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Effect of TiO_2 addition on the stability of t-ZrO_2 in mullite–ZrO_2 composites prepared from various starting materials

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Abstract

Mullite–zirconia composite materials were prepared by reaction sintering of α-alumina and aluminium nitrate as alumina sources, and zircon powder. Different effects were observed on sintering, densification and microstructure of composites prepared by various alumina sources by adding TiO_2. The formation temperature and retention of tetragonal zirconia phase were found to differ in composites with and without TiO_2. The more fraction of t-ZrO_2 was retained from the reaction sintering of alumina nitrate and zircon without TiO_2 addition. The same trend was observed for the combination of α-alumina and zircon containing 3.5 wt.% TiO_2 below 1550 °C. The microstructural analysis show enlarge ZrO_2 particles in compositions containing TiO_2; that is the reason for the reduction of t-ZrO_2 concentration.

Keywords: B. Composites; D. Mullite; D. ZrO_2; D. TiO_2

1. Introduction

Many workers have studied the system ZrO_2–Al_2O_3–SiO_2–TiO_2 [1–3]. As proved, TiO_2 is the most effective additive for improving sintering and mechanical properties [4]. In zircon/alumina/titania composition densification occurs through the formation of a transitory liquid phase. Moya et al. [5] found that for the composition located inside the solid solubility limit (0.25 mole TiO_2) the reaction-sintering process takes place in the absence of any liquid phase. Conversely, in the composition with the higher TiO_2 content than the solid solubility limit, the transitory formation of $ZrTiO_4$ occurs at temperatures around 1300 °C.

The aim of the present study is to examine the retention of tetragonal zirconia phase in reaction-sintered mullite-zirconia composites prepared from different alumina sources. In addition, the effect of TiO_2 on reaction sintering, densification and microstructure of these composites was investigated and correlated to the retention of tetragonal zirconia phase.

2. Experimental procedures

Four compositions were prepared by the mixing of α-alumina (CS-400M; MARTOXID, Germany), aluminium nitrate ($Al(NO_3)_3.9H_2O$, >99.9%, Merck), zircon (Zircosil 5; Cookson Matthey Ceramics and Materials) and TiO_2 (Merck), Table 1. AZ and AZT powders were mixed for 1 h by a planetary mill in isopropanol using yttria-stabilised tetragonal zirconia pot and balls. Then a hot stirrer at 80 °C dried the obtained slurries. ANZ and ANZT powders were prepared by dissolving of aluminium nitrate in deionized water, and zircon and TiO_2 powders gradually added into the obtained solution. The pH of the mixture was adjusted to 3 by adding dilute HNO_3 acid. After stirring the mixture for 4 h, it was dried at 80 °C and a paste compact was obtained. The compact was calcined at 900 °C for 3 h. The calcined powders were wet milled for 1 h under the conditions already mentioned for AZ and AZT powders. The mixed powders were compacted by uniaxial pressing at 190 MPa. PVA (1 wt.%) was used as binder, and granulation was made by passing the dried mixtures through 180 μm sieve. Density and porosity measurements of sintered samples were carried out according to ASTM-C20. In all cases, the progress of the chemical reaction between alumina sources, zircon and TiO_2 was examined by X-

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ray analysis with a Philips X' Pert System with Ni-filtered CuK_α radiation. As-sintered samples were used for X-ray analysis due to tetragonal → monoclinic zirconia phase transformation by polishing and grinding effects [6]. The retained tetragonal fraction of ZrO_2 was obtained from the ratio of intensity of the (111) tetragonal peak to the sum of the intensities of the (111) and $(\bar{1}11)$ monoclinic and (111) tetragonal peaks [7]. The grain size of ZrO_2 particles in sintered samples was determined from counts of 170 grains by scanning electron microscopy using a stereoscan 360, Lecia Cambridge instrument.

3. Results and discussion

The more retention of tetragonal zirconia phase is found in ANZ sample than AZ sample (Fig. 1) which can be attributed to the formation of zirconia phase at lower temperatures (Fig. 2) and low density (Fig. 3) of this sample [8,9]. As Fig. 2 illustrates the dissociation of zircon and the formation of zirconia occur at lower temperatures in ANZ sample than AZ sample. Extents of reaction in ANZ sample is confirmed by considering Fig. 4 which demonstrates no additional alumina powder at 1600 °C, while in AZ sample alumina powder remains partially unreacted. The reaction evolution of ANZ sample can be attributed to the homogeneity of the mixture of alumina precursor and zircon powder. Addition of 3.5 wt.% TiO_2 to the composition of AZ and ANZ samples causes the significant change in the dissociation of zircon in AZ sample and improvement of densification in ANZ sample. The observed changes alternately affect on the retention of t-ZrO_2 in these samples. The reaction between alumina and zircon enhances by introducing TiO_2 (Fig. 2), and the dissociation of zircon and formation of zirconia are shifted to the lower temperatures. Fig. 4 indicates further evidence of the enhance effect of TiO_2 in the dissociation of zircon and formation of mullite and zirconia. As Fig. 1 reveals, adding 3.5 wt.% TiO_2 leads the sharp change of t-ZrO_2 concentration in AZ sample at low sintering temperature (e.g. 1400 °C). Presumably, the formation of t-ZrO_2 at lower temperatures implies the existence of

Table 1
Composition of mixed-powder samples

	α-Al_2O_3	$Al(NO_3)_3.9H_2O$	$ZrSiO_4$	TiO_2
AZ	*	—	*	—
AZT	*	—	*	*
ANZ	—	*	*	—
ANZT	—	*	*	*

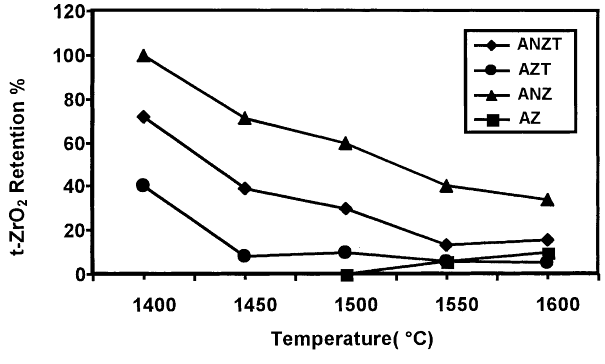

Fig. 1. Tetragonal zirconia fraction in reaction-sintered samples as a function of sintering temperature after 2 h.

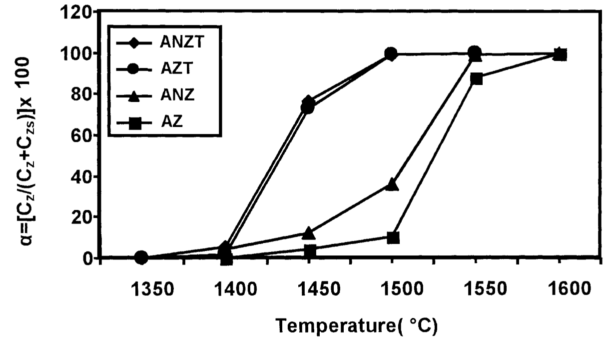

Fig. 2. Zirconia formation versus sintering temperature after 2 h heating. C_z and C_{zs}, the concentration of zirconia and zircon, respectively. α gives the value of zircon dissociation.

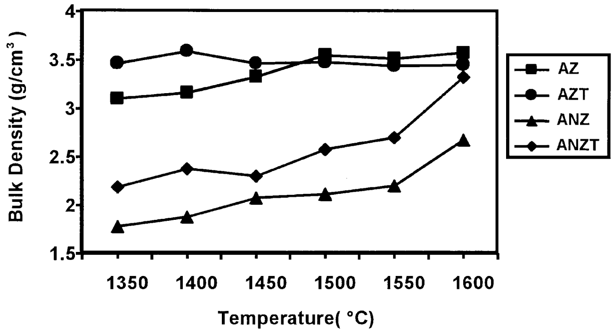

Fig. 3. Bulk density of composites under various sintering conditions after 2 h heating.

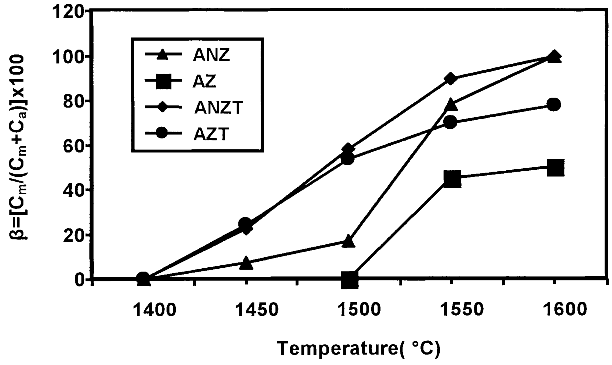

Fig. 4. Mullite formation versus sintering temperature after 2 h heating. C_m and C_a, the concentration of mullite and alumina, respectively. β gives the value of mullite formation.

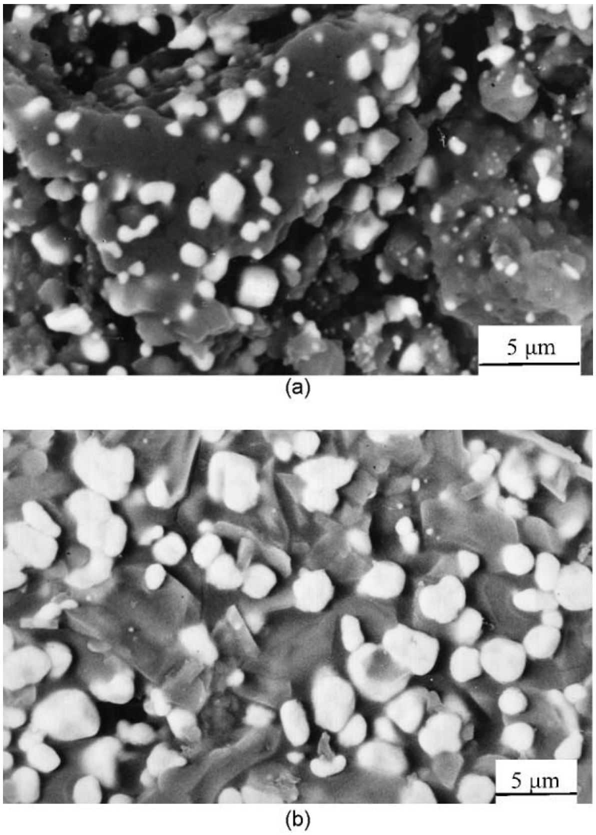

Fig. 5. Scanning electron micrographs of the thermal etched surface of (a) AZ and (b) AZT samples sintered at 1600 °C for 2 h.

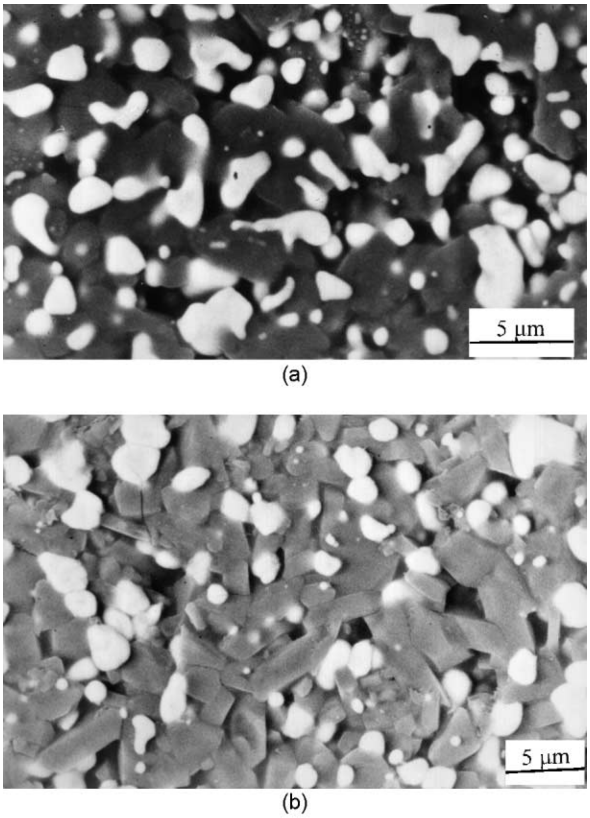

Fig. 6. Scanning electron micrographs of the thermal etched surface of (a) ANZ and (b) ANZT samples sintered at 1600 °C for 2 h.

some particles below the critical size for transformation. This result is consistent with reducing of the tetragonal phase concentration by increasing sintering temperature (Fig. 1). The further attention to Fig. 1 reveals that the formation temperature of t-ZrO_2 in AZ sample begins above 1500 °C. X-ray diffraction analysis showed only monoclinic zirconia as the crystalline phase at this temperature. By increasing the sintering temperature the more tetragonal phase preserved in AZ sample. This result is consistent with the fact that the more tetragonal particles entrapped by growing the mullite grains. Since as reported earlier [10], the ZrO_2 particles are intragranular in mullite-ZrO_2 composites fabricated by reaction-sintering of alumina and zircon powder mixtures. Thus, it can be postulated that the tetragonal particles remain below the critical size for transformation due to the increasing of diffusion distances by increasing the mullite layer [11]. The SEM micrographs corresponding to AZ and AZT samples (typically, Fig. 5a and b) show the elongated mullite grains and enlarge zirconia particles (2.1 ± 1.1 μm) in AZT sample, while AZ sample contains the smaller zirconia particles (1.7 ± 0.7 μm) surrounded by mullite grains.

The present results suggest that the addition of TiO_2 gives rise to the reduction of t-ZrO_2 concentration in ANZ sample by increasing the sintering temperature. This can be possibly attributed to the decreasing of tetragonal→monoclinic transformation temperature by the formation of solid solution of TiO_2 in t-ZrO_2 [12] and the enlargement of zirconia particles higher than the critical size of tetragonal→monoclinic transformation [13]. The electron microscope images of ANZ and ANZT samples (typically, Fig. 6a and b) show the two different size of zirconia particles, 0.9 ± 0.5 and 2.8 ± 0.8 μm, respectively.

From the results of Figs. 1 and 3, one would expect to distinguish a connection between t-ZrO_2 retention and density of the composites sintered at the different temperatures. As can be seen, the lower compact composites obtain the higher t-ZrO_2 concentration. This effect has been noted previously [9] and the possible explanation is the reduction of compaction tension, which enhances tetragonal to monoclinic transformation.

4. Conclusions

The present experimental results indicate that the addition of TiO_2 to mullite-ZrO_2 composites prepared from different alumina sources leads to change of reaction sintering, densification and microstructure which can alternately alter the formation temperature and retention of t-ZrO_2 phase in these composites. The tetragonal phase is not detected in the mixture of α-alumina and zircon sintered below 1500 °C, while by adding TiO_2 due to the extent of reaction t-ZrO_2 peaks appear at low sintering temperature (e.g. 1400 °C). In this mixture, no significant change of t-ZrO_2 concentration is noted in composites containing TiO_2 and without it in the final sintering temperature (1600 °C). At all sintering temperatures the composites derived from aluminium nitrate as the alumina source have higher t-ZrO_2 concentrations than when alumina is used (with and without TiO_2). The concentration of t-ZrO_2 decreases by introducing TiO_2 in aluminium nitrate derived composites.

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