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Synthesis and characterization of mullite–zirconia nanostructured composite by combined mechanical activation and reaction sintering

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ABSTRACT

The objective of present study was to produce mullite–zirconia nanostructured composite by mechanical activation of zircon–alumina powder mixture followed by reaction sintering. The results showed that mechanical activation up to 60 h led to no phase change. Complete formation of mullite–zirconia composite was observed after 60 h of mechanical activation and subsequent reaction sintering at 1400 °C for 2 h. This temperature is about 200–250 °C lower than the temperatures commonly used in the reaction sintering of zircon–alumina powder mixture. Density measurements showed that the relative density of green bodies was ~78%, which increased to values above 90% after reaction sintering. It was also observed that the relative density of reaction sintered samples increased with an increase in the mechanical activation time. The produced composite showed a hardness value of 11.1 GPa, which is comparable with the hardness value of mullite–zirconia composites obtained by other methods.

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1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$), which is the only stable compound in the alumina–silica system at ambient conditions, is a suitable compound for high temperature applications owing to its excellent properties like high melting point, low coefficient of thermal expansion, high chemical stability, high creep resistance and sufficient hardness [1–3]. However, mullite by itself suffers from low fracture toughness (~2 MPa m$^{1/2}$) at room temperature and difficulties in sintering to full density [4,5]. In order to improve its fracture toughness and sinterability, other ceramic components such as zirconia, silicon carbide, alumina and etc. have been introduced into mullite. Among these composites, mullite–zirconia has attracted the greatest attention because of its superior fracture toughness, high hardness and strength at room temperature [6].

Mullite–zirconia composites have been fabricated by various methods like plasma-spark [7], laser floating zone (LFZ) directional solidification method [5], sol–gel [8] and reaction sintering [9]. From these methods, reaction sintering has been proved to be an inexpensive and simple method to obtain mullite–zirconia composites with enhanced mechanical properties. Furthermore, reaction sintering is the only method in which natural minerals like zircon can be used as starting material. Nevertheless, this process needs very high temperatures (>1600 °C) to reach complete mullitization [2,10].

Mechanical activation is an effective method to enhance the contact and interaction of the reactants by decreasing their particle size and increasing their homogeneity by the milling process, which facilitates formation of new phases in the subsequent thermal treatment. This process can also produce powders in the nanometer size range [11]. In recent years, mechanical activation with subsequent thermal treatment has been successfully employed by researchers to synthesis ceramic materials with nanometer grain size [12,13].

Some works has been performed to obtain mullite zirconia composite by reaction sintering of zircon and alumina powders. [10,14]. As mentioned earlier, complete formation of mullite during the reaction sintering of zircon–alumina mixture takes place in temperatures higher than 1600 °C, which can be difficult to reach in industry. Therefore, the objective of the present study was to obtain mullite–zirconia nanostructured composite using mechanical activation and reaction sintering. The effect of mechanical activation time on the formation of phases during the reaction sintering was also investigated. Finally, the hardness of reaction sintered samples was measured and compared with those reported for mullite–zirconia composites processed by other methods.

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2. Materials and methods

The materials used in this study were calcined alumina (α-alumina, supplied by Merck) and zircon (ZrSiO$_4$, supplied by Accer) powders with the chemical compositions listed in Table 1. Fig. 1 shows the X-ray diffraction (XRD) patterns of initial powders. The morphology of the as-received powders is shown in Fig. 2. The alumina powder agglomerates were spherical with a mean size of ∼7 μm. Zircon agglomerates had angular morphology with mean size of ∼2 μm.

In order to synthesis the mullite–zirconia composite, the alumina and zircon powders were mixed with a molar ratio of 3:2 (stoichiometric) and then mechanically activated for 5 min, 10, 20, 40 and 60 h in a planetary ball mill (Fritsch P7 type) at room temperature. The rotation speed was 500 rpm and a ball–powder-mass ratio of 10:1 was employed. The milling media consisted of five zirconia balls each with a diameter of 20 mm confined in a 120 mL zirconia vial. No process control agent was used during the milling process. Phase transformation during the milling was evaluated by XRD (Philips XPERT MPD diffractometer) using filtered Cu Kα radiation (λ = 0.15406 nm). The XRD patterns were recorded in the 2θ range of 10–70° (step size 0.05°, time per step 1 s). Morphology of powder particles was studied by scanning electron microscopy (SEM) using a Philips XL30 at an accelerating voltage of 30 kV. The particle sizes of milled powders were estimated from SEM images by using Image J software. In this regard, the sizes of at least 40 particles were measured, and the mean value was reported as the average particle size.

The milled powders were cold pressed into pellets of Φ 10 mm × 2 mm under pressure of 600 MPa and then sintered at 1400 °C for 2 h. Crystallographic changes after the sintering were determined by XRD. The Williamson–Hall equation was employed to evaluate the crystallite size of sintered samples [15]:

$$\beta \cos \theta = \frac{K\lambda}{D} + 2A\varepsilon \sin \theta \tag{1}$$

where θ is the Bragg angle, D is the crystallite size, ε is the average internal strain, λ is the wavelength of the X-ray (0.15406 nm) and β is the peak full width at half maximum intensity. Density of sintered samples was evaluated by Archimedes technique. Vickers microhardness of the reaction sintered specimens was evaluated using a Vickers indentation machine (Buhler) at the load of 1 kg.

3. Results and discussion

3.1. Structural changes during mechanical alloying

Fig. 3 shows the XRD patterns of the initial powder mixture after various times of mechanical activation. The diffraction peaks of pure crystalline α-alumina and zircon phases were present after 5 min of mechanical activation. No new phase diffraction pattern was observed by increasing the milling time to 10 h and only some broadening of α-alumina and zircon diffraction peaks and a reduction in their intensities were observed. This can be attributed to grain size refinement and straining during the milling [16].

By increasing the milling time, the intensity of alumina and zircon peaks decreased gradually. After 60 h of milling, most of the zircon diffraction peaks disappeared. This indicates that
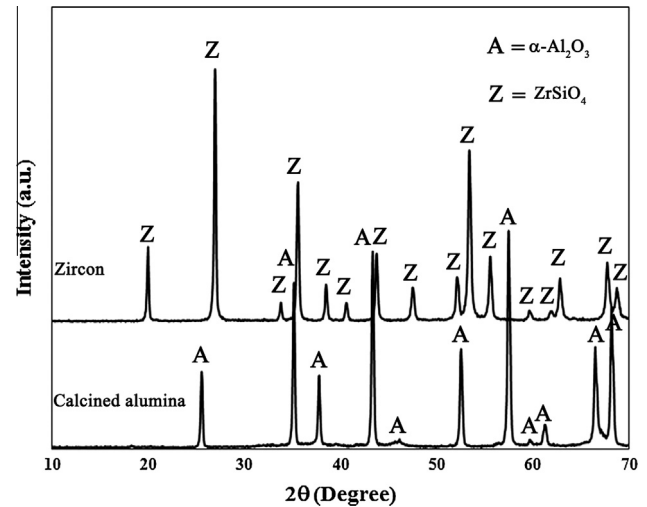

Fig. 1. XRD patterns of α-alumina and zircon powders.

mechanical activation gradually drives zircon to an amorphous state. However, the peaks of alumina phase still remained, indicating that this phase was in crystalline form even after long times of mechanical activation.

3.2. Structural changes during reaction sintering

To obtain mullite–zirconia composite, the milled powders were cold pressed to pellets of Φ 10 mm × 2 mm and then sintered at 1400 °C for 2 h. Cold compression increases the contact surface between the powders and provides diffusion paths for atoms involving in the chemical reaction, and therefore enhances the formation of mullite–zirconia composite in the subsequent sintering process.

Zircon and alumina react according to the following reaction to form mullite–zirconia composite [10]:

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 2ZrO_2 + 3Al_2O_3 \cdot 2SiO_2 \tag{2}$$
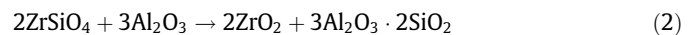
$$\Delta G = (73.75 - 0.05375T)\text{kJ mol}^{-1}$$

The first step in the formation of mullite–zirconia composite during the reaction sintering of zircon–alumina mixture is the dissociation of ZrSiO$_4$ according to following reaction [17]:

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2 \tag{3}$$

$$\Delta G = (26.8 - 0.0126T)\text{kJ mol}^{-1}$$

Afterwards, SiO$_2$ starts to dissolve Al$_2$O$_3$ to aluminosilicate glass. Nucleation of mullite takes place after a critical Al$_2$O$_3$ concentration is exceeded in the glass phase [14,17]:

$$2SiO_2 + 3Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 \tag{4}$$
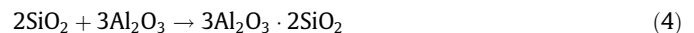
$$\Delta G = (20.15 - 0.02855T)\text{kJ mol}^{-1}$$

It has been understood that only chemical reactions with negative Gibbs free energy change at room temperature can be done during mechanical activation [18]. The Gibbs free energy change for all the above reactions is positive at room temperature. Therefore, they cannot be done during the mechanical alloying process. According to the Gibbs free energy change for reaction (2), the onset temperature for mullite–zirconia formation is ∼1100 °C. However, this is a theoretical temperature and in practice, mullite formation during reaction sintering starts at temperatures higher than ∼1450 °C [10].

Table 1
Chemical composition of raw materials.

Material	Al$_2$O$_3$	SiO$_2$	ZrO$_2$	CaO	MgO	Na$_2$O	TiO$_2$	Fe$_2$O$_3$
Zircon	0.5	37.7	61.3	0.04	0.03	0.2	0.2	0.05
α-Alumina	99.73	0.04	–	0.01	0.11	0.1	0.01	–