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Zirconia–mullite materials prepared from semi-colloidal route derived precursors

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Abstract

A semi-colloidal technique was used to synthesize a precursor powder of zirconia–mullite composites using an aqueous suspension of sillimanite powder and zirconium oxychloride solution and adding micron sized aluminium powder to the precipitate (calcined) thus obtained. The precursor powder was compacted in presence of MgO and CeO_2 additives and fired at different temperatures. The physico-mechanical properties of the sintered compacts were influenced both by the firing temperatures and the nature of additives present in the compacts. MgO was found to exert a greater influence on the physico-mechanical properties of the composites than CeO_2.

Keywords: Semi-colloidal technique; Zirconia–mullite; Additives

1. Introduction

Mullite–zirconia composites find extensive applications due to a combination of several advantageous properties, such as, refractoriness, chemical inertness, low thermal expansion and mechanical properties. Many workers studied the synthesis of mullite–zirconia composites by different routes to improve their thermo-mechanical properties through the controlling of microstructure. These reported routes have different advantages. Prochazka et al. [1] prepared ZrO_2–mullite composites by a conventional mixing of fused mullite and zirconia powder by attrition milling, the samples were fired at 1600 °C and it was observed that the addition of ZrO_2 was effective in enhancing densification and retarding grain growth of mullite. Mizuno et al. [2] prepared zirconia–mullite composites by sol–gel methods using mullite and zirconia sol as starting material; the density reached nearly 100% by firing at 1550 °C, which was lower temperature than that used in the conventional sintering method. Das and Banerjee [3] developed zirconia–mullite composites of appreciable flexural strength and fracture toughness using zircon sand and beach sand sillimanite with dysprosia additive, the reaction-sintered material was observed to possess an improved microstructure. Bhattacharjee et al. [4] used thermal plasma for the preparation of zirconia–toughened mullite achieving superb high temperature mechanical properties. Jin et al. [5] studied the effects of Nb_2O_3 addition on the sinterability, microstructure and mechanical behaviour of zirconia toughened mullite alumina composites. Porous mullite bodies were infiltrated with $ZrOCl_2$ and $Al(NO_3)_3$, $9H_2O$ solution and densified bodies showed enhanced mechanical properties.

In most of the previous studies for the synthesis of zirconia–mullite composites, either synthetic materials, like organic and inorganic salts of aluminium and zirconium were used as starting materials for colloidal (sol–gel or co-precipitation) route, or, naturally occurring materials, like, sillimanite, zircon sand, etc. were used as the starting materials for reaction sintering process. But not much work was done on the combination of synthetic and natural materials and a combination of colloidal techniques and reaction sintering processes. In the present investigation, a new route, that of semi-colloidal processing was used to synthesize zirconia–mullite composites. In addition the influence of two different additives, MgO and CeO_2, was

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examined for their role on the fired properties of the fabricated composites.

2. Experimental

An aqueous solution of zirconium oxychloride was added to a suspension of sillimanite ($Fe_2O_3 \sim 0.27\%$) powder ($d_{50} \sim 19$ μm) and zirconium hydroxide was slowly allowed to precipitate and deposit on the sillimanite powder through the addition of ammonium hydroxide solution. The precipitated mass was filtered and washed thoroughly with de-ionized water to make it free from associated impurities, then dried at (110 ± 5)°C for 24 h and calcined at 850 °C for a period of 2 h to eliminate water and other volatile impurities. Micronized aluminium powder ($d_{50} \sim 12$ μm) was added in requisite proportion to the calcined mass by thorough mixing. The powder was divided into three parts. In one part no additive was used. In the second and third part light calcined MgO (L.R. grade) and CeO_2 (L.R grade) were added, respectively. The samples were compacted at 400 kg/cm^2 using a hydraulic press and fired at 1400, 1500 and 1600 °C (heating rate was 10 °C/min up to 1000 °C and 5 °C/min from 1000 °C to the final temperature firing) with 2 h soaking time at each firing temperature in an electrically heated muffle furnace. The fired samples were cooled at the rate of 2 °C/min. Firing shrinkage, bulk density, apparent porosity, specific gravity and flexural strength of the compacts were measured following procedures described in BS 1902, Part 1A, 1966. For each measurement five pieces of each sample were used. Both XRD analyses (with a Seifert XDAL 3000 diffractometer) and SEM analyses (with Leo, Cambridge, UK microscope) were carried out.

3. Results and discussion

At elevated temperature sillimanite is converted into mullite and silica. Aluminium powder added to the batch is converted to Al_2O_3 by oxidation at elevated temperature. The Al_2O_3 thus formed reacts with available silica to form mullite. Oxidation of aluminium powder generates considerable amount of heat ca., about 268.4 kcal/mol [6], which helps the sintering process of the composite providing additional thermal energy.

The batch composition was so proportioned as to develop 93.5% mullite and 6.5% zirconia in the sintered mass (Table 1). Refractoriness of such composition will be more than 1800 °C (as evident from the ZrO_2–Al_2O_3–SiO_2 ternary phase diagram [7]). With respect to ZrO_2, 9 mol% MgO was added to the batches. This composition after firing contains solid solutions of cubic and tetragonal zirconia (as evident from the ZrO_2–MgO binary phase diagram [8]). ZrO_2 is formed in the batches from the dissociation of zircon after firing the compacts. MgO can stabilize zirconia and it can form different liquid phases on reaction with silica, which will affect different physico-mechanical properties of the composites after firing. The cubic phase is formed first forming solid solution with MgO, from which some tetragonal phase is precipitated. CeO_2 used in the present investigation (10 mol% with respect to the ZrO_2 content) would form solid solution with ZrO_2 during firing, causing a stabilization of the tetragonal and cubic phase to lower temperature region. The presence of CeO_2 causes an increase in the unit cell of all the crystal forms due to the substitution of smaller Zr^{4+} (0.84 Å) by larger Ce^{4+} (0.97 Å). The system would give rise to high toughness owing to stress induced tetragonal to monoclinic phase transformation [9]. So from theoretical point of view both the additives can influence the physico-mechanical properties of zirconia–mullite composite.

The degree of oxidation of Al powder used in the batches with temperatures was calculated from the difference in the theoretical and actual weight gain of the batches after firing. With an increase in the firing temperatures (Fig. 1), the degree of oxidation of Al powder increased. The maximum oxidation of Al powder (about 98%) was observed in the batch containing CeO_2. But unlike the other batches, in this case percent oxidation did not increase with the increase in firing temperature from 1500 to 1600 °C. Considering the high bond strength of other oxides present in the system, like MgO, ZrO_2 and CeO_2 (all have higher melting points than Al_2O_3), the reduction of other oxides is the least likely reason for the Al oxidation, particularly when water vapor is present in the system as a result of the dehydration of zirconium hydroxide with the increase in temperature and the oxidation becomes kinetically controlled. In all the cases, therefore, a very high degree of Al-oxidation (on an average >90%) was observed. The un-oxidized, un-vaporized, trace quantity of Al remained in the fired batch (as detected in the XRD diagram of the fired sample), probably in the form of Al–Al_2O_3 cermet composite.

All the samples showed volume expansion after firing (Fig. 2). This also can be related to the oxidation of aluminium particles. The maximum expansion took place at the sintering temperature of 1500 °C for all the batches and

Table 1
Starting materials for different batches

Batch	$ZrOCl_2 \cdot 8H_2O$ (wt.%)	Sillimanite (wt.%)	Al-powder (wt.%)	MgO	CeO_2
I	18	70	12	–	–
II	18	70	12	0.2 parts[a]	–
III	18	70	12	–	0.9parts[a]

[a] Parts means added over 100% as parts per hundred (wt.%).

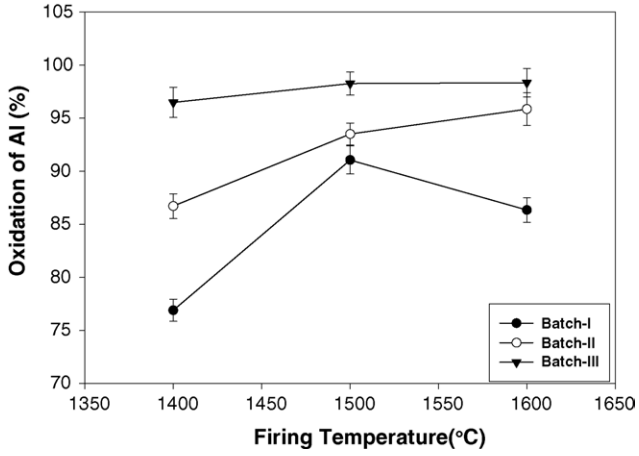

Fig. 1. Percent oxidation of Al in the samples with firing temperatures.

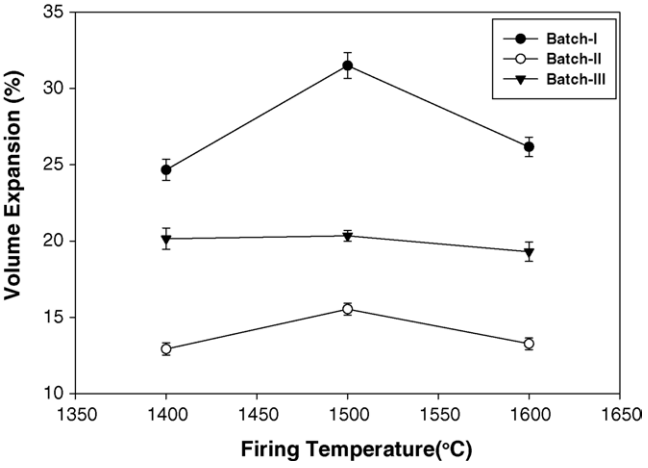

Fig. 2. Volume expansion of the samples with firing tempearture.

then it decreased at 1600 °C. It suggested the formation of some liquid phases in all the batches at the temperature range 1500–1600 °C which assisted in the densification through a liquid phase sintering approach. This densification somewhat reduced the magnitude of expansion. The

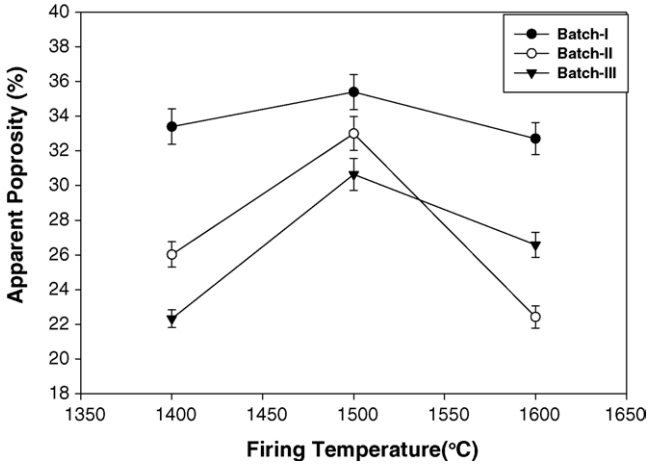

Fig. 3. Variation in apparent porosity with firing temperature (°C).

expansion data at 1500 °C indicated that there is a maximum conversion of Al to alumina and hence a volume expansion occurred and above 1500 °C, sintering assists the densification, which caused a volume reduction [10]. As sillimanite contains trace quantity of CaO and Fe_2O_3, the liquid phase composition most likely contained calcium aluminosilicate and iron silicate phases. Again the batch without any additive showed the maximum volume expansion at all the firing temperatures. It suggested the formation of more liquid phases in the batch containing additives. Batch with MgO additive showed the minimum volume expansion at all the three firing temperatures in the present investigation.

The maximum apparent porosity values of the samples were also observed at 1500 °C and it decreased at 1600 °C (Fig. 3). The batch without additive showed the maximum value of apparent porosity and the least exothermic reaction. The minimum value was observed with the batch containing MgO additive, which might be due to the formation of more liquid phases in the batch with MgO additive, acting to assist as pore closure through sintering. As a consequence to this change in porosity values, bulk density of the samples was also observed to be the minimum at the firing temperature of

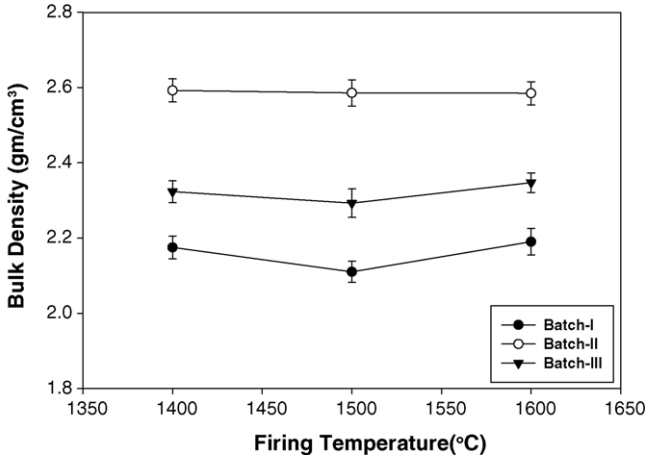

Fig. 4. Bulk density of the samples with firing temperatures.

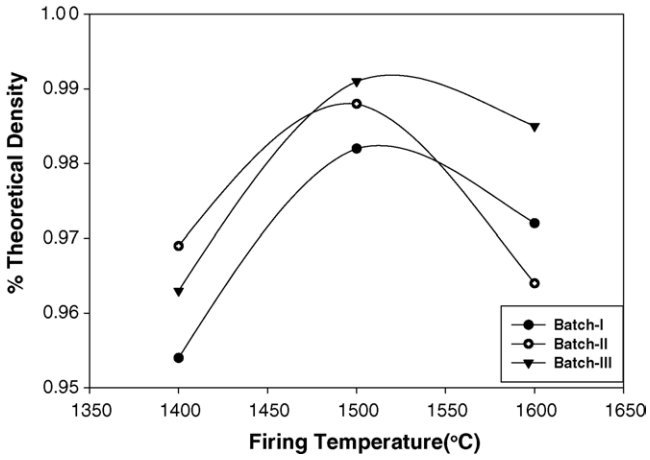

Fig. 5. Variation in percent theoretical density with firing temperature (°C).

1500 °C and maximum at the firing temperature of 1600 °C, respectively (Fig. 4). The batch without any additive had the lowest bulk density and the batch with MgO additive had the highest bulk density. A further detailed study on the kinetics of Al-oxidation in this system is, therefore, required for an optimal control of porosity and expansion of the fired samples. Theoretical density of the samples is 3.30 gm/cc (taking into account the sum of densities of all the theoretically developed phases) and all the samples had a true density (powder density) of more than 3.15 gm/cc, which indicated the formation of considerable amount of crystalline phases in the sintered masses. All the sintered masses contained some silica bearing liquid phases as a result of which, complete theoretical density was not achieved. Under the experimental condition, most likely the samples did not attain equilibrium phase compositions. The fractional densification, i.e., the ratio of actual true density and theoretical density was plotted as a function of the firing temperature (Fig. 5). The maximum densification was observed at the firing temperature of 1500 °C for all the samples. It indicated the formation of the maximum amount

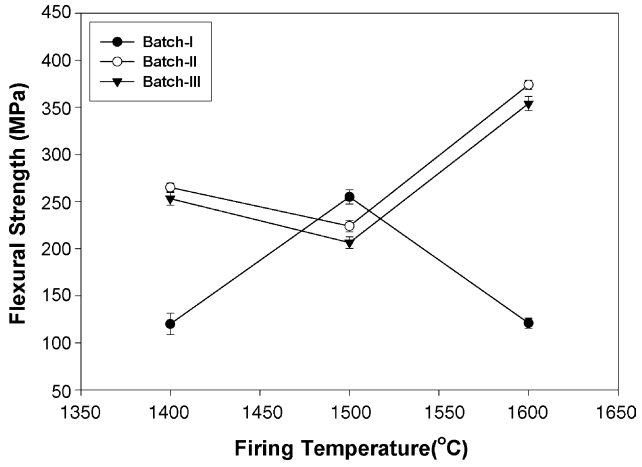

Fig. 6. Variation in flexural strength of the samples with firing temperature (°C).

of crystalline phases at this temperature. But this also resulted in the formation of maximum amount of porosity at this temperature. A decrease in true density values at the firing temperature of 1600 °C for all the samples suggested the generation of relatively more amount of amorphous silica bearing phases and here also the effect was the maximum for the batch with MgO additive. Apparent porosity values of the samples were also found to be less at this temperature.

For the sample without any additive, the maximum flexural strength was observed with samples fired at 1500 °C, whereas, for the samples containing the additives, the same was the minimum after firing at this temperature (see Fig. 6). For the sample without any additive the increase in the sintering temperature further decreased flexural strength significantly for the fired sample without any additive, but increased for both the fired samples with additives. Formation of calcium aluminosilicate and iron silicate type liquid phases at the intermediate firing temperature could be a reason for the deterioration of flexural strength. The liquid phase subsequently devitrified with the formation of more interlocking crystals (reinforcement of mullite matrix by inter-granular zirconia), which raised the flexural strength further. This effect was more prominent with the batch containing MgO additive. The decrease in flexural strength for the batch without additive, fired at higher temperature, is associated with the formation of segregated amorphous phase at the concerned temperature range.

XRD data of the sintered samples (not shown here) showed that mullite was the major crystalline phase in the sintered sample followed by corundum and zirconia. The relative proportions of the different crystalline phases were determined, see Table 2 [11] and it was observed that the proportion of mullite was the maximum in the batch containing MgO additive (Table 2). A considerable amount of corundum was observed in all the batches. Mainly tetragonal and monoclinic polymorphic zirconia was present in all the batches. The proportion of tetragonal zirconia was relatively more in the batches containing additives, particularly with CeO_2 due to the greater stabilization of the tetragonal zirconia phase within this composition and firing temperature. The average grain size of the batch without additive as calculated using Scherrer's formula [12] was observed to be 100 μm (standard deviation 4.83 μm) and in the batch with MgO was determined to be 93 μm (standard deviation 5.19 μm). In the batch with CeO_2 additive it was calculated to be 97 μm (standard deviation 4.47 μm). The smaller grain size of the batch containing MgO additive could be due to the pinning of grain boundaries of zirconia and mullite by MgO. From the SEM photographs of the samples it was observed that (Fig. 7A–C) fully developed mullite, zirconia and corundum crystals were present in the microstructure of all the batches. Distribution of different phases including the porosity was found to be more uniform in the microstructures of the batch

Table 2
Identified crystalline phases in the fired samples and their approximate relative proportion by XRD (firing temperature 1500 °C)

Batch number	Phases present and their approximate relative proportion
I	Mullite (74%), corundum (13%), *m*-ZrO_2 (6%), *t*-ZrO_2 (4%), cristobalite (2%), Al (1%)
II	Mullite (84%), corundum (6%), *m*-ZrO_2 (4%), *t*-ZrO_2 (5%), Al (trace <1%)
III	Mullite (79%), corundum (11%), *m*-ZrO_2 (2%), *t*-ZrO_2 (6%), *c*-ZrO_2 (1%), Al (trace <1%)

with MgO additive, for which the relative proportion of mullite phase was also found to be higher. The crystalline phases remained as interlocked in the microstructure and in the mullite-corundum inter-granular spaces zirconia grains existed in the form of clusters. Mean grain sizes of the samples were also rechecked from the microstructures [13].

4. Summary and conclusions

Precursor powder of zirconia–mullite composite was prepared precipitating zirconium hydroxide on the grains of sillimanite from an aqueous solution of zirconium oxychloride. Aluminium powder was used in the precursor material to form incipiently formed alumina by oxidation during heat treatment. Nearly complete oxidation of Al particles took place in the batches. Role of two different additives namely, CeO_2 and MgO on the microstructure and physico-mechanical properties of these composites were investigated.

From the different results it was concluded that

- Zirconia–mullite composites with incipiently formed high proportion of mullite phase can be prepared by this technique

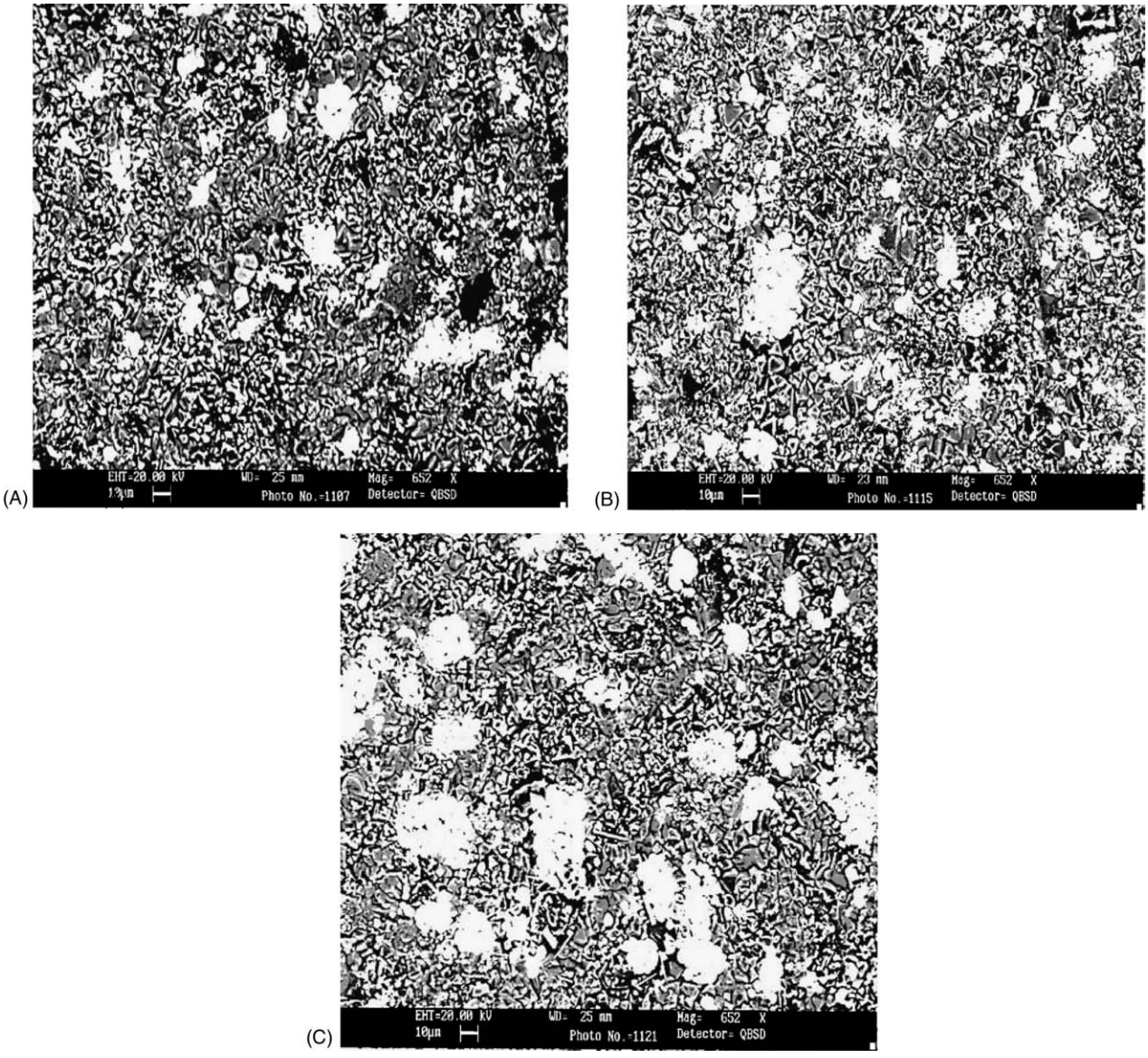

Fig. 7. SEM photograph of (A) batch-I (at 1600 °C); (B) batch-II (at 1600 °C); and (C) batch-III (at 1600 °C).

- The relative proportion of Al powder in the composition, firing temperature and soaking time requires to be optimized for the control of porosity and bulk density of the fired batches, which seems to be a problem for the technique used here.
- MgO as an additive was observed to assist in the formation of more mullite phase and lesser grain-sized microstructure in the fired material
- CeO_2 as an additive assisted in the formation of more tetragonal zirconia phase in the fired material.

Based on these conclusions samples with higher mullite content have better mechanical properties.

References

[1] S. Prochazka, J.S. Wallace, N.C. Claussen, Microstructure of sintered mullite–zirconia composites, J. Am. Ceram. Soc. 66 (1983) C125–C127.

[2] M. Mizuno, M. Shiraishi, H. Saito, Preparation and properties of mullite–ZrO_2 composites, in: Abstracts of the Annual of the Ceramic Society of Japan, paper no. 3F29, Ceramic Society of Japan, Tokyo, 1988.

[3] K. Das, G. Banerjee, Mechanical properties and microstructures of reaction sintered mullite–zirconia composites in the presence of an additive dysprosia, J. Eur. Ceram. Soc. 20 (C) (2000) 153–157.

[4] S. Bhattacharjee, S.K. Singh, R.K. Galgali, Preparation of zirconia toughened mullite by thermal processing, Mater. Lett. 43 (1–2) (2000) 77–80.

[5] X.H. Jin, L. Gao, R.R. Chen, Q.M. Yuan, Effects of Nb_2O_5 addition on the sinterability, microstructure and mechanical behaviour of JTM-Al_2O_3, J. Eur. Ceram. Soc. 20 (12) (2000) 2115–2119.

[6] T.A. Ring, Fundamentals of Ceramic Powder Processing and Synthesis, Academic Press, New York, 1996, p. 145.

[7] C.C. Sorrell, C.A. Sorrell, The Al_2O_3–SiO_2–ZrO_2 liquidus surface: a discussion, J. Am. Ceram. Soc. 60 (1-2) (1977) 93–94.

[8] D.J. Green, R.H.J. Hannink, M.V. Swain, Transformation Toughening of Ceramics, CRC Press, Boca Raton, FL, 1989.

[9] M. Yashima, T. Hirose, S. Katano, Y. Suzuki, Structural changes of ZrO_2–CeO_2 solid solutions around the monoclinic–tetragonal phase boundary, Phy. Rev. B. 51 (13) (1995) 8018–8025.

[10] N. Claussen, S. Wu, D. Holz, Reaction bonding of aluminium oxide (RBAO) composites: processing, reaction mechanisms and properties, J. Eur. Ceram. Soc. 14 (1994) 97–109.

[11] B.D. Cullity, Elements of X-ray Diffraction, Addison–Wesley Publishing Company, Inc., USA, 1959, pp. 388–392.

[12] B.D. Cullity, Elements of X-ray Diffraction, Addison–Wesley Publishing Company, Inc., USA, 1959, p. 99.

[13] J. White, Phase distribution in ceramics, in: R.M. Fulrath, J.A. Pask (Eds.), Ceramic Microstructure, their Analysis, Significance and Production, John Wiley and Sons, 1968, pp. 729–762.