Studies on MgO-Doped Reaction-sintered ZrO_2-Al_2O_3-SiO_2 Refractory Materials

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Extremely dense zirconia-mullite-alumina composite refractories have been prepared by reaction sintering of zircon flour and calcined alumina mixes in different ratios. High-purity MgO powder was used in different proportions as an additive for these mixes. The isostatically pressed powder mixes were sintered at 1550 °C with 3 h soaking time. The sintered specimens were characterized by measuring their bulk density, apparent porosity, modulus of rupture, hot modulus of rupture, hardness, elastic modulus, abrasion, and corrosion resistance. The microstructure of polished sections of the sintered specimens was examined with an optical microscope and the phases developed in the sintered specimens were identified with XRD. It has been observed that the fabricated compacts exhibited exceptionally high sintered density, mechanical strength and corrosion resistance. The Al_2O_3/ZrO_2 ratios and the proportions of the MgO additive content were also found to significantly influence the physico-mechanical properties of the composites.

1 Introduction

Ceramic materials with improved mechanical strength are desirable for structural engineering applications. Among these materials, mullite has been considered as one of the best candidates as it exhibits a low thermal expansion coefficient, high melting temperature, very strong resistance to high-temperature creep, high thermal stability, outstanding thermal shock resistance, excellent chemical stability and low specific gravity [1]. The stable forms of alumina, i.e. corundum also has several high-temperature advantageous properties and therefore mullite and mullite-alumina composite matrices with another dispersed phase like zirconia, have been widely used for high-temperature applications. Different physico-mechanical properties of these composites are of paramount importance [2]. The mechanical properties of mullite-alumina matrix composites can be enhanced by the dispersion of zirconia grains, which can be generated by reaction sintering of zircon and alumina powders. To obtain fully dense zirconia-mullite-alumina composites, reaction sintering is used to synthesize the compacts, i.e. dissociation of zircon with the production of dispersed ZrO_2 and mullite and the simultaneous densification of the ceramic. Reaction sintering of zirconia-mullite composites results in the development of mullite matrix composites with excellent flexural strength as a result of adequate toughening in the matrix.

But to obtain reaction-sintered zirconia-mullite composite from zircon and alumina mixtures in stoichiometric proportions, high isostatic pressure and a high sintering temperature are required. To reduce the firing temperatures, sintering aids can be used. These additives can reduce the sintering temperature either with the formation of a permanent liquid phase or the formation of solid solution or the formation of transitory liquid phase [3].

In the case of liquid-phase additives, formation of inter-granular phases may cause degradation of the high-temperature properties of the composites. But the use of solid-solution additives does not create this type of problem and microstructures developed in the sintered compacts can be modified significantly.

A number of papers have reported on the synthesis and characterization of zirconia-mullite composites by many researchers. Selected important works in this connection are presented here.

Ebadzadeh and *Ghasemi* [4] prepared mullite-zirconia composite materials by reaction sintering of α-alumina, aluminium hydroxide and aluminium nitrate as alumina sources along with zircon powder. The morphology of the inter-granular ZrO_2 particles was found to be dependent on the growing conditions owing to the use of different starting materials. *Haldar* [5] prepared zirconia-mullite composites with 4 – 8 mol-% magnesium oxide from Indian coastal sillimanite beach sand. Miranzo et al. [6] prepared fully dense zirconia-toughened ceramics with a mullite matrix based on the quaternary sys-

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Tab. 1 Batch composition of the samples

	Zircon flour : calcined alumina (weight ratio)	MgO additive [mass-%]
Batch 1	1:4	2,5 5,0 7,5 10,0
Batch 2	1:5	2,5 5,0 7,5 10
Batch 3	1:6	2,5 5,0 7,5 10,0

Tab. 2 Physico-chemical properties of the starting materials

Chemical composition [%]	Zircon flour	Calcined alumina	Calcined magnesia
ZrO_2	65,40	–	–
Al_2O_3	0,60	98,61	0,10
MgO	-	-	98,30
SiO_2	31,5	0,19	0,20
CaO	-	0,18	0,75
Fe_2O_3	0,75	0,16	0,50
TiO_2	0,37	0,24	-
Physical properties			
Particle size, mean [µm]	369,016	0,512	0,953
Specific surface [m^2/g]	0,19	14,16	12,06

tem ZrO_2–Al_2O_3–SiO_2–MgO in the temperature range as low as 1450 to 1550 °C by reaction sintering of zircon-alumina-magnesia mixtures. The shrinkage, advance of reactions, microstructure, densification mechanism and mechanical properties of the composites have been explained in terms of transitory and permanent liquids that appear at ≤ 1425 °C and ~ 1450 °C respectively. *Biswas* and *Chaudhury* [7] prepared several zirconia-mullite and alumina-zirconia composites and determined their physical, chemical, mechanical and thermal properties. They observed that the thermal shock resistance of clay-based zirconia-mullite composites and alumina-zirconia composites was almost on par. *Lin* [8] synthesized mullite-zirconia composites by reaction sintering of powder mixtures of α-alumina, amorphous silica and 3 mol-% Y_2O_3-stabilized zirconia and found that the addition of 3 mol-% yttria-zirconia improves sintering and lowers the mullitization temperature. *Yaroshenko* and *Wilkinson* [9] studied the combined effects of zirconia and mullite seeds on the crystallization process and microstructural development in zirconia-mullite composites. They observed that when zirconia is added without seeding, mullite formation proceeded through the formation of transient zircon, which provided a lower-energy barrier for mullite nucleation. *Ibarra Castro* et al. [10] sintered mixtures of aluminium dross and zircon and obtained a homogeneous mullite matrix with small zirconia particles by sintering at 1500 °C for 6 h.

A survey of existing literature revealed that no information is available about the sintering behaviour of isostatically pressed zirconia : alumina : silica in different proportions of the constituents in presence of different additives. In the present work therefore, we investigated the influence of MgO additive in different proportions on the microstructure and mechanical properties of reaction-sintered zirconia-alumina-mullite composites prepared from zircon flour and calcined alumina in different proportions.

2 Experimental

Micro-fine (–325 mesh) calcined alumina of *ALCOA* and zircon flour (–170 mesh) from *Indian Rare Earth Ltd (IREL)* were used as starting materials. Calcined MgO powder

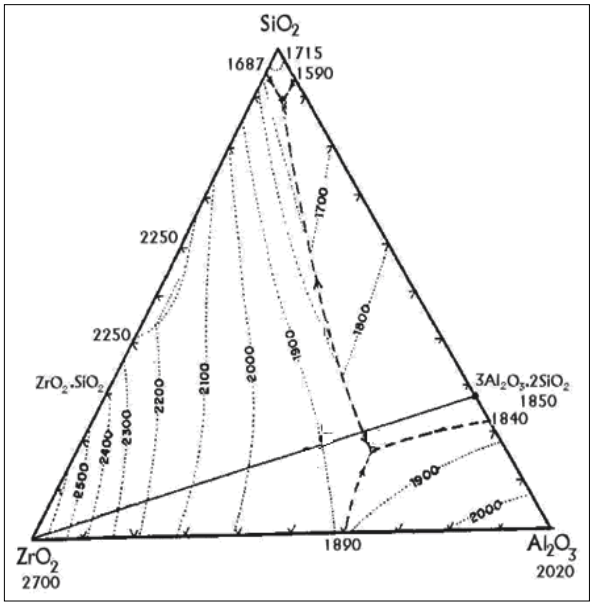

Fig. 1 Phase equilibrium diagramme of ZrO_2–Al_2O_3–SiO_2 for liquidus projection [°C]

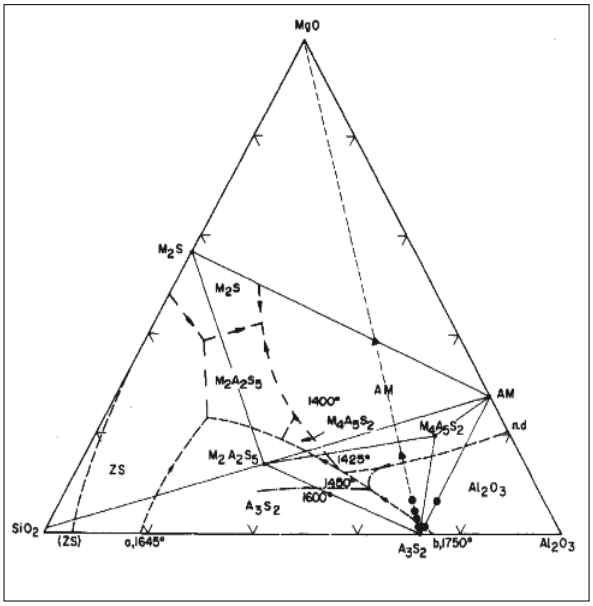

Fig. 2 Projection of the primary volume of crystallization of ZrO_2 in Al_2O_3–MgO–SiO_2 ternary phase diagramme

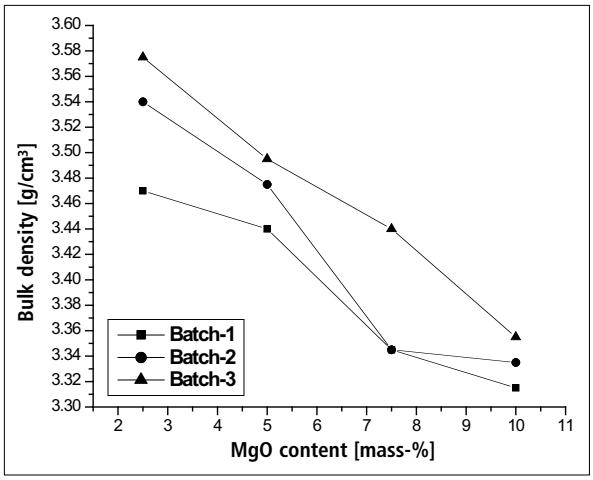

Fig. 3 Variation in bulk density with MgO content for the sintered specimens

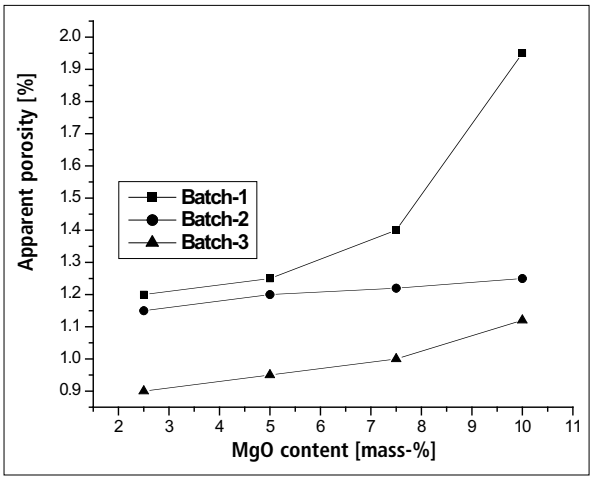

Fig. 4 Variation in apparent porosity with MgO content for the sintered specimens

(*SWM,* Netherlands) was used as an additive. The physico-chemical properties of the starting materials are given in Tab. 1. The ingredients were mixed in different proportions and the batch compositions are detailed in Tab. 2. The powders were mixed in a dry mixer with the required amount of binder and moisture for better workability during pressing. The mixes were compacted by means of isostatic pressing at 1500 bar. These compacted specimens were dried at (105 ± 5) °C for 24 h and sintered at 1550 °C for 2,5 h. Different physico-mechanical properties of the sintered specimens like bulk density, apparent porosity, specific gravity, MOR, HMOR, abrasion resistance, hardness and corrosion resistance were measured in compliance with BS 1902, Part 1A, 1966 specification. The phase compositions in the sintered specimens were ascertained with XRD analyses using a diffractometer (Philips, PW 1383) with CuK_α radiation. Phase distributions in the sintered compacts were analyzed with an optical microscope (Leitz, Germany, labour Lux 12MEST) and polished sections.

3 Results and discussion

The physico-chemical properties of the starting materials are shown in Tab. 1. In both the alumina and magnesia specimens the content of alumina and magnesia was > 98 %. The zircon sand contained more than 65 % ZrO_2. The specific surface of calcined alumina was the maximum among the ingredients. The different compositions of the batches are shown in Tab. 2. Three different ratios of alumina and zircon sand were investigated in the present study. For all these compositions it is apparent from the ZrO_2–Al_2O_3–SiO_2 ternary diagramme (Fig. 1) that the refractoriness of the batches was > 2100 °C.

The reaction sintering process has been utilized for the development of many high-density high-performance ceramic materials. In this process compacted starting materials are subjected to solid-state-reaction-induced sintering at suitable elevated temperatures to develop a superior microstructure in the product.

The solid-state reaction between zircon flour and alumina at elevated temperature can be presented in the following way,

$3\,Al_2O_3 + 2\,ZrSiO_4 =$
$(3\,Al_2O_3 \cdot 2\,SiO_2) + 2\,ZrO_2 +$ extra phase

In all the batches, the proportions of the additive MgO content have been varied from 2,5 to 10 mass-%. In the presence of MgO additive, the system became a quaternary one, ZrO_2–Al_2O_3–SiO_2–MgO and stoichiometrically the solid-state reactions can be presented in the following way [9, 10].

$2\,ZrSiO_4 + 3\,Al_2O_3 + x\,(Al_2O_3 + MgO) \rightarrow$
$2\,ZrO_2 + Al_6Si_2O_{13} + x\,Al_2MgO_4$

The value of x varies from 0,3 to 1. The two compositions considered are located in the primary phase field of ZrO_2. For the secondary phase field, with MgO content above 2,5 mass-% the secondary phase is alumina, and for a lower content, the corresponding secondary phase field is mullite [9].

In the case of non-dissociated zircon, the original mixtures consist of two crystalline compounds, $ZrSiO_4$ and α-Al_2O_3. The reaction of mullitization is expected to be concomitant with the zircon dissociation. This means the development of crystalline mullite will be associated with the progressive consumption of zirconia and alumina. However, some non-crystalline phases can exist during a transient period.

From the ZrO_2–Al_2O_3–SiO_2–MgO quaternary phase diagramme (Fig. 2), a transient liquid would appear below 1400 °C, corresponding to the invariant point denoting the co-existence of sapphire–spinel–cordierite–zirconia. Below 1425 °C, another transient liquid would also appear, corresponding to the invariant point denoting the co-existence of sapphire–spinel–mullite–zirconia. At a temperature above 1450 °C, the formation of a permanent liquid phase would take place. At temperatures below 1350 °C, no liquid phase formation took place and Al_2MgO_4 spinel would form as a result of solid-state reaction. It has been observed that in the case of zirconia-mullite compositions, the transitory liquid partially left the bulk and appeared on the surface of the sintered compact owing to capillary forces. These phenomena did not take place in the case of the free-alumina-containing compacts.

With the increase in the Al_2O_3 content, the proportion of mullite phase increased in the batches. In a particular batch, with the increase in the proportion of MgO content, initially the proportion of MgO-SiO_2- and MgO-Al_2O_3-SiO_2-bearing liquid phases increased, which at higher temperature dissociate, resulting in the formation of more mullite and spinel phases in the structure.

As a result of cold isostatic pressing, a high value of specific gravity (> 3,9 g/cm³) in

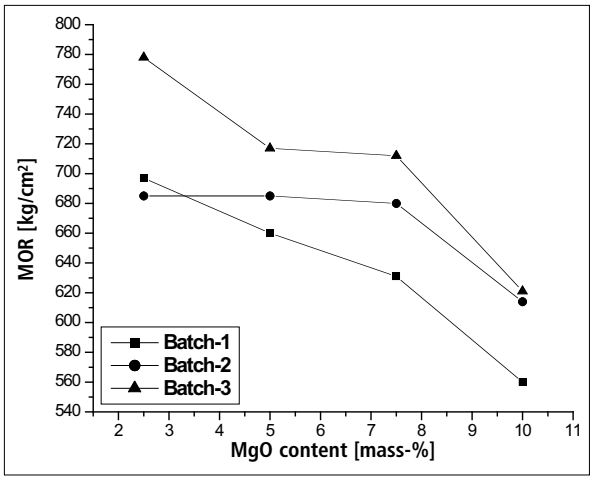

Fig. 5 Variation in modulus of rupture with MgO content for the sintered specimens

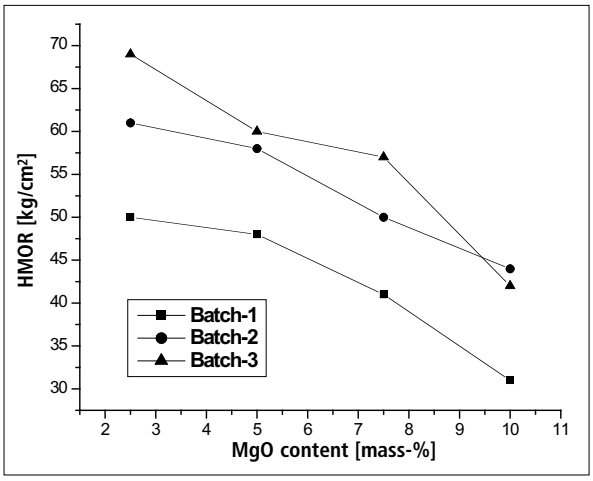

Fig. 6 Variation in hot modulus of rupture with MgO content for the sintered specimens

all the sintered compacts was developed. The apparent porosity developed in the samples after heat treatment was very low (< 2,5 %), which suggests the formation of incipient liquid phase during reaction sintering in presence of MgO. From Figs. 3 and 4 it is apparent that the bulk density of the batches increased with the increase in the proportion of Al_2O_3. For a particular batch, with the increase in the proportion of the MgO content the bulk density values decreased. This might be related to more devitrification in the batches with higher MgO content resulting in the development of more crystalline phases, like spinel. Consequently, the apparent porosity value of the sintered samples increased slightly with the increase in MgO content. It might be related to the peritectic transformation of the extra liquid phase at elevated temperature.

The composites exhibited a very high value of modulus and hot modulus of rupture (Figs. 5 and 6). The development of a high value for the modulus of rupture in all the samples can be related to the absence of significant porosity in the samples, which improved the modulus of elasticity of the samples (Fig. 7). With the increase in the proportion of alumina the modulus of rupture and elasticity values increased. This might be related to the formation of more interlocked mullite and less zirconia-transformation-induced strain in the microstructure. It suggests the strengthening of the grain boundaries of zirconia-mullite-alumina composites by the re-crystallization of MgO at the interfacial grain boundary. With the increase in MgO content, the modulus of rupture values decrease slightly, which could be related to the increase in porosity in the structure as a result of the increase in spinel phase. The increase in porosity also resulted in the reduction of the modulus of elasticity values of the samples.

The hardness of the samples in Moh's scale was found to be >7. The hardness of the samples were also measured in Rockwell's C scale (Fig. 8) by means of the indentation method with 120°-diamond cone. The hardness values of the samples increased with the increase in the proportion of alumina in the batches. For a particular batch, the hardness increased with the increase in the MgO additive content. This can be related to the formation of more corundum and mullite phases in the microstructure with the increase in Al_2O_3 and MgO content. As a result of improved hardness the samples exhibited exceptional abrasion resistance (Fig. 9). For this property, MgO as an additive also ex-

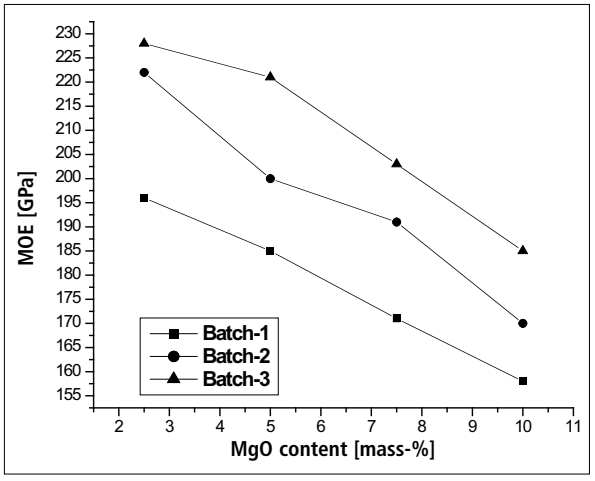

Fig. 7 Variation in modulus of elasticity with MgO content for the sintered specimens

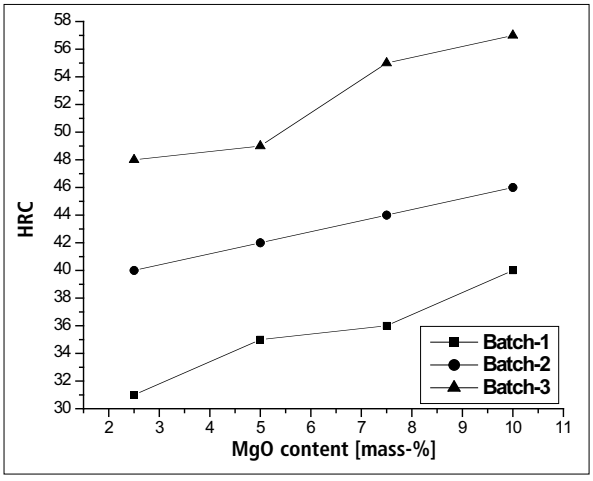

Fig. 8 Variation in hardness with MgO content for the sintered specimens

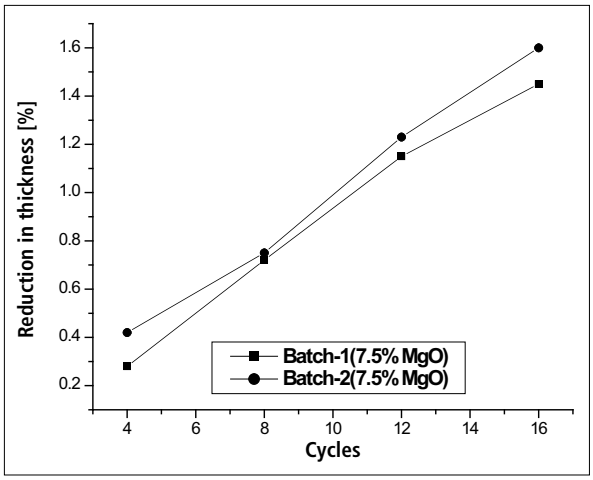

Fig. 9 Variation in abrasion resistance with number of abrasion cycles

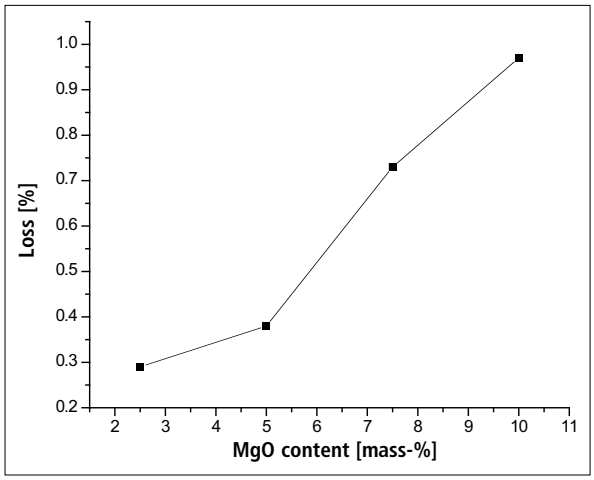

Fig. 10 Variation in corrosion resistance with MgO content for batch 3

hibited a similar influence. Even after 16 cycles of abrasion the loss in thickness in the samples was observed to be negligible and the abrasion resistance behaviour followed similar trends in terms of composition.

The corrosion resistance behaviours of the specimens were measured in a drum test at 1500 °C with four taps using a synthetic slag. The slag was basically soda-lime-silica glass. All the samples exhibited exceptional corrosion resistance. This can be related to the superior density and compact microstructure of the samples. Corrosion (loss in thickness) of the sample in the rotary drum test was found to be about 0,03 – 0,13 mm, which may be considered negligible. The corrosion resistance also increased with the increase in the proportion of Al_2O_3 content in the batches. This might be related to the formation of more mullite and corundum phases. Again with the increase in the MgO content, the corrosion resistance was also slightly improved as the increase promoted the formation of more crystalline phases in the microstructure (Fig. 10).

The microstructures of the samples are presented in Fig. 11. From the microscopic study it was observed that mullite and zirconia were homogeneously distributed in the microstructure and corundum precipitates existed in the higher alumina batches. Intergranular locking and irregular-shaped zirconia inclusions in different positions of the microstructure were observed. Mullite exhibited equiaxed grains in the higher alumina batches and mixed (acicular and equiaxed) grains in the lower alumina batches. This can be related to the presence of a liquid phase during sintering of the samples. Zirconia inclusions were found to be rounded or coarsened to a bead-like form in the intermediated alumina-containing batch.

The XRD pattern of the fired sample exhibited clear, sharp and long peaks of different phases (Figs. 12 and 13). This suggests the absence of significant glassy phases in the microstructure. The major phases detected in the sintered samples were mullite, corundum and zirconia (monoclinic). In presence of MgO additive, the crystallinity of the specimens has been improved further. It was noticed from the XRD diagrams that with the increase in the MgO content, the proportion of spinel phase increased and mullite phase decreased. The ingredient reactive Al_2O_3 reacted with MgO prior to the dissociation temperature of zircon. Therefore the alumina

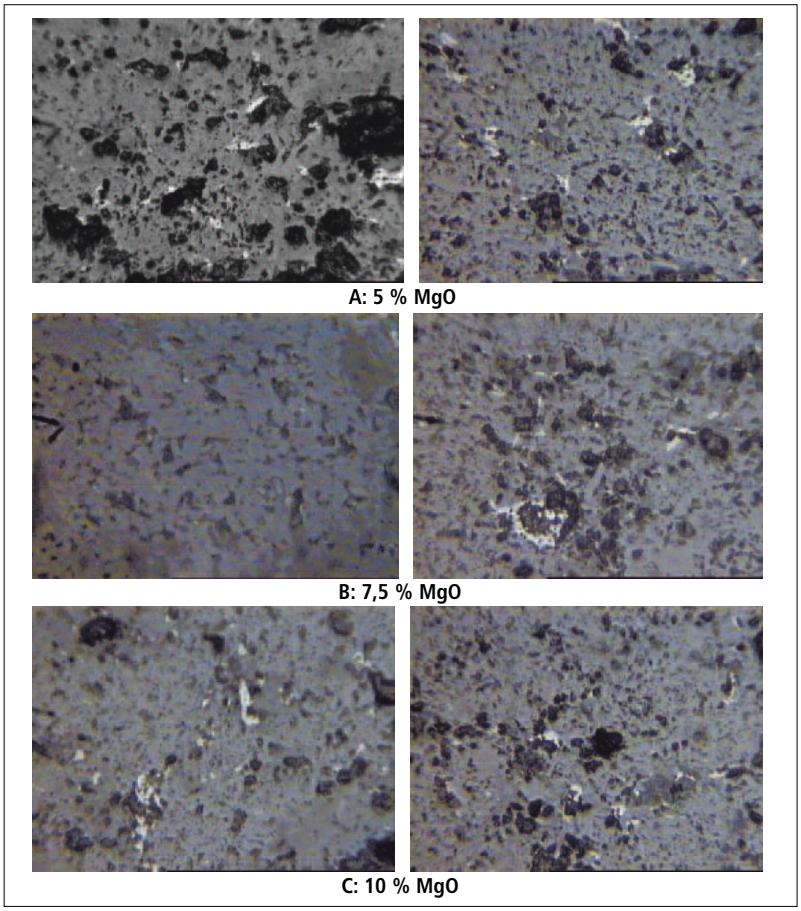

Fig. 11 Photomicrograph of the batch 3 specimens after acid etching (x 100)

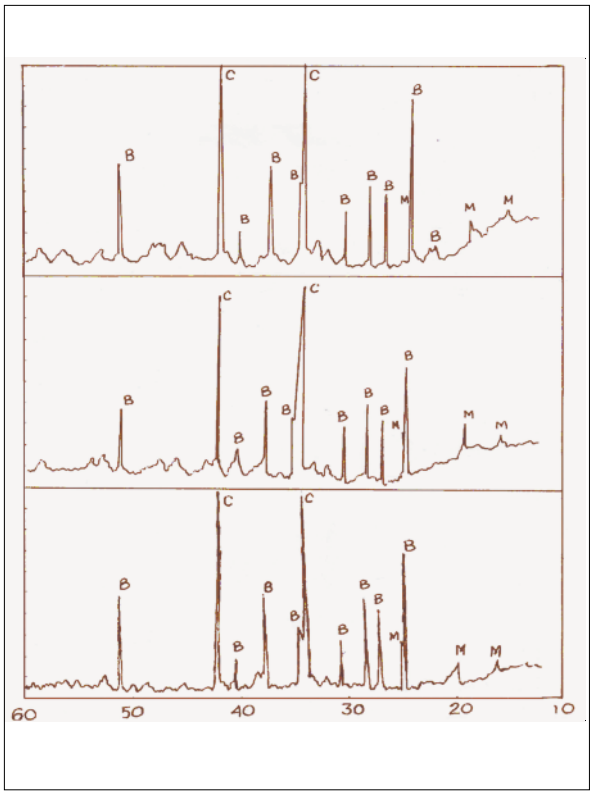

Fig. 12 XRD diagramme of the sintered specimens (top to bottom: batch 3, batch 2, batch 1) without additive (B = ZrO_2(m), M = mullite, C = corundum)

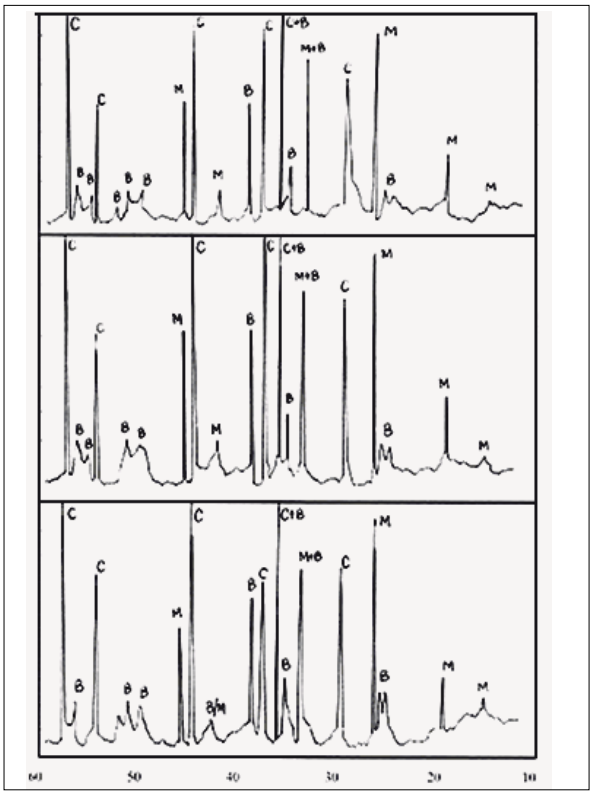

Fig. 13 XRD diagramme of the sintered specimens of batch 3 with MgO (top to bottom: 5 % MgO, 7,5 % MgO and 10 % MgO) additive (B = ZrO_2(m), M = mullite, C = corundum, S = spinel)

could form a lower amount of mullite phase by reaction with the silica generated from the dissociation of zircon. As this reaction reduced the availability of MgO for the stabilization of ZrO_2, the presence of only monoclinic ZrO_2 was detected in the sintered compacts.

4 Summary and conclusion

Reaction sintered zirconia-mullite-alumina compacts were prepared from zircon flour and calcined alumina by isostatic pressing with different zircon and alumina ratios. MgO was used as an additive for these composites. The materials exhibited exceptionally high density, modulus and hot modulus of rupture, abrasion resistance and corrosion resistance. The physico-mechanical properties of these materials were slightly affected by the relative proportion of Al_2O_3 content and the amount of additive used for densification. The microstructures of the materials consisted of uniformly distributed zirconia and mullite grains with intergranular corundum precipitate. In relatively higher alumina batches equiaxed mullite and in relatively lower alumina batches both acicular and equiaxed mullite grains were observed. At elevated temperature MgO promoted peritectic transformation of the vitreous phase to crystalline phases, like spinel. As a result, properties like bulk density, modulus of rupture and modulus of elasticity of the sintered samples decreased slightly with the increase in the MgO additive, whereas properties like abrasion resistance, hardness and corrosion resistance improved with the increase in MgO content.

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