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Ceramics International 34 (2008) 429–434

CERAMICS INTERNATIONAL

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In situ formation of zirconia–alumina–spinel–mullite ceramic composites

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Received 27 March 2006; received in revised form 27 June 2006; accepted 3 November 2006
Available online 8 December 2006

Abstract

A study was made to prepare and characterize multicomposite containing zirconia–mullite–spinel [ZrO_2–$Al_6Si_2O_{13}$–$x$$MgAl_2O_4$ ($0.25 \leq x \leq 4$)]. This multicomposite was prepared by reaction sintering of relatively pure commercial grades of zircon, alumina and magnesium carbonate. Spinel and mullite could be in situ formed, while ZrO_2 evolved mainly in monoclinic polymorph. The sintering properties in terms of bulk density (BD) and apparent porosity (AP) were measured. The formed phases were identified by X-ray diffraction pattern (XRD). Cold crushing strength (CCS) of the fired and thermally shocked bodies was evaluated. The fractured surfaces of the fired compacts were scanned by SEM. The results showed great dependence on the firing temperature as well as zircon content, type and amount of glassy phase. XRD exhibited that all samples contain m-ZrO_2 and Al_2O_3 and with decreasing the amount of MgO and increasing zircon, the spinel phase decreases while mullite begins to form at high zircon contents. Batches containing mullite, ZrO_2 and Al_2O_3 gave higher mechanical properties. Also, all samples retained more than 90% of their original strength after being subjected to 20 cycles of thermal shock ($\Delta t = 1000\ ^\circ C$).

Keywords: B. Composites; Engineering ceramics; High temperature application; Advanced materials

1. Introduction

It is widely accepted that the fabrication of composite materials is a rational strategy to design materials with properties that cannot obtained for a monolithic material. The appropriate selection of a matrix phase and the combinations made from various grains to form ceramic composites with better strength and toughness has become widely recognized as a method for producing materials suitable for high temperature and engineering applications. Among most of the studied composites, ZrO_2 bearing materials are considered as one of the most promising materials in refractory ceramics candidates. Recently, several studies on the systems alumina/zirconia [1], mullite/zirconia and cordierite/zirconia [2–13] have shown that fine ZrO_2 dispersions in a ceramic matrix can affect the sinterability and considerably improve the mechanical properties. Magnesium aluminate spinel ($MgAl_2O_4$) and mullite ($3Al_2O_3{\cdot}2SiO_2$) based ceramics can exhibit outstanding high temperature strength, low thermal expansion coefficients, good creep resistance and excellent chemical stability. However, the poor mechanical properties at room temperature rather than their difficult densification may limit their field of applications. This has led to a range of approaches involving sintering of their precursors, i.e. mixture of components rather than pure monoliths. Also, spinel and mullite exhibit significant grain growth, which inhibit sintering kinetics. Micrometric zirconia powder additions to spinel and mullite can overcome all the disadvantages resulting from individual spinel or mullite. However, most attention was paid to study of ZrO_2/mullite and ZrO_2/spinel composites [14–22], but up to the best of our knowledge, very few published works have been concerned with the ZrO_2–spinel–mullite multicomposite.

The present work studies an in situ formation of ZrO_2–spinel–mullite multicomposite by a simple one step reaction sintering of commercial grades of zircon, alumina and magnesium carbonate according to the following reaction:

$$2ZrSiO_4 + (3 + x)Al_2O_3 + xMgO \rightarrow 2ZrO_2 + 3Al_2O_3{\cdot}2SiO_2 + xMgAlO_4$$

This reaction depends primarily on the reaction of both alumina and magnesia to form spinel and on the ease of

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doi:10.1016/j.ceramint.2006.11.002

dissociation of zircon to form zirconia and mullite. The use of relatively pure commercial grades of the starting materials is believed to bring the reaction toward completion due to the presence of contaminating oxides that may ease both reactions to yield ceramic materials suitable for high temperature structural and engineering ceramics applications as well as their utilization as direct or permanent in situ bonds between the aggregate constituents of the refractory linings of metallurgical vessels.

2. Materials and experimental procedures

The materials used in this study were relatively pure, commercial grades of zircon sand (>98.5% $ZrSiO_4$, Australian zircon sand flour Westralian Sand, West Perth, Western Australia), calcined alumina (>99% Al_2O_3, Alcoa, UK) and a local chemical grade magnesium carbonate (>98.5% $MgCO_3$, El Nasr Pharmaceutical Co.). The particle size of used zircon and alumina raw materials was determined using a Mastersizer 2000, Malven (UK). The mean particle sizes of these materials (D_{50}) were 1.38 and 4.47 μm, respectively. The surface area was carried out by BET method using an (ASAP200) Micromeritics GmbH Moenchengladbach using N_2 absorpant gas. The specific surface areas of zircon and alumina were 6.08 and 1.18 m^2/g, respectively. The particle size and surface area of $MgCO_3$ were not determined. The chemical composition of these materials is illustrated in Table 1. $2ZrO_2$–$3Al_2O_3 \cdot 2SiO_2$–$xMgAlO_4$ composition was made by mechanical mixing of stoichiometric amounts of zircon, alumina and magnesium carbonate to give the desired x-mole of spinel (x = 4, 2, 1, 0.5 and 0.25 mol). Accordingly, five batches were designed and their compositions are represented in Table 2. Each batch was carefully weighed and mixed using high-speed attrition mill (2000 rpm) in deionized water medium using 1–2 mm Mg-stabilized ZrO_2 balls. The dried slurries were ground and passed through 100 μm US standard testing sieve. The powders were uniaxially pressed under pressure of 100 MPa into cylindrical compacts of 2.5 cm diameter and 2.5 cm height. The compacts had more than 60% relative density based on the calculated green densities. Their calculated values are inserted in Table 2. Firing of the formed compacts were conducted in an electrically heated furnace at 1400–1550 °C with 50 °C intervals, and 2 h soaking at the peak temperature. The densification parameters in terms of bulk density and apparent porosity of the fired compacts were determined at each firing temperature according to ASTM-C20 method. The developed high temperature phases formed at maximum firing temperature were detected by X-ray using a Philips 1730 diffractometer with Ni filtered Cu Kα radiation at a scan speed of 0.5 min^{-1}. The obtained microstructure was examined using scanning electron microscope (Philips XL 30) of gold coated fractured samples. The samples were thermally etched for 1/2 h at 1350 °C before scanning. Cold crushing strength (CCS) was determined using a hydraulic testing machine for both as-fired samples and those after 20 cycles of thermal shock ($\Delta t = 1000$ °C) using water as quenching medium. The latter strength value is considered as an estimation of the thermal shock behavior of the prepared compositions.

Table 1
Chemical analysis of staring materials

Oxide	Chemical composition (wt.%)		
	Zircon	Al_2O_3	$MgCO_3$
SiO_2	35.37	0.03	–
Al_2O_3	<1.0	99.80	–
ZrO_2	62.64	–	–
TiO_2	0.15	–	–
Fe_2O_3	0.15	0.04	–
CaO	–	0.03	–
MgO	–	–	45
Na_2O	–	0.1	–
SO_4^{2-}			<1.2
L.O.I	–	–	51.6

Table 2
Batch composition, green and theoretical densities of the prepared composites

Mix no.	Batch composition (wt.%)			Formed spinel content	Density (g/cm^3)		
	Zircon	Al_2O_3	MgO		P_1	P_2	P_{obs}
1	29.53	57.49	12.99	4	3.91	3.84	2.41
2	38.31	53.27	8.42	2	4.06	3.92	2.52
3	45.0	50.06	4.95	1	4.17	3.99	2.67
4	49.30	47.99	2.71	0.5	4.25	4.03	2.77
5	51.78	46.80	1.42	0.25	4.30	4.05	2.84

P_1: theoretical green density (of reactants); P_2: theoretical fired density (of products); P_{obs}: observed green density.

3. Results and discussion

3.1. Sintering of prepared composites

Based on the previous equation, complete reaction of zircon with alumina and magnesia give products of relatively lower densities than those of the reactants. Taking into consideration the difficulty of such reaction completion, fully dense compacts are not expected to be obtained under these conditions. This is clearly seen from Table 2 where the calculated green densities (reactants) of all batches are higher than that of their fired counterparts (products). However, the observed green densities are lower than the calculated ones. The observed green density is largely dependent on other factors including particles fineness, shape, geometry, homogeneity and forming pressure. Fig. 1 shows the bulk density of the fired compacts at different temperatures. In general, the bulk densities are lower than the theoretical densities which steadily increase with increasing zircon content. On the other hand, increasing the firing temperature led to fully sintered compacts and increased the bulk density. The effect of firing temperature is greatly pronounced in low and high zircon contents while it has a little effect in intermediate zircon contents. This may be due to the zircon/MgO ratio which plays an important role in zircon dissociation. For all the batches, the increase in firing temperature from 1500 to 1550 °C had a nearly negligible

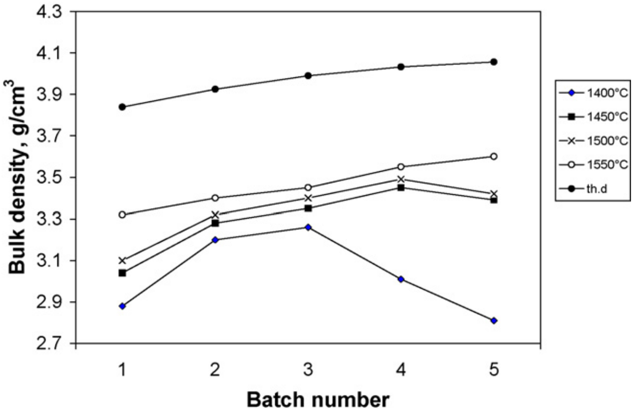

Fig. 1. Bulk density of the fired compacts at different temperatures.

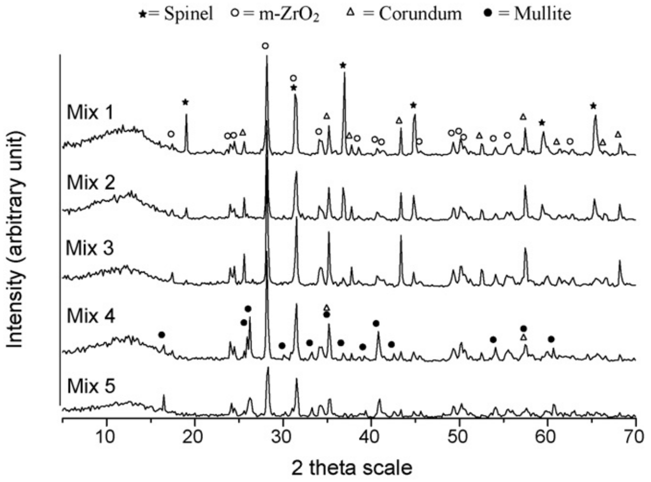

Fig. 3. XRD patterns of the formed phases after sintering at 1550 °C.

effect on the sintering process. This proved the completeness of reaction at this stage. Further increase in firing temperature is believed to lower all the properties of the fired compacts. Fig. 2 shows the apparent porosity of the fired specimens. A noticeable decrease in the porosity is obtained by increasing either zircon content or firing temperature. All samples exhibit apparent porosity less than 5%, especially after sintering ≥1450 °C.

3.2. Phase composition and mechanical properties

Fig. 3 shows XRD patterns of the phases formed at 1550 °C. In mix 1, monoclinic zirconia polymorph and spinel are the major phases beside a lesser corundum one. Mullite phase formed only in mixes 4 and 5, while spinel phase is gradually decreased with increasing zircon content. As Reynen and Filatli [23] pointed out; it is thought that the spinel formed by a reaction between Al_2O_3 and the stabilizer (MgO) of MSZ, hampered densification and caused microcracks inside the sintered bodies by stabilization of ZrO_2. No spinel lines were detected in mix 5. In fact, the presence of MgO beside Al_2O_3 led to the complete dissociation of zircon. The lack of mullite formation in the first three mixes indicates that the SiO_2 liberated from zircon dissociation is partially or totally consumed in the formation of Mg–Al–silicate glassy phases. The consumed part of MgO to form these glassy phases, leads to a corresponding part of corundum to appear as free phase. The formation mechanism of mullite from zircon and alumina [24] comprises the following steps:

(1) initial formation of glassy phase from the present impurities with partially thermal dissociated zircon;
(2) dissolution of zircon into this glassy phase;
(3) dissociation of zircon and the formation of ZrO_2 and higher SiO_2-rich glassy phases;
(4) dissolution of Al_2O_3 in this glassy phase and its concentration in the melt increases until the stoichiometric composition of mullite is obtained.

In fact, the dissolution of ZrO_2 in the glassy phase increases its viscosity which acts as a physical barrier for the mobility of solid particles in this melt and once mullite is formed, it will crystallize rapidly. In contrast, fluid glassy phases (higher flux/SiO_2 ratio) may lead to formation of amorphous or poor crystalline mullite. It seems that mixes 4 and 5 fulfill the

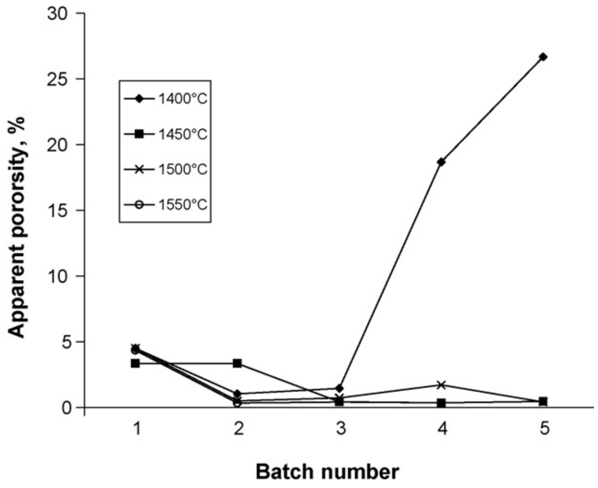

Fig. 2. Apparent porosity of the fired compacts at different temperatures.

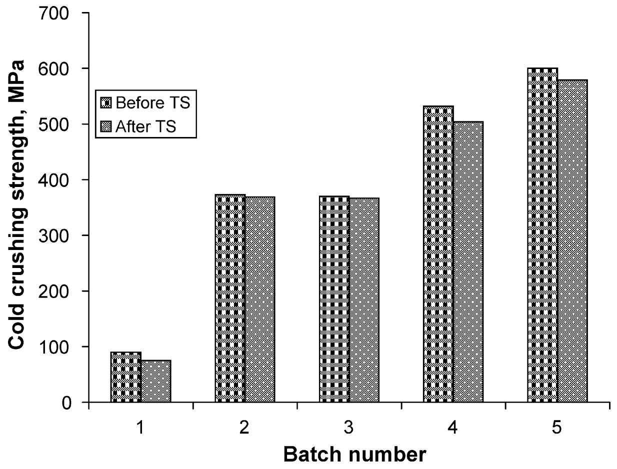

Fig. 4. Cold crushing strength of the composites sintered at 1550 °C after and before thermal shock test.

mullitization and sinterability increase with the incorporation of fluid and/or high amount glassy phases. In addition, the cold crushing strength values are exceptionally high for mixes 4 and 5 (Fig. 4 before thermal shock) which indicated the effect of the presence of mullite beside zirconia and corundum phases. Also, the type and amount of liquid phases as well as the microstructure of the fired bodies plays an important role in this concern.

It is well known [1] that alumina–zirconia sintered composites in the region with excess of alumina have higher strength and toughness than alumina itself. These composites have also excellent mechanical properties without any stabilizers as well as when using yttria as a stabilizer. However, in compounding alumina and magnesia stabilized zirconia (MSZ) which is applied to metal extrusion dies, etc., because of its high toughness and thermal shock resistance among zirconia sintered bodies, sufficient densification is difficult due to the formation of $MgAl_2O_4$. Therefore, excellent mechanical properties have not been provided.

As a trial to estimate the thermal shock resistance of these bodies, the retained strength of compacts subjected to 20 sudden heating–cooling cycles is compared with that of the original samples (Fig. 4 after thermal shock). Since all compositions gave 20 cycles with retention of more than 90% of their original strength, the resulting bodies are recommended for applications where extensive temperature fluctuations may exist.

3.3. Microstructure

Scanning electron micrographs of fractured surfaces of the compacts fired at 1550 °C are shown in Figs. 5 and 6. Fig. 5 exhibits photomicrographs of mixes 1–3. High homogeneity spinel (Point S) and zirconia grains (Point Z) beside less corundum (Point A) ones are appeared in mix 1 (micrograph 1b). Zirconia appeared in fine minute rounded particles (white) with grain size of about 2–3 μm. Euhedral spinel grains (2–4 μm) also appeared and did not undergo grain growth due to the presence of ZrO_2. Spinel crystals were interlocked by prismatic corundum crystals with different sizes. Both of these phases are direct bonded. In mix 2, fewer spinel grains could be detected beside the ZrO_2 (white) and corundum (gray) grains.

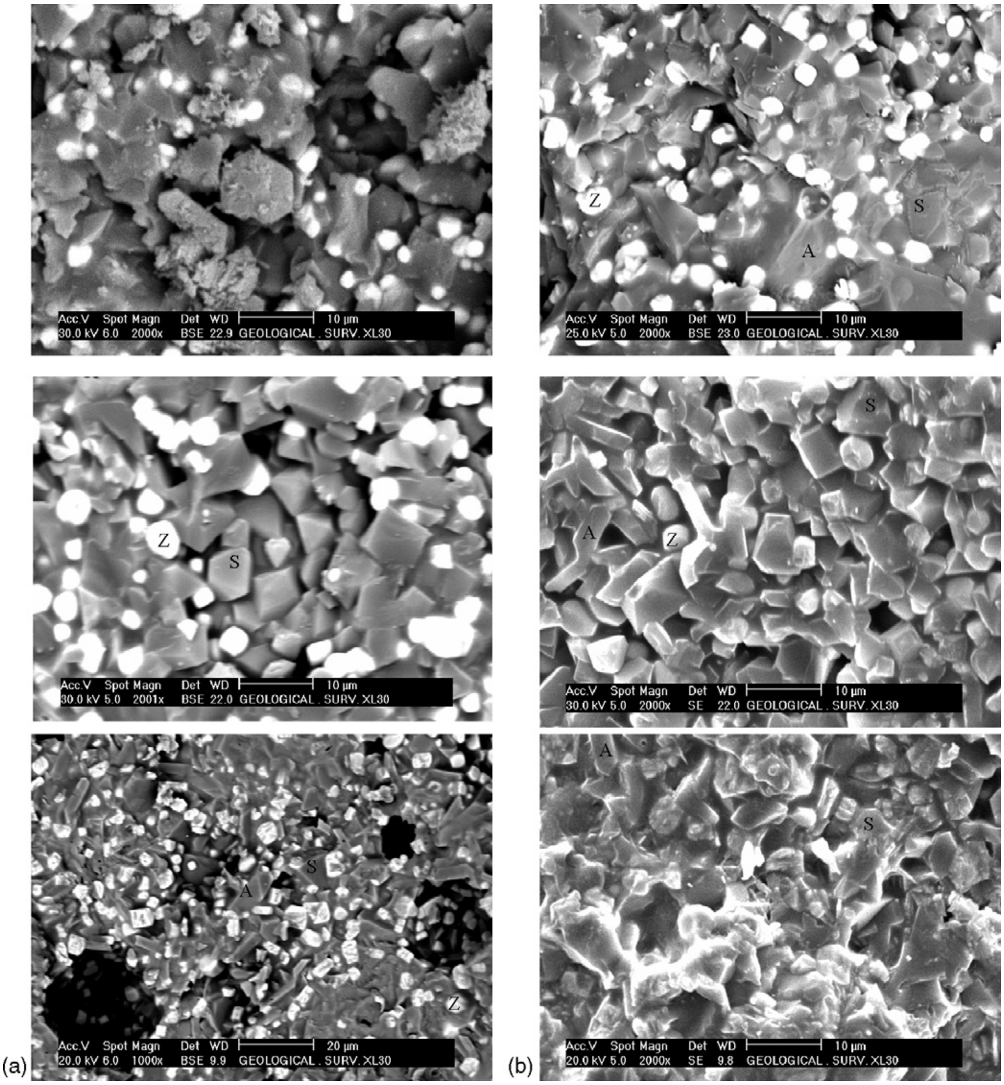

Fig. 5. SEM micrographs of the composites sintered at 1550 °C at two magnifications (batch nos. 1–3).

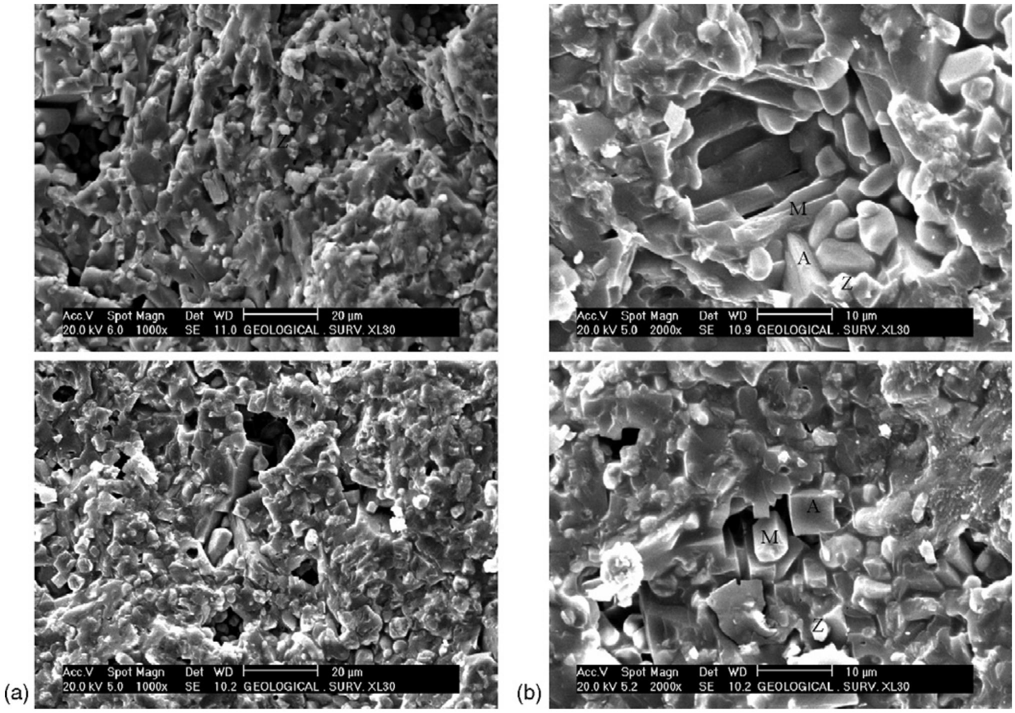

Fig. 6. SEM micrographs of the composites sintered at 1550 °C at two magnifications (batch nos. 4 and 5).

The corundum grains started to loose their edges and higher glassy phase appeared in mix 3 where the grains are connected to each other in homogeneous network. Mullite is formed as rectangular prisms (may be due to the growth of mullite needles or lathes) or equiaxed grains in mixes 4 and 5 (Fig. 6). Where the spinel is difficult to detect in mix 4, and completely absent in mix 5, rigid structure with grains sealed together (with no rims) is appeared indicating high glassy phase formation.

4. Conclusion

The addressed compositions could be used to produce zirconia–spinel–mullite ceramic composite through in situ reaction sintering. The sinterability is greatly dependent on both firing temperature and zircon content, which undergoes complete dissociation in all compositions. Zirconia is the major phase evolved in the studied composites beside alternative amounts of spinel and corundum. Mullite formation is independent on the Al_2O_3/SiO_2 ratio, but greatly dependant on the type and amount of glassy phase present. The incorporation of lower MgO and Al_2O_3 and higher ZrO_2 contents led to the formation of excellent high temperature multicomposites. Batches containing mullite, ZrO_2 and Al_2O_3 gave higher mechanical properties. Also, all sample retained more than 90% of their original strength after subjected to 20 cycles of thermal shock.

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