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Ceramics International 30 (2004) 923–926

CERAMICS
INTERNATIONAL

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Effect of Al_2O_3 addition on ZrO_2 phase composition in the Al_2O_3–ZrO_2 system

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Received 20 June 2003; received in revised form 28 August 2003; accepted 12 October 2003

Abstract

Al_2O_3–ZrO_2 powders with 15, 50 and 85 wt.% Al_2O_3 were prepared by mixing high purity α-alumina powder with $Zr(OH)_4$ gel synthesized by the precipitation method. The obtained mixture was calcined for 2 h at temperatures ranging from 400 to 1300 °C. The effect of the addition of Al_2O_3 on ZrO_2 phase composition in the Al_2O_3–ZrO_2 system was characterized by means of differential thermal analysis, X-ray diffraction and transmission electron microscopy.

Keywords: A. Calcination; D. Al_2O_3; D. ZrO_2; Phase composition; Crystallite size

1. Introduction

It is well known that the tetragonal and/or cubic ZrO_2 can be retained to room temperature by doping small amount of stabilizing oxides (e.g. Y_2O_3, MgO, CaO, and some rare-earth oxides) [1]. In addition, the metastable tetragonal zirconia without dopants can also be prepared in the form of fine particles that are smaller than the critical size [2–4]. It is reported that the critical particle size is about 30 nm if the elastic strain energy is considered, or about 10 nm if the elastic strain energy is ignored [5]. In practice, however, m-ZrO_2 phase is often obtained using undoped zirconia powders after calcination because of higher crystallite growth rate than that of doped zirconia [6–8].

Recently, many studies [7–10] indicated that Al^{3+} cations could present in the ZrO_2 lattice, leading to a formation of metastable Al_2O_3–ZrO_2 solid solutions with a cubic or tetragonal structure at low temperatures when the Al_2O_3–ZrO_2 powders were synthesized by the alkoxide route where the mixture of zirconium isopropoxide and aluminium isopropoxide was used, or by the aqueous co-precipitation route, starting with a mixture of zirconium oxychloride and aluminium chloride. However, as indicated by the phase diagram of the Al_2O_3–ZrO_2 system [11,12], the solubility of alumina in the fluorite lattice of zirconia is less than 2 mol% at temperatures lower than 1400 °C. Large-scale replacement of Zr^{4+} with Al^{3+} is difficult to understand [13,14]. Meanwhile, based on the experiment and simulation, Kikkawa et al. pointed out that the Al^{3+} ion seemed not substituting into the Zr^{4+} site in tetragonal zirconia [15]. On the other hand, Shi et al. [16] prepared zirconia–alumina composite powders by a method of spray-drying mixed oxalate complex solutions and their results showed that high alumina contents led to retarded grain growth of tetragonal zirconia and the enhanced critical size for the phase transformation from tetragonal to monoclinic. Those experimental results mentioned above were based on solution methods to prepare zirconia–alumina composite powders. Further studies should be carried out in the Al_2O_3–ZrO_2 system.

In the present work, the Al_2O_3–ZrO_2 powders are prepared by mixing high purity α-alumina powder with $Zr(OH)_4$ gel, which is synthesized by the precipitation method. In this case, it is impossible for Al^{3+} cations to enter into the ZrO_2 lattice. The major objective of this study is to investigate the effects of the Al_2O_3 content and the calcination temperature on the ZrO_2 phase composition in the as-calcined Al_2O_3–ZrO_2 powders.

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doi:10.1016/j.ceramint.2003.10.014

2. Experimental procedure

The Al_2O_3–ZrO_2 powders with 15, 50 and 85 wt.% Al_2O_3, named respectively as A, B, and C, were prepared. α-Alumina powder (TM-DAR grade, mean particle size of 0.2 μm, purity of 99.99%, Taimei Chemical Co., Ltd., Japan), zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, 99.0%, Kishida Chemical Co. Ltd., Japan) and aqueous ammonia (28 wt.%) were used as the starting materials. Zirconium oxychloride solution was prepared by dissolving in distilled water. The solution was thoroughly stirred at room temperature, and then precipitated by adding ammonia to get $Zr(OH)_4$ gel. The gel was washed with water–ammonia mixtures until chloride ion was free (as tested by $AgNO_3$ solution) while the pH value was kept at about 10.0. Between each washing step, the gel was settled and the clear supernatant liquid was removed. The Al_2O_3 powder and a little amount of polyethylene glycol (PEG) as surfactant were added into the gel and this mixture was ball milled for 24 h. The filtered slurry was washed with ethanol to remove the free water and then dried in oven at 110 °C. The obtained powders were passed through 100 mesh sieve and then calcined at temperatures between 400 and 1300 °C for 2 h at a heating rate of 5 °C/min. For reference, the pure ZrO_2 powder was also prepared by the same route.

The crystallite sizes of zirconia and phase composition of the Al_2O_3–ZrO_2 composites were measured by means of X-ray diffraction (XRD) using Cu Kα radiation with a Rigaku RAD-2C diffractometer. The mean crystallite size D was obtained from the Scherrer formula:

$$D = \frac{(k\lambda)}{(\beta\cos\theta)} \qquad (1)$$

where $k = 0.9$, $\lambda = 1.5418$, θ is the diffraction peak angle, and β denotes the full width at half maximum of the corresponding diffraction peak.

The volume fraction of monoclinic zirconia (V_m) was calculated according to the following equation:

$$V_m = \frac{I_{(\bar{1}11)_m} + I_{(111)_m}}{I_{(\bar{1}11)_m} + I_{(111)_m} + I_{(111)_t}} \qquad (2)$$

where I is the integral intensity and the subscripts m and t refer to the monoclinic and tetragonal phase, respectively. The intensities were corrected for the background.

Differential thermal analysis (DTA, Rigaku Thermo Plus TG8120, Japan) for the powders was carried out in air at a heating rate of 5 °C/min using ultra-pure Al_2O_3 as reference. Microstructural evolution of the powder was observed using transmission electron microscopy (TEM, Hitachi H-9000).

3. Results and discussion

DTA curves for the pure ZrO_2 and the Al_2O_3–ZrO_2 powders are shown in Fig. 1. The exothermic peak represents the crystallization temperature for Zirconia. It can be seen that there is a slight increase in the crystallization temperature of ZrO_2 with increasing the Al_2O_3 addition. This trend is in good agreement with the results reported by Inamura et al. [9]. However, the exothermic peak is not detected for powder C due to the fact that there is only 15 wt.% ZrO_2. Fig. 2 shows the XRD patterns of powder C calcined at different temperatures, indicating no sign of crystallization at 450 °C.

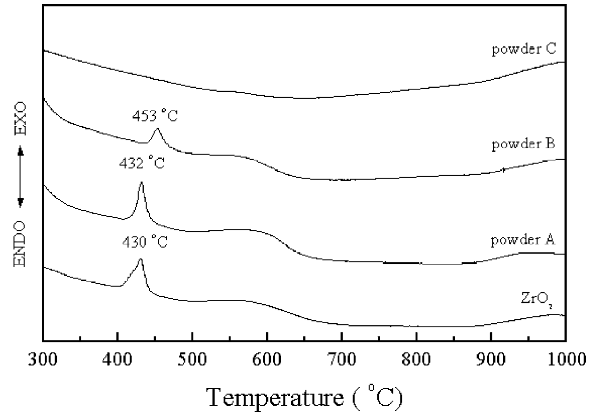

Fig. 1. DTA curves for the pure ZrO_2 and the Al_2O_3–ZrO_2 powders.

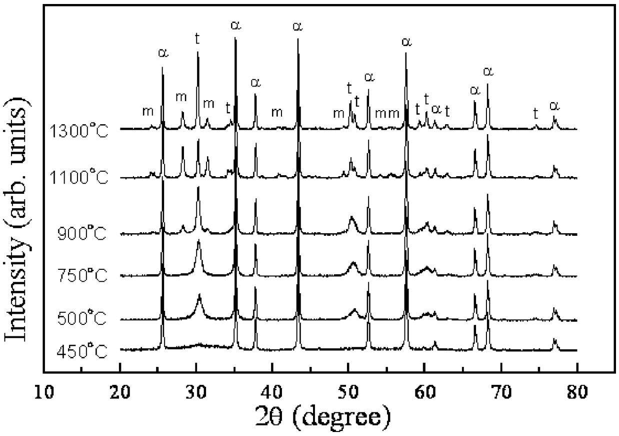

Fig. 2. Phase evolution of powder C with increasing calcination temperature.

Table 1
Crystallite size and phase composition of ZrO_2 of powder C calcined at different temperatures

Calcination temperature (°C)	ZrO_2 phase composition	Crystallite size (nm)
450	–	–
500	t-ZrO_2	7
600	t-ZrO_2	9
700	t-ZrO_2	10
750	t-ZrO_2	11
800	≥95 vol.% t-ZrO_2; ≤5 vol.% m-ZrO_2	14
900	82 vol.% t-ZrO_2; 18 vol.% m-ZrO_2	18
1000	31 vol.% t-ZrO_2; 69 vol.% m-ZrO_2	22
1100	37 vol.% t-ZrO_2; 63 vol.% m-ZrO_2	31
1200	56 vol.% t-ZrO_2; 44 vol.% m-ZrO_2	35
1300	66 vol.% t-ZrO_2; 34 vol.% m-ZrO_2	37

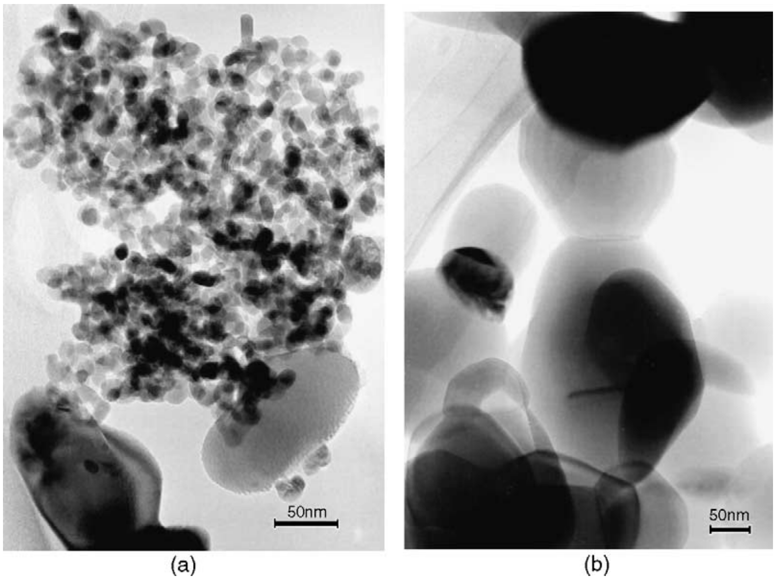

Fig. 3. TEM micrograph of powder C calcined at (a) 600 °C and (b) 1200 °C.

Table 1 summarizes the XRD-identified phase composition and crystallite size of ZrO_2 of powder C after calcination at different temperatures. As expected, the crystallite size of ZrO_2 increases with increasing calcining temperature. This is clearly demonstrated in Fig. 3. Meanwhile, metastable t-ZrO_2 phase has been obtained in the $Al_2O_3-ZrO_2$ system after calcination at temperatures ranging from 500 to 750 °C. It reveals that the high alumina content can effectively inhibit the nucleation and the grain growth of zirconia. When the powder is calcined at 600 °C, the apparent crystallite size of 9 nm, which is calculated using the Scherrer equation, is almost the same as that observed by TEM in Fig. 3a.

The effects of the Al_2O_3 content and the calcination temperature on the ZrO_2 phase composition in the Al_2O_3–ZrO_2 powders are showed in Fig. 4. It is quite clear that Al_2O_3 has a great influence on the grain growth of zirconia and the stability of tetragonal zirconia. At the same calcination temperature, the volume fraction of tetragonal zirconia increases with Al_2O_3 content. In pure ZrO_2 as well as powders A and B, the volume fraction of tetragonal zirconia continuously decreases with increasing calcination temperature due to the increasing particle size of ZrO_2. In powder C, however, metastable t-ZrO_2 phase has been obtained after calcination at temperatures ranging from 500 to 750 °C. When the calcination temperature is over 800 °C, some ZrO_2 particles with size larger than the critical size have transformed into m-ZrO_2. Thus, tetragonal zirconia continuously decreases with increasing calcination temperature between 800 and 1000 °C. When the calcination temperature is over 1100 °C, a large amount of hard agglomerates exist in the powder. In this case, tetragonal zirconia continuously increases with calcination temperature between 1100 and 1300 °C, resulting from high alumina content and the higher Young's modulus of alumina.

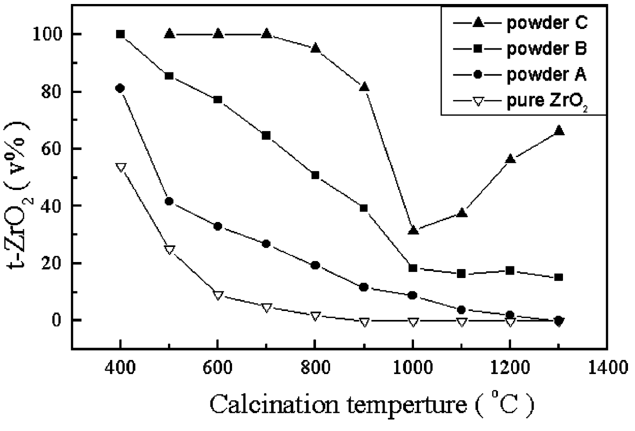

Fig. 4. Effects of the Al_2O_3 content and the calcination temperature on the ZrO_2 phase composition.

4. Summary

Incorporation of 85 wt.% Al_2O_3, metastable t-ZrO_2 with a crystallite size smaller than 11 nm has been obtained after calcination at temperatures ranging from 500 to 750 °C due to the fact that alumina with high content can effectively inhibit the nucleation and the grain growth of zirconia. With addition of 15 or 50 wt.% Al_2O_3, the volume fraction of tetragonal zirconia continuously decreases with increasing calcination temperature.

Acknowledgements

One of the authors (P.R.) acknowledges the financial support of Japan Science and Technology (JST) and Guangdong Natural Science Foundation (Grant number 031446).

We thank Dr. Satoshi Ichikawa for assistance with TEM observation.

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