributed to the unreacted fly ash. When the temperature was increased to 1200 ºC, more puncheons were embedded in the vitreous phase and fewer pseudomorph appeared (Fig. 3b) because there is less fly ash in the final product. At 1300 ºC (Fig. 3c), there are relatively better-developed and numerous cubic puncheon-shaped crystals with aspect ratios of 4–6. Fig. 3d shows a larger tetragonal section of the puncheon, with an aspect ratio of about 6 at 1500 ºC, which indicates a higher growth rate at this temperature. According to energy dispersive X-ray spectroscopy analysis (Fig. 3d inset), the calculated formula unit of the mullite product was Al₃.₉₆Fe₀.₁₂Ti₀.₀₈V₀.₀₂Si₁.₈₂O₉.₉₁. When the percentage of V₂O₅ increases to 10 mol% and 20 mol%, mullite crystal grows into longer...
To confirm the phase transition in this process, the samples were analyzed with X-ray diffraction (XRD; X’PERT SW). Peaks of mullite appeared in the sample sintered at 1100 °C with 5 mol% V2O5 (Fig. 4), but the α-Al2O3 and cristobalite peaks were also found. The amorphous background of the profile was derived from the unreacted glass phase of the original fly ash. As the sintering temperature was increased to 1300 °C, all the samples showed complete mullitization. All the diffraction peaks were perfectly indexed to the orthorhombic mullite structure. The mullite lattice constants calculated from the XRD data are given in Table 2, and are larger than those for Joint Committee on Powder Diffraction Standards (JCPDS) no. 15-0776. Taking into account that the incorporation of an octahedral transition metal is associated with the removal of Al3+ from the structure, the entry of cations with varying oxidation states, i.e. V3+ or V4+, results in a reduction in V2O5 by the components of the fly ash and also compensates for the excess positive charge introduced by the impurities in the fly ash and bauxite [25]. The subsequent lattice parameters are larger than those of the original mullite because the radii of V3+ (0.74 Å) and V4+ (0.63 Å) are larger than that of Al3+(0.53 Å).

4. Conclusions

In this research, we produced low-cost mullite ceramics at a relatively low sintering temperature using high-alumina fly ash and bauxite as raw materials. The effects of doping with V2O5 on the properties of the mullite ceramics are described. The apparent porosity and water absorption decreased with an increase in the V2O5 content at 1500 °C. The prepared mullite mainly existed in the shape of long parallelepipeds when doped with V2O5. It underwent a transition from small puncheons to large cuboids with an increase in temperature, until an aspect ratio of about 6 was reached at 1500 °C. Doping with V2O5 enlarges the cell lattice parameters of the mullite, because of the entrance of V3+ or V4+ and the substitution Al3+ in the cells of the mullite. This research should facilitate the utilization of fly-ash waste in the production of highly pure mullite ceramics.

Acknowledgments

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References


Table 2

Calculated lattice parameters of mullite prepared under different conditions.

<table>
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<tr>
<th>Temperature (°C)</th>
<th>V2O5 (mol%)</th>
<th>Laue parameter</th>
<th>α0 (Å)</th>
<th>β0 (Å)</th>
<th>γ0 (Å)</th>
<th>Volume (Å³)</th>
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