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Preparation and characterization of Al_2O_3–25 mol% ZrO_2 composites

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Abstract

Al_2O_3–ZrO_2 (AZ_x), with 25 mol% ZrO_2 content, was prepared using the co-precipitation method. Synthesized powders were characterized by thermal reaction using a differential thermal analysis technique (TG–DTA) and were investigated by phase formation using X-ray diffraction. It indicated that the reaction occurred at 850 °C; cubic (c)-ZrO_2 phase and Al_2O_3 were obtained. By increasing temperature to 1100 °C, tetragonal (t)-ZrO_2 phase was detected. The Al_2O_3–25 mol% ZrO_2 was sintered for 2 h in the temperature range of between 1300 and 1600 °C. The majority phases of ceramics were m-ZrO_2 and α-Al_2O_3, although a t-ZrO_2 phase also appeared as a minor phase and decreased with higher temperature. Moreover, morphology and particle size evolution have been determined via the SEM technique. SEM showed that the particles of powder are agglomerated and basically irregular in shape. An SEM micrograph of ceramics exhibits uniform microstructure without abnormal grain growth.

Keywords: A. Grain growth; A. Sintering; D. Al_2O_3; D. ZrO_2

1. Introduction

Al_2O_3 ceramics is one of the most widely used engineering ceramic materials due to its high elastic modulus, high wear resistance and chemical corrosion resistance, high temperature stability and the retention of strength at high temperatures [1]. It is well known that the mechanical properties of alumina ceramics can be considerably increased by the incorporation of fine zirconia particles [2]. Therefore, the alumina–zirconia system (AZ_x with 15–30 mol% ZrO_2) is interested to study [3,4]. As a structural oxide ceramic, zirconia has received much attention due to its high toughness while alumina is known as a hard, low-cost ceramics with high thermal conductivity [5,6]. The toughening mechanisms associated with zirconia toughened alumina are mainly based on the stress-induced transformation tetragonal-monoclinic martensitic transformation toughening and micro crack toughening. The extent of a stress-induced transformation toughening depends on the dispersion of tetragonal zirconia in an alumina matrix, its volume fraction and transformability. On the other hand, a uniform distribution of ZrO_2 ceramic matrix is an important factor for optimization of micro crack nucleation-induced toughening [7,8]. The phase composition structure is the key to control material properties.

In this work, Al_2O_3–25 mol% ZrO_2 samples were prepared by a co-precipitation route and the influence of heat treatment on phase compositions and microstructure were investigated.

2. Experimental

The Al_2O_3–ZrO_2 powders with 25 mol% ZrO_2, respectively were synthesized using aluminum chloride ($AlCl_3{\cdot}6H_2O$, 99.9% pure), zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, 99.9% pure) and ammonia solution (NH_4OH, 28%) as raw materials. Aluminum chloride and zirconium oxychloride were mixed and dissolved in distilled water. The solution was thoroughly stirred at room temperature, and then precipitated by adding ammonia to get $Zr(OH)_4$ gel. The precipitate was washed repeatedly using distilled water to remove all the chloride ions (as tasted by $AgNO_3$ solution), and then dried in air at 100 °C. The samples from the precipitate were investigated by thermal analysis using TA instruments (SDT Q600, USA) and after, they were calcined at different temperatures between 700 and 1100 °C. Then, various sintering conditions were employed by varying the sintering temperatures from 1300 to 1600 °C for 2 h. The crystallized phase of the Al_2O_3–ZrO_2 solid solution was

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measured by X-ray diffraction (XRD) using CuKα radiation (Philips PW 1729 diffractometer, Netherlands). Microstructural evolution of the powders and ceramics were observed using the scanning electron microscopy: SEM (JEOL, JSM 840A, Japan).

3. Results and discussion

Fig. 1 shows the TG and DTA curves of the Al_2O_3–ZrO_2 (AZ_x) mixed powders, with $x = 25$ mol% ZrO_2 content. It can be seen that the TG curve demonstrates three distinct weight losses below 600 °C. The first weight loss occurs below 230 °C, the second between 240 °C and 290 °C and the third above 300 °C. In the temperature range of room temperature to ~150 °C, the sample shows an endothermic peak in the DTA curve at ~100 °C, which relates to the first weight loss. This DTA peak is attributed to the elimination of water. The second weight loss between 240 °C and 290 °C were observed, which corresponded to endothermic peak at 282.50 °C on DTA curve. Previous works reported that the crystallization of t-ZrO_2 is obtained at 280 °C [7]. The third weight loss was found above 300 °C, and related to a small exothermic peak at 398 °C in the DTA curve. This result indicates the boiling point of the derivative product and corresponds to the transformation of $Al(OH)_3$ and γ-AlOOH into γ-alumina, consistent with other works [8]. The phase transformation from γ-AlOOH to α-Al_2O_3 follows the following path as reported by a number of workers [9].

$$\gamma\text{-ALOOH}\xrightarrow{400\,^{\circ}\mathrm{C}}\gamma\text{-}Al_2O_3\xrightarrow{800\,^{\circ}\mathrm{C}}\delta\text{-}Al_2O_3\xrightarrow{1000\,^{\circ}\mathrm{C}}\theta\text{-}Al_2O_3\xrightarrow{1200\,^{\circ}\mathrm{C}}\alpha\text{-}Al_2O_3 \quad (1)$$

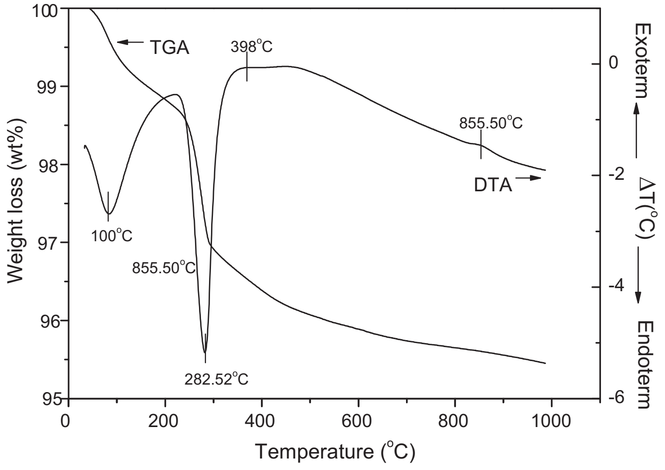

Fig. 1. A TG–DTA curve for the mixture of Al_2O_3–25 mol% ZrO_2 powders.

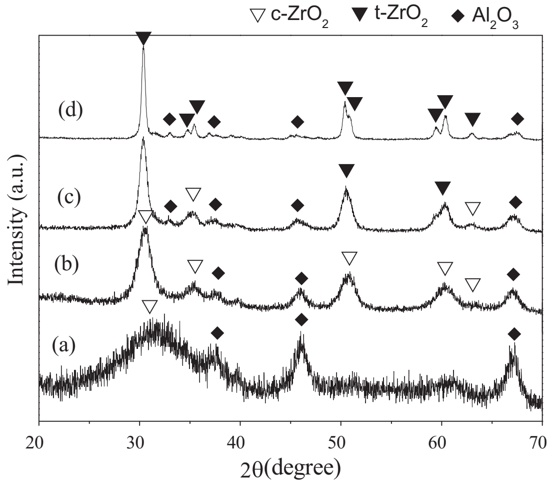

Fig. 2. XRD patterns of Al_2O_3–25 mol% ZrO_2 powders at various calcinations temperatures for 2 h: (a) 700 °C, (b) 850 °C, (c) 900 °C, and (d) 1100 °C.

The relationship between the TG curve and the DTA curve between 300 and 700 °C (Fig. 1) reveals a loss in the weight of raw material (TG), and a corresponding loss in the reaction of zirconium hydroxyl and aluminum hydroxyl (DTA). The DTA curve displays a sharp exothermic peak at 855 °C, which is the formation of a crystal line phase of Al_2O_3–ZrO_2 solid solution. Similar change in the crystallization temperature of Al_2O_3–ZrO_2 system were also observed by the same research group in earlier works [3,4,10,11]. These curve data were used to select the ranges of temperatures (700–1100 °C) for XRD investigation. To study the effect of heat treatment temperatures on Al_2O_3–25 mol% ZrO_2, the precursor powders were calcined between 700 and 1100 °C for 2 h. All calcined powders were examined by XRD in order to investigate the phase development. As shown in Fig. 2(a), phase formation of Al_2O_3–25 mol% ZrO_2 calcined at 700 °C. X-ray peaks of θ-Al_2O_3, δ-Al_2O_3, and very broad peaks of c-ZrO_2 phase are present, indicating incomplete reaction. So the sample was calcined at 850 °C and the resulting XRD patterns are shown in Fig. 2(b). Due to the broad peak observed at 855 °C (Fig. 1) and the clear intensity peaks of the c-ZrO_2, θ-Al_2O_3 and δ-Al_2O_3 phases (Fig. 2(b)) it was concluded that 850 °C would complete the Al_2O_3–ZrO_2 phase. XRD pattern in Fig. 2(b) exhibits very broad peaks confirming a small crystallize size. As the temperature increase to 900 °C, the phases present are θ-Al_2O_3, c-ZrO_2 and t-ZrO_2. At this temperature, t-ZrO_2 were appeared. Agreement with previous reported that alumina could stabilize the cubic zirconia (c-ZrO_2) and the tetragonal zirconia (t-ZrO_2) if the Al_2O_3–ZrO_2 powders were prepared by the aqueous co-precipitation route, starting with mixture of zirconium oxychloride and aluminum chloride [1]. In general, the c-ZrO_2 → t-ZrO_2 phase transformation took place at about 900 °C confirming their phase and being consistent with other work [11]. When heating further to higher temperature (1100 °C), zirconia phases are composed mainly of t-ZrO_2. The presence of tetragonal phases of ZrO_2 is detected by the presence of high intensity peak at $2\theta = 30^{\circ}$ and splitting of peaks at around $2\theta = 50^{\circ}$. It is indicated the c-ZrO_2 phase transformed to complete t-ZrO_2 phase. From the little detection of θ-Al_2O_3 and δ-Al_2O_3 peaks, it was suspected that some Al_2O_3 phase still existed in an amorphous state even at 1100 °C and incompletely transformed to α-Al_2O_3. Fig. 3 shows the morphological evolution of all samples as a function of calcination conditions. For all the samples, the micrographs revealed foamy agglomerated particles. Powders calcined at 700 °C (Fig. 3(a)) shows more agglomeration state and irregular in

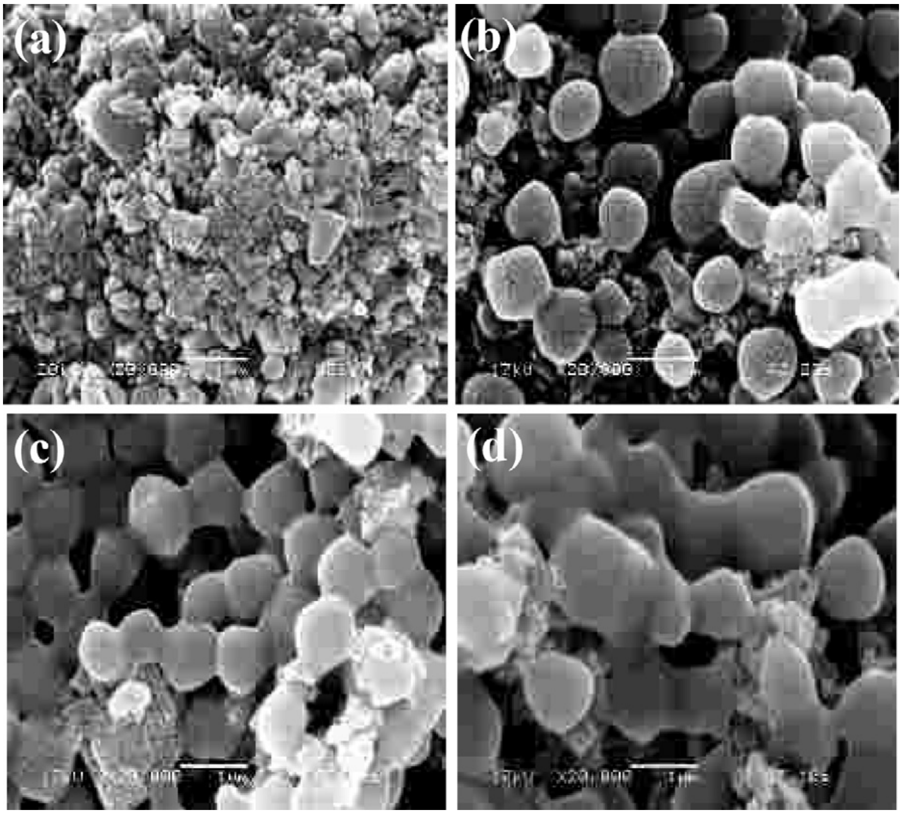

Fig. 3. SEM micrograph of the Al_2O_3–25 mol% ZrO_2 powders calcined at (a) 700 °C, (b) 850 °C, (c) 900 °C, and (d) 1100 °C.

shape, with a substantial variation in particle sizes which probably have resulted from incomplete reaction. The result was agreed with XRD pattern in Fig. 2(a). SEM micrographs of powders calcined at higher temperature (in Fig. 2(b) and (c)) show spherical particles, it is likely to correspond to TEM photograph reported by Sarkar et al. [12]. The size of the particles tends to increase when the calcination temperature is increased. However, the smallest particle size estimated from SEM micrograhps was ~0.20 μm. The phase formations of the sintered ceramics at sintering temperatures ranging from 1300 to 1600 °C are presented via XRD patterns in Fig. 4. XRD patterns of crystalline products revealed that they contain three crystalline oxides phase of α-Al_2O_3, m-ZrO_2 and t-ZrO_2. Thus, at higher temperatures the ZrO_2 phase changed to become mainly monoclinic (m), while t-ZrO_2 decreased by a few degrees with increased heat-treatment. The particle size of many zirconia may exceed the critical size and so a transformation from t → m takes place. According to the stabilization of tetragonal phase of zirconia at room temperature is proved to be due to small crystallite size as well as constraining effect of matrix phase of Al_2O_3 [11]. Fig. 5 shows SEM images of as-received Al_2O_3–25 mol% ZrO_2 as sintering conditions were varied between 1300 and 1600 °C for 2 h. Almost no abnormal grain growth was observed. The addition of ZrO_2 helped to control the abnormal grain growth in Al_2O_3 ceramics [13]. In Fig. 5(a) and (b) the free surfaces showed many pores. However, at the higher temperatures similar microstructural characteristics were observed, i.e., uniformly sized grains with well-packed and continuous grain structure (Fig. 5(c) and (d)). It can be seen that ceramics sintered at 1300–1400 °C exhibited grain size range of about 0.25–1.10 μm, while ceramics sintered at 1500–1600 °C exhibited grain size range of about 1.22–2.87 μm. The results indicate that the average grain size tend to increase with sintering temperature. It is to be noted that the stabilization of the tetragonal phase, which may be ascribed to the smaller particle-size and low temperature, is consistent with other works [10,12,14,15].

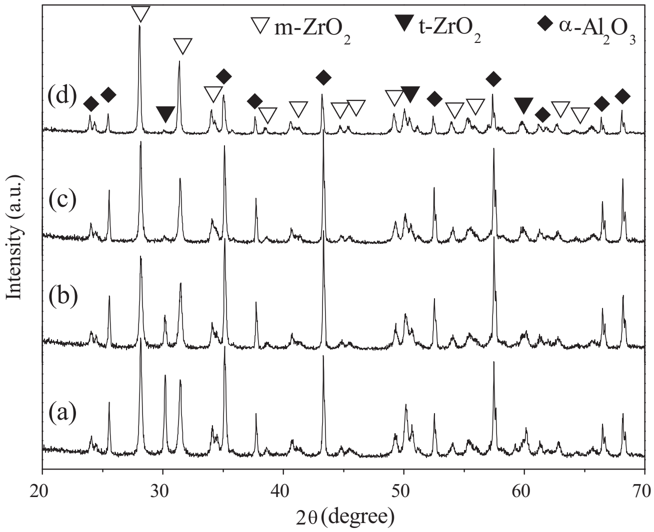

Fig. 4. XRD patterns of Al_2O_3–25 mol% ZrO_2 ceramics at various sintering temperatures for 2 h: (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, and (d) 1600 °C.

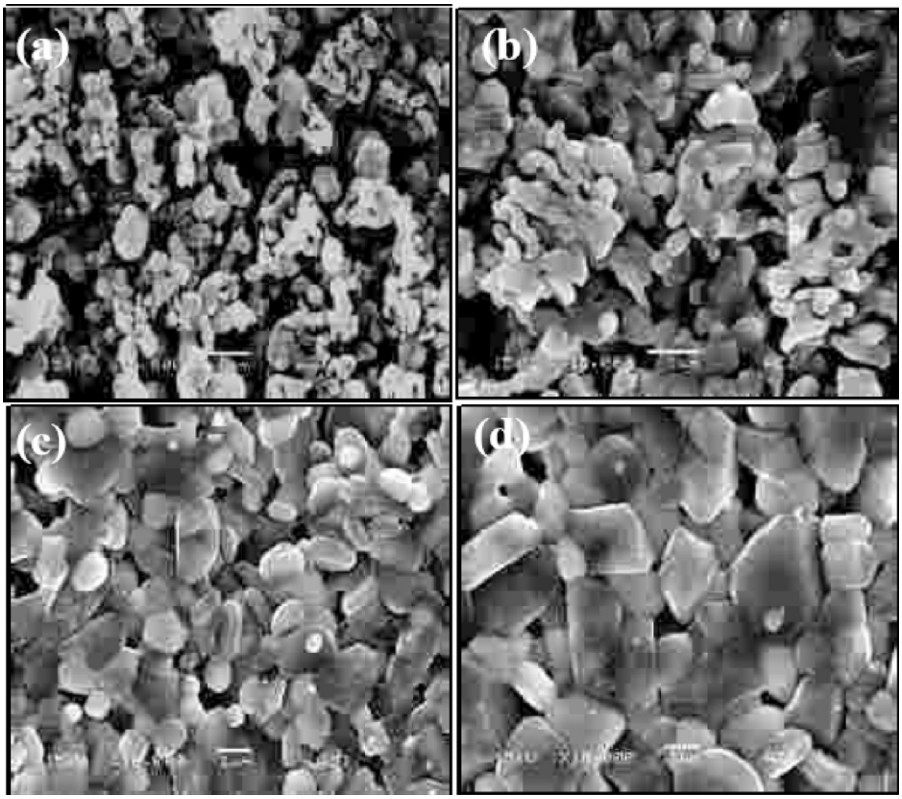

Fig. 5. SEM micrograph of the Al_2O_3–25 mol% ZrO_2 ceramics sintered at (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, and (d) 1600 °C.

4. Conclusions

The effect of heat treatment on phase formation and microstructure of Al_2O_3–25 mol% ZrO_2 synthesized by the co-precipitation method was investigated. This work demonstrated that Al_2O_3–25 mol% ZrO_2 calcined powders obtained main phase of c-ZrO_2 and combined with some θ-Al_2O_3 and δ-Al_2O_3 phases. At higher calcination temperatures (850–1100 °C), t-ZrO_2 were detected. The sintered ceramics showed the major crystalline phase of α-Al_2O_3 combined with m-ZrO_2 and t-ZrO_2; further, it was found that t-ZrO_2 decreased by a few degrees with increased heat-treatment. The resulting Al_2O_3–25 mol% ZrO_2 powders consisted of a variety of agglomerated particle sizes, depending on calcination conditions. Al_2O_3–25 mol% ZrO_2 grain ceramics exhibited irregular shaping and growth of grain, both of which increased with higher temperatures.

Acknowledgements

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