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Porous mullite–ZrO_2 composites from reaction sintering of zircon and aluminum

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Abstract

Mullite–zirconia porous bodies were prepared by reaction sintering of zircon and alumina derived from oxidation reaction of Al at sintering temperatures between 1200 and 1600 °C. The results show that the incorporation of TiO_2 improves the oxidation reaction of Al, dissociation of zircon subsequently formation of mullite and zirconia. Composites containing TiO_2 obtain a high tetragonal concentration at 1500 °C, which reduces by increasing sintering temperature to 1600 °C. No tetragonal zirconia phase was detected at 1500 °C in TiO_2-free composites while tetragonal concentration was increased over this temperature. The major oxidation reaction of Al proceeds with a liquid–gas mechanism that is suitable for producing low dense ceramics. In spite of the higher porosity of the composites containing TiO_2, they possess almost the same flexural strength values as obtained from the TiO_2-free composites.

Keywords: B. Composites; D. Mullite; D. Zirconia; D. TiO_2; Porous materials; Aluminum; Zircon

1. Introduction

Porous ceramics can be used as lightweight structural components, catalysts carriers for chemical plants and automobiles, heat exchangers, acoustic absorbers, dust collectors, filters and electrods [1]. Several studies have been carried out to obtain ZrO_2–Al_2O_3–SiO_2 system with and without addition of TiO_2. As known, TiO_2 is the most effective additive for improving sintering in mullite–zirconia composites [2]. It seems that no attempt has been made for producing porous ceramics in ZrO_2–Al_2O_3–SiO_2 system by the reaction sintering of zircon and aluminum using TiO_2 additives for improving oxidation reaction of Al. Fabrication of porous mullite–zirconia composites is due to the fact that the transformation of Al to α-alumina leads the 28% volume expansion and by the formation of alumina particles, the reaction sintering of alumina and SiO_2 of the zircon conducts the formation of mullite. The directed oxidation of molten Al and reaction bonding of aluminum oxide in Al/Al_2O_3 composites has been reported [3,4]. The reaction-bonded alumina (RBAO) process involves milling of a mixture of Al metal and various ceramic oxide powders follows by heat-treating of the compacted powders in air such that the metal is oxidised to small Al_2O_3 particles which sinter and thereby bond the large ceramic powders [5,6]. In this work, the reaction sintering of zircon and aluminum for obtaining porous ceramics in the ZrO_2–Al_2O_3–SiO_2 system is studied. In addition, the effect of TiO_2 on reaction sintering, densification, mechanical strength, oxidation reaction of Al and retention of tetragonal zirconia phase was investigated.

2. Experimental procedures

The raw materials were zircon powder (Zircosil 5; Cookson Matthey Ceramics & Materials) with average particle size 4 μm, aluminum powder (local supply, passed through 200 mesh sieve) and TiO_2 (Merck). Three compositions were prepared by the mixing of zircon and aluminum powders with summarized names ZAL, ZALT and ZALT1 (0, 1.5 and 3 wt.% TiO_2, respectively). Powder compositions

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were mixed for 20 min by a planetary mill. The mixed powders were uniaxially pressed at 80 MPa. The pellets were reaction-sintered in an electrical temperature-controlled box furnace with molybdenum disilicide elements in air at a heating rate of 10 K/min to a maximum temperature and held for 2 h. Density and porosity measurements of sintered specimens were determined by the Archimedes method using distilled water. The progress of the chemical reaction between aluminum and zircon was examined by X-ray analysis with a Philips' Diffractometer Simens D-500 System, using Cu Kα radiation. In as-sintered samples the area of the peaks (1 1 0) of orthorhombic mullite, (1 1 3) of α-alumina, (2 0 0) of zircon and (1 1 1), ($\bar{1}$ 1 1) of monoclinic zirconia was used for phase evolutions. The retained tetragonal fraction of ZrO_2 was obtained from the ratio of intensity of the (1 1 1) tetragonal peak to the sum of the intensities of the (1 1 1) and ($\bar{1}$ 1 1) monoclinic and (1 1 1) tetragonal peaks [7]. The X-ray results were examined three times and the error of the intensity measurements was estimated to be ±4%. Flexural strength tests were carried out on rectangular cross-section bars 52 mm × 14 mm × 4 mm (10 bars) at room temperature by using 4-point bending with a 20 mm span between the inner rods and 40 mm span between the outer rods. The scatter of probability of failure was estimated at $F \sim n/(N+1)$, where n is the ranking of the sample and N the total number of samples, and plotted versus the measured strength value for each value of n. The microstructure observations were carried out by scanning electron microscopy (Stereoscan 360, Leica Cambridge) on polished thermally etched surfaces (100 °C below the sintering temperature for 30 min).

3. Results and discussion

Figs. 1 and 2 illustrate the formation of zirconia and mullite from the reaction sintering of oxidized aluminum with zircon. As can be seen and previously reported [8] the formation of zirconia and mullite promotes in the ZALT and ZALT1 compositions at the final sintering temperature. The X-ray diffraction patterns revealed the greater retention of tetragonal zirconia phase in the ZALT1 and ZALT samples between 1400 and 1500 °C (Fig. 3), which may be attributed to the formation of zirconia phase at the lower temperatures (Fig. 1), and because of that it is postulated that the size of tetragonal particles remains below the critical size for tetragonal to monoclinic zirconia transformation [9,10]. By increasing the sintering temperature to 1600 °C, the concentration of tetragonal phase reduces in samples containing TiO_2, while increases in ZAL sample due to the dissociation of zircon over 1500 °C (Fig. 1). As Fig. 4 shows, the weight gain due to the oxidation reaction of Al is more in samples containing TiO_2 than the TiO_2-free sample. It is noteworthy that there is a small increase of the weight gain during the holding of sintering temperature over 1500 °C in the samples containing TiO_2, which indicates the intimate completion of oxidation reaction. As reported [11], the oxidation of Al takes place at temperatures over 380 °C and dominant reaction mechanism is the solid–gas reaction of Al particles with the diffusion of oxygen along grain boundaries in the large particles and via microcracks in the oxide skin of smaller particles. The microcrack formation is due to a large difference in thermal expansion coefficient between Al_2O_3 (8.3×10^{-6} K^{-1}) and Al (25×10^{-6} K^{-1}), and subsequently a large volume expansion (28%) as the result of Al to Al_2O_3 transformation. Furthermore, the formation of relatively large hollow channels was reported

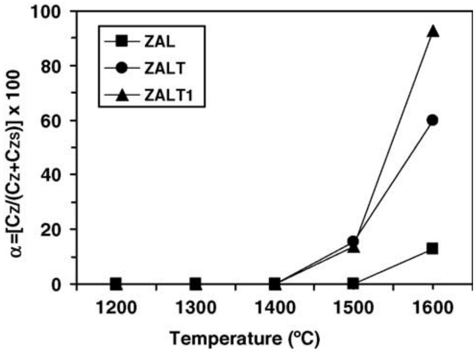

Fig. 1. Zirconia formation vs. temperature after 2 h heating. C_Z and C_{ZS} are the concentration of zirconia and zircon, respectively. α gives the value of zircon dissociation.

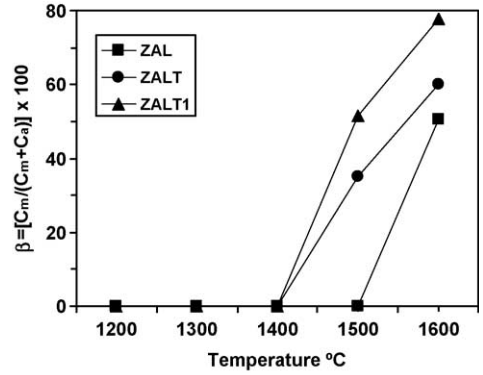

Fig. 2. Mullite formation vs. temperature after 2 h heating. C_m and C_a are the concentration of mullite and alumina, respectively. β gives the value of mullite formation.

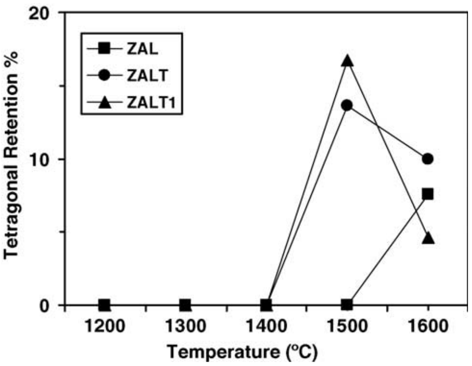

Fig. 3. Tetragonal zirconia fraction in reaction-sintered samples as a function of heating temperature after 2 h.

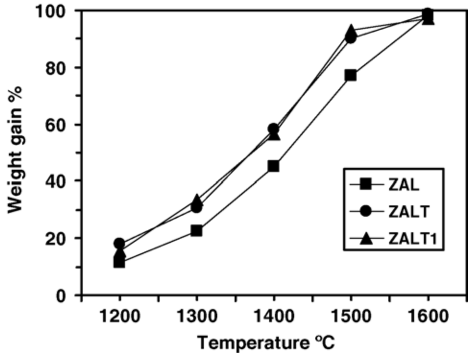

Fig. 4. Weight gain of the samples as a function of heating temperature (one sample was used in each measurement).

[12,13] probably due to the melt coagulation or sweating of the Al above its melting point during the reaction process. At 660 °C, the rest of Al melts and the oxidation reaction continues by a liquid–gas mechanism [13]. As Fig. 4 further reveals, the significant oxidation reaction of Al occurs between 1200 and 1500 °C sintering temperature, which implies that the oxidation reaction continues by a liquid–gas mechanism. This mechanism is suitable for producing low dense ceramics, since as reported [11] in producing dense RBAO ceramics, the process parameters are usually chosen that the oxidation step (up to 90% oxidation) takes place in the solid–gas regime. According to Holz et al. [14] for the oxidation reaction to occur within the solid–gas domain, all the Al particles should be smaller than 1 μm. In the present work, the major oxidation reaction of Al (nearly between 80 and 90%) occurs at temperatures over 1200 °C, since Al particle size is selected lower than 75 μm and this particle size confirms the liquid–gas mechanism for the most Al particles. As reported [11] the oxidation of small Al particles ($<r_c$) would dominate in the temperature regime between 450 and 520 °C. The retardation of Al oxidation in the present mixtures (Fig. 4) can be attributed to the large size of Al particles, since the oxide film covering the Al particles always serves as a protective layer and the complete oxidation cannot be achieved [15]. It has, therefore, become apparent that the oxidation reaction of Al particles inside of the pressed sample is more difficult and oxidation accelerates just when the microcrackes are formed. The enhancement of Al oxidation in samples containing TiO_2 can be attributed to the formation of aluminum ion vacancies by the substitution of aluminum ions by tetravalent titanium ions. These ion vacancies are the suitable paths for the diffusion of oxygen ions [16]. The bulk density measurements of sintered specimens (Fig. 5) show that samples containing TiO_2 have higher density than ZAL sample up to 1500 °C and above this sintering temperature the reverse is observed. This behaviour can be explained by the fact that in samples containing TiO_2 the applied heating energy consumes more in the densification of the sample rather than the oxidation reaction of Al, which occurs at lower temperatures, and besides, the reaction between alumina and zircon enhances by introducing TiO_2. The results of Table 1 show that in spite of the increase of porosity in specimens sintered at 1600 °C with increasing of TiO_2 content (the increase of 4.8 and 5.6% porosity in ZALT and ZALT1 specimens, respectively, relative to TiO_2-free sample), the flexural strength data are almost the same. The observed strength behaviour can be attributed to the more completion reaction between formed alumina and zircon in the ZALT and ZALT1 specimens rather than ZAL sample, as X-ray diffraction investigations confirmed (Figs. 1 and 2). Fig. 6 suggests that almost 50% values of the measured strength of the specimens containing TiO_2 are very close to the mean strength value while in ZAL sample no strength value is found.

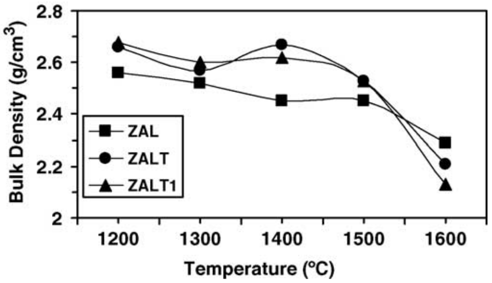

Fig. 5. Bulk density of the samples as a function of heating temperature (standard deviation: <0.03).

Table 1
Apparent porosity and Weibull parameters of specimens sintered at 1600 °C

	Apparent porosity (%)	σ_o	*m*
ZAL	49.3 ± 0.5	14.2	4.9
ZALT	51.8 ± 0.2	13.7	10.9
ZALT1	52.2 ± 0.6	13.9	6.6

The SEM micrographs corresponding to samples containing 0, 1 and 3 wt.% TiO_2 heated at 1600 °C for 2 h are shown in Fig. 7. TiO_2 additions increase the size of mullite grains rather than TiO_2-free samples, which are acircular and round. The morphology of round mullite grains implies the higher probability to grow in the presence of Al liquid. Further evidence of the mentioned above is demonstrated by considering the oxidation curves of the samples (Fig. 4). Since the oxidation behaviour of Al is retarded in ZAL samples, it can be postulated that the mullite grains remain in Al liquid for a longer time in ZAL rather than ZALT and ZALT1 samples. Because of the effect of TiO_2 addition on

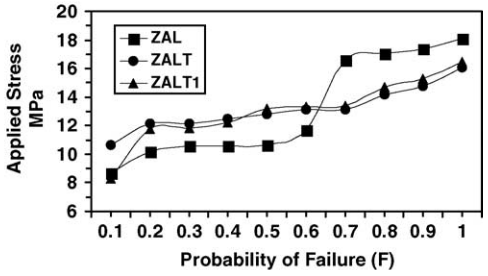

Fig. 6. Probability of failure vs. applied stress.

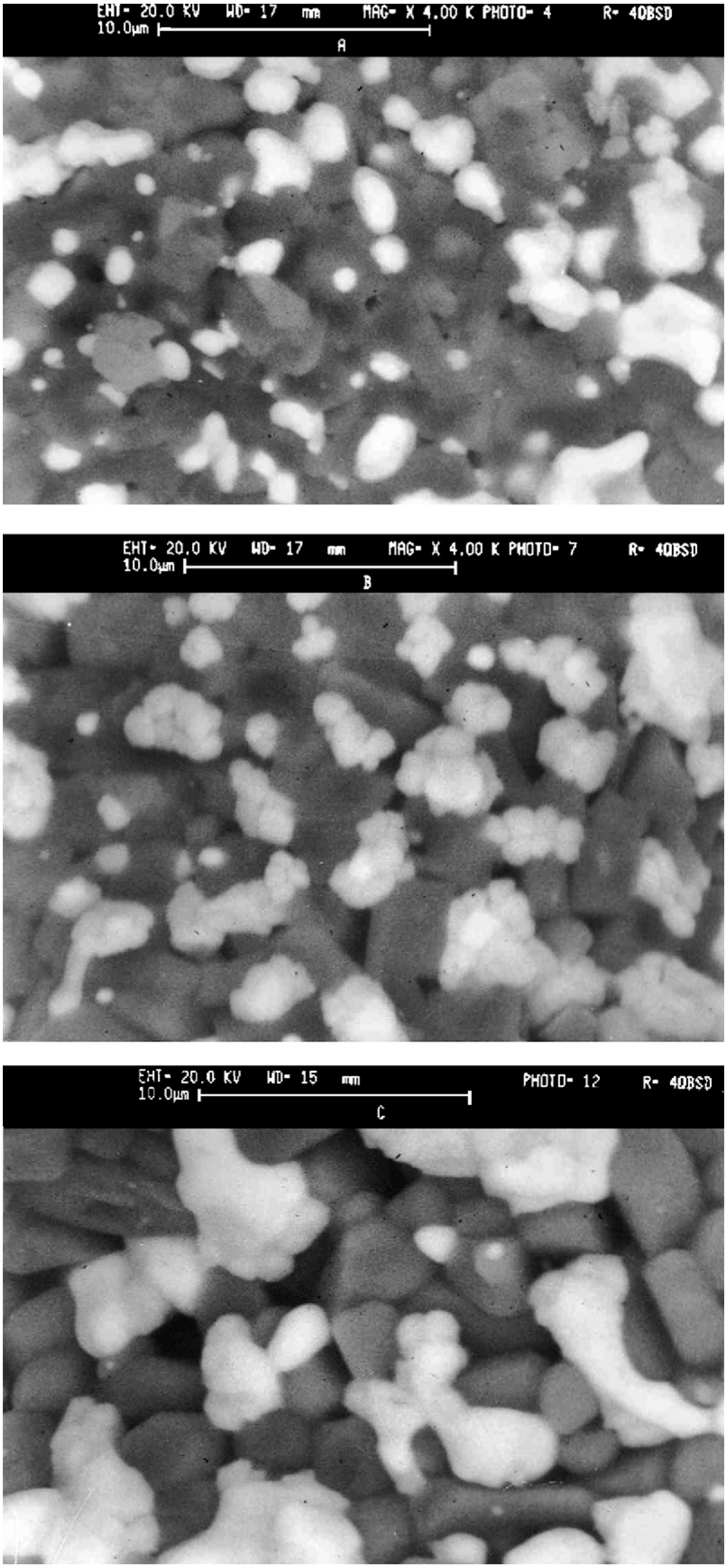

Fig. 7. SEM images of (a) ZAL, (b) ZALT and (c) ZALT1 samples sintered at 1600 °C for 2 h.

crystallization and microstructure of the composites it seems very probable that the improvement of strength of ZALT and ZALT1 samples in spite of the increase of porosity (Table 1) can be attributed to the further increase of mullite and ZrO_2 phases in these samples by the increase of TiO_2 content, as the Figs. 1 and 2 confirm.

4. Conclusions

Porous mullite–zirconia composites (45–47% porosity) can be produced by the mixture of zircon and aluminium powders sintered at 1600 °C in oxidizing atmosphere. TiO_2 addition accelerates the oxidation reaction of aluminium and the reaction between zircon and formed alumina powder. Over 80% of the oxidation reaction of Al occurs at a high temperature (over 1200 °C) and implies a liquid–gas mechanism, which is suitable for producing low dense ceramics. In spite of the higher porosity of composites containing TiO_2 they show almost the same flexural strength values like TiO_2-free composites.

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