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Fabrication and characterization of multi phase ceramic composites based on zircon–alumina–magnesia mixtures

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ABSTRACT

Five composites were prepared from zircon, alumina and magnesia. The variation of densification parameters, phase composition, thermo-mechanical properties, and microstructure with the firing temperatures were investigated. The rate of zircon dissociation was very low in the free magnesia composite, while it increased abruptly when 2.5 mass% MgO was added, then changed gradually in the followed batches. At low silica content, the formation of magnesium silicate and magnesia alumina spinel was more preferred than the mullite. Firing at 1300 °C did not show remarkable variations in the sintering of the investigated composites, while great discrepancies were observed at higher temperature. Firing at 1500 °C resulted in dense bodies (1–5.5% apparent porosity) for all composites excepting the magnesia free one (26% apparent porosity). The optimum properties were attained by the composite prepared from 62.5% zircon, 35% alumina and 2.5% magnesia, when fired at 1500 °C, 2 h.

1. Introduction

Composite materials have an important industrial and technological role. The designing capability of the manufacturer in properties and behaviors is enhanced by combining two or more different materials. However the final properties will not always be between the pure material ones. Once the constituent phases and the processing conditions are chosen the phase's proportion becomes one of the most important processing variables [1].

Zircon ($ZrSiO_4$) is a good refractory material because it does not undergo any structural transformation until its dissociation at about 1450–1700 °C, depending on the present impurities. It exhibits many attractive properties such as excellent chemical stability, a very low thermal expansion coefficient ($4.1 \times 10^{-6}\,°C^{-1}$ from room temperature to 1400 °C) and low heat conductivity coefficient (5.1 W/m °C at room temperature and 3.5 W/m °C at 1000 °C). In addition, zircon is a very hard material as its hardness is ranging from 7 to 8 Moh. These properties make this material a potential candidate as a useful structural ceramic. Thermal shock resistance is a behavior that affects the performance of Zircon ceramics due to the important extent of damage or degradation of the material. Hence Zircon based dense materials degradation by a thermal shock condition is sometimes the limiting property for its applications [2–4].

Zircon based ceramics have been processed in several ways, for example by room temperature pressing, hot pressing, sol–gel and slip casting. Zircon materials sintered in the range between 1500 °C and 1650 °C achieved densities over the 99% of the theoretical depending on the processing route. There are several studies of composites with zircon as the principal phase [1].

Garvie [5] demonstrated the positive effect of adding zirconia (ZrO_2) on the zircon mechanical properties while they were mutually compatible on all proportions up to the zircon dissociation temperature. The major effect of adding zirconia was the improvement of the composite thermal shock resistance. Ying et al. [6] concluded that the addition of 20% volume of stabilized zirconia (Y-TZP) in a zircon matrix resulted in a considerable increase of toughness and strength (about 40% and 20% respectively).

Zheng et al. [7] prepared zircon toughened alumina from zircon and $CaO–Al_2O_3–SiO_2$ ceramic powder. The fracture toughness of 95 wt.% alumina ceramics at first increased with the content of zircon then decreased at the point of 3.5 wt.%. The fracture toughness of the composite reached the peak 6.13 MPa $m^{(1/2)}$ with 3.5 wt.% addition.

On the other hand, zirconia–mullite ($3Al_2O_3 \cdot 2SiO_2$) composites revealed widespread applications due to their excellent properties such as high melting point, high strength and fracture toughness as well as good wear and thermal shock resistance [8–10]. Although zircon and mullite are different from the chemical and crystallographic point of view, their mechanical properties are similar [1].

The dispersion of zirconia in the mullite matrix improves the thermo-mechanical properties, leading to toughness by transformation and microcracking. Various methods were followed to prepare zirconia–mullite composites such as sintering of mullite and zirconia, reaction sintering of alumina and zircon, and reaction sintering

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of alumina, silica and zirconia. Due to their characteristic microstructure, composites prepared from alumina and zircon revealed some unique features, e.g. higher fracture toughness [11].

In addition, zirconia-toughened alumina (ZTA) ceramics have been widely studied because of their excellent mechanical properties [12].

Also, zirconia–spinel ($MgAl_2O_4$) composites resulted in highly compacted bodies with a good fracture toughness and flexural strength [13].

Heat treatment of zircon and magnesia was used to produce zirconia toughened forsterite. Hot pressing yields dense, fully reacted, materials with 35% of the zirconia present in the tetragonal form; these materials have strengths (>350 MPa) substantially greater than those of conventional forsterite ceramics [14].

Reports that 390% tensile strain can be achieved in 4 s at 1650 °C for a three phase zirconia–alumina–spinel ceramic composite demonstrated the advantages of using a three phase system for enhancing super plastic behavior in ceramics. Grain growth is severely constrained by second and third phases and the fine grain microstructure required for super plastic deformation is maintained. Super plasticity may be further enhanced by cations supplied from the additional phases which enhance diffusion along the ZrO_2 grain boundaries [15].

In view of the benefits of this three phase concept, the present work aims at preparing multi-phase composites based on zircon, alumina and magnesia. The effect of composition and firing temperature on the phase evolution, microstructure and technological properties of the investigated bodies was thoroughly studied.

2. Experimental procedure

Starting powders were zircon with ZrO_2 = 65.74 wt.%, SiO_2 = 34.01 wt.%, Fe_2O_3 = 0.1 wt.% and TiO_2 = 0.15 wt.%, $D_{0.5}$ = 1.0 μm, (Kreutzonit Super FF, Helmut Kreutz, Germany), commercial calcined alumina with Al_2O_3 = 98.2 wt.%, SiO_2 = 0.74 wt.%, Fe_2O_3 = 0.41 wt.%, TiO_2 = 0.23, CaO = 0.27 wt.%, Na_2O = 0.1 wt.%, MgO = 0.07 wt.% and K_2O = 0.05 wt.%, $D_{0.5}$ = 90 μm, (Alexandria company for refractories, Alexandria, Egypt) and high purity magnesia with 95 wt.% MgO, (Prolabo, Rhône-Poulenc, France).

Five batches, Z1–Z5, were formulated according to Table 1. The powders were mixed in a ball mill and then uniaxially semi-dry pressed at 150 MPa. The formed specimens were dried overnight at 110 °C and fired at 1300–1500 °C with a soaking time of 2 h.

The densification parameters in terms of bulk density and apparent porosity were determined by the Archimedes method according to ASTM C373 [16]. The linear shrinkage was calculated by the measure of the samples diameter before and after firing. A thermal shock test was conducted by subjecting the fired specimens to 20 cycles of 1000 °C/air quenching, 15 min each. The thermal shock resistance was identified both qualitatively by visual inspection and quantitatively through the variation of cold crushing strength after the thermal shock tests. A hydraulic press machine (SEIDNR-Riedlinger type, Germany) was used to evaluate the cold crushing strength according to ASTM C133 [17] while the hardness were determined by means of a knoop indenter with a load of 2 kg and dwell time of 40 s as defined by BS EN 14205 [18]. Phases and their relative mass fractions (not including the remaining glass) of either raw materials or fired specimens were estimated by X-ray diffraction (Philips 1730 with Ni filtered Cu Kα radiation at a scanning speed of 1° 2θ/min, S-Q software). Exactly weighed samples were used at similar lab conditions for the semi-quantitative way of comparison. The microstructure and microchemistry of the specimens were carried out by means of scanning electron microscope (SEM; JXA-840A electron probe microanalyzer, JEOL, Japan) attached with an EDAX unit.

Table 1
Investigated batches compositions.

Batch	Composition, mass%		
	Zircon	Alumina	Magnesia
Z1	54.5	45.5	–
Z2	62.5	35	2.5
Z3	68.5	27	4.5
Z4	73	21.5	5.5
Z5	76.5	17	6.5

3. Results and discussion

3.1. Phase compositions

Figs. 1–3 represented the XRD patterns of the fired specimens while Table 2 showed their semi-quantitative mineralogical compositions. After firing at 1500 °C, free magnesia samples were

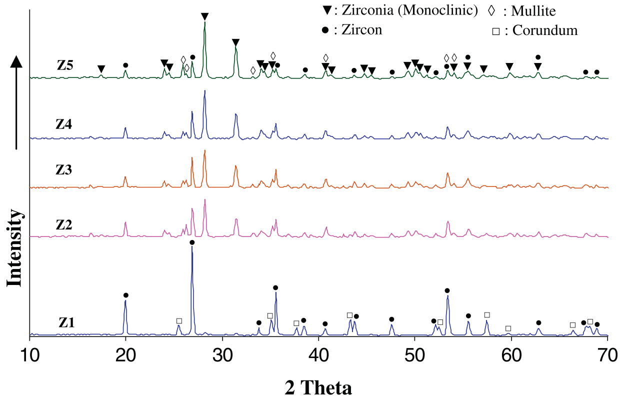

Fig. 1. XRD patterns of Z1–Z5 fired at 1500 °C, 2 h.

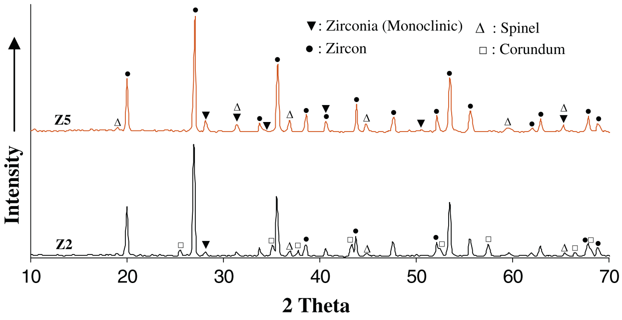

Fig. 2. XRD patterns of Z2, Z5 fired at 1400 °C, 2 h.

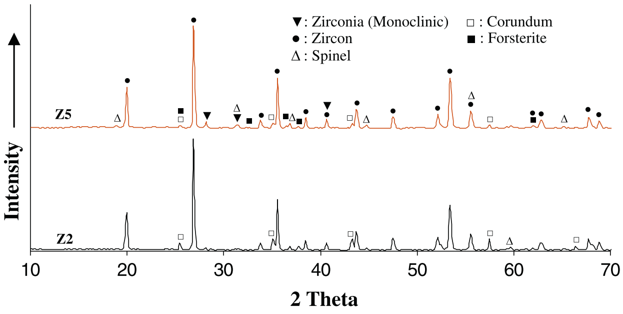

Fig. 3. XRD patterns of Z2, Z5 fired at 1300 °C, 2 h.