

Effect of Yttria on Mechanical and Microstructural Properties of Reaction Sintered Mullite–Zirconia Composites

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Abstract

Mullite–zirconia composites containing 0 to 7 mol% yttria were prepared by reaction sintering process from Indian coastal zircon flour and calcined alumina. The main raw materials were attrition milled. Samples were isostatically pressed and sintered at temperatures of 1400 to 1650°C with 2 h soaking time. The resulting composites were characterised in terms of phase compositions, martensitic start (M_S) temperature, mechanical properties and microstructural features. The presence of yttria results in a dense composite material at a comparatively low temperature. Addition of yttria increases the tetragonal zirconia fraction and reduces the M_S temperature. Yttria goes into solid solution which was detected by EDX analyses. The effect of yttria on thermal expansion coefficient, room temperature flexural strength, hardness, fracture toughness is discussed. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Mullite–zirconia composites can be prepared through several routes. Of these the important ones are (a) from mechanical mixture of fired mullite/active premullite and zirconia powder;^{1,2} (b) coprecipitation;³ (c) sol–gel method of preparation^{4–6} and (d) reaction sintering.⁷

Among the different techniques of preparation the reaction sintering route is the only method by which the relatively pure raw zircon sand can be used directly. Thus this method is inexpensive and simple. This is a process in which the chemical reaction amongst the starting materials and the

densification or the removal of porosity in the powder compact can be attained in a single heat treatment.⁸ But the shortcoming of the method is the more or less constant phase composition. This impedes the study of the optimum mechanical behaviour with respect to zirconia content.

The effect of different additives on the formation as well as thermal and mechanical properties of mullite–zirconia composites was studied. The additives commonly studied are magnesia, calcia, titania, yttria and ceria. Small amount of magnesia addition (2 wt%) to the batch enhanced the reaction and zircon decomposition rate. This is supposed to be due to the appearance of a small amount of liquid phase.^{9,10} It was reported that for CaO content greater than 4 wt%, the secondary phase is alumina and for lower amounts the corresponding phase is mullite.¹¹ At high temperature, a permanent liquid phase was present together with alumina, mullite and zirconia. TiO_2 forms solid solution with zirconia and mullite and its solid solubility in zirconia and mullite, was about 4 wt%.¹² Addition of CeO_2 enhances the formation of mullite and also increased the fraction of tetragonal zirconia. CeO_2 essentially forms solid solution with zirconia.¹³ It was observed that Y_2O_3 favoured the dissociation of zircon and consequently the formation of zirconia. It helps t-ZrO_2 stabilisation by formation of a solid solution of $\text{ZrO}_2\text{--Y}_2\text{O}_3$.¹⁴

In the present study, Indian coastal zircon flour and calcined alumina are selected as principal raw materials. The objective of the present work was to study the influence of Y_2O_3 on mechanical, thermal and microstructural characteristics of reaction sintered mullite–zirconia composites using Indian coastal zircon flour and calcined alumina. The advantage of using this type of additive is to avoid the appearance of any additional phases.

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2 Experimental

The starting materials, Indian zircon flour (obtained from beach zircon sand, supplied by Indian Rare Earth Ltd, Bombay, India) and Calcined alumina (supplied by Associated Cement Company, Bombay, India) were ground together in an attritor (in 2:3 molar ratio) for 6 h with zirconia balls in isopropyl alcohol medium. Chemical analyses of the raw materials are listed in Table 1. The batch composition of four composites are summarised in Table 2. The slurry from the attritor was dried, granulated by sieving and subsequently uniaxially pressed into bars ($60 \times 6 \times 6 \text{ mm}^3$) and discs (diam 25 mm) at $\sim 100 \text{ MPa}$ followed by cold isostatic pressing at 275 MPa using 10% PVA as binder. For thermal expansion measurement, 40 mm length and 5 mm diameter cylindrical rods were fabricated. The pressed samples were dried and sintered at temperatures ranging between 1400 and 1650°C with 2 h soaking period. 3, 5 and 7 mol% yttria was added to the mixture with respect to the zirconia content. The sample codes used for the samples are also described in Table 2.

The bulk density of the sintered composites was measured by water displacement method. True density was measured with powdered sample in a pycnometer. The t-ZrO₂ fraction content was determined on the as sintered surfaces from the ratio of XRD (Philips PW-1010) integrated peak intensity of t-ZrO₂ (111) to m-ZrO₂ (11 $\bar{1}$) and m-ZrO₂ (111) following Garvie and Nicholson's equation.¹⁵

Linear thermal expansion was performed on fired cylindrical bars using BAHR 804 dilatometer up to 1400°C with 6°C min^{-1} rate of heating. The flexural strength at room temperature (RT) was measured on the fired rectangular bars by three point bending method using an Instron-1185 Universal Testing Machine. The span was 45 mm and

Table 1. Chemical analyses and physical properties of Indian coastal zircon flour and calcined alumina

Constituents	Zircon flour	Calcined alumina
SiO ₂	31.94	0.34
ZrO ₂	59.74	—
Al ₂ O ₃	6.76	99.17
Fe ₂ O ₃	0.17	—
TiO ₂	Trace	—
HfO ₂	0.03	—
CaO	1.03	—
MgO	Trace	—
K ₂ O	Trace	—
Na ₂ O	0.07	0.37
XRD analyses		
(phases)		
Major	Zircon	α -Alumina
Minor	Anorthite	γ -alumina, β -alumina

Table 2. Batch composition and sample codes for different additives

Additive (mol%)	(wt%)	Zircon flour (wt%)	Calcined alumina (wt%)	Sample code used
nil	nil	59.00	41.00	MZ
3	1.86	57.89	40.24	3MZY
5	3.00	57.22	39.76	5MZY
7	4.12	56.57	39.30	7MZY

the cross head speed was 0.5 mm min^{-1} . The fracture toughness (K_{IC}) was examined by the Vicker's Indentation method following the equation of Anstis *et al.*¹⁶ using Wolpert Hardness Tester, Germany.

Microstructural analyses was performed on the mirror polished surface after thermal etching. Thermal etching was done at a temperature 50°C less than the sintering temperature for 20 min. A JEOL SEM with Kevex EDX was used for energy dispersive X-ray analyses.

3 Results and Discussions

The present study was carried out on two main raw materials—Indian beach zircon and calcined alumina. The chemical analyses (Table 1) shows that wt ratio of ZrO₂ to SiO₂ is 1.87 instead of 2.086 for stoichiometric zircon indicating silica rich zircon. The other impurities are alumina and calcium oxide. Calcined alumina contains soda and silica as impurities. X-ray diffraction analyses confirmed the presence of small amount of anorthite in zircon and small amount of γ -Al₂O₃ and β -Al₂O₃ in calcined alumina as minor phases.

The relative density of the composites as a function of sintering temperature are shown in Fig. 1. The reaction sintering of zircon and alumina in the absence of any additive mainly occurs by solid state diffusion of reactants.¹⁷ The low reaction rate in this composite thus requires a high sintering temperature. Figures 2 and 3 showed the X-ray diffraction pattern of control composite, i.e. the one without any additive and yttria containing one (3MZY) at 1550 and 1600°C , respectively. 3MZY completes decomposition of zircon and formation of mullite at 1550°C which is supported by the absence of zircon and alumina peaks but MZ completes the same at 1600°C . MZ attains maximum relative density at 1550°C whereas yttria containing composites show highest density at 1500°C . This can be due to reduction in porosity. As the development of mullite in reaction sintered mullite-zirconia composites is always accompanied with a decrease in density, the completion of reaction decreases the relative densities of all composites although their apparent porosities are very

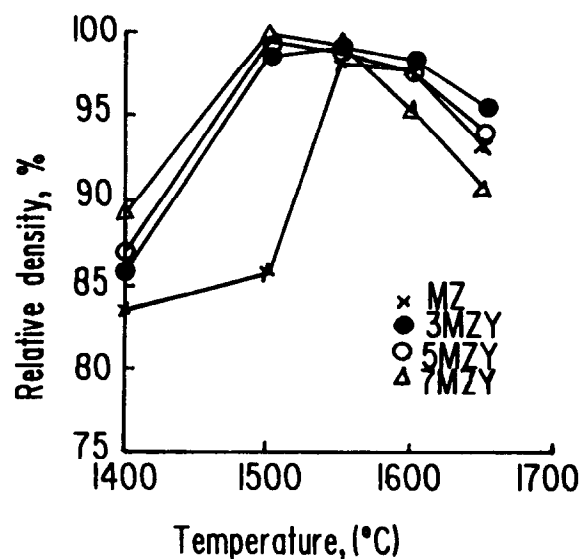


Fig. 1. Densification of reaction sintered mullite-zirconia (MZ) composites as a function of sintering temperature with yttria (Y). 3, 5 and 7 represents the mole% of yttria in composites.

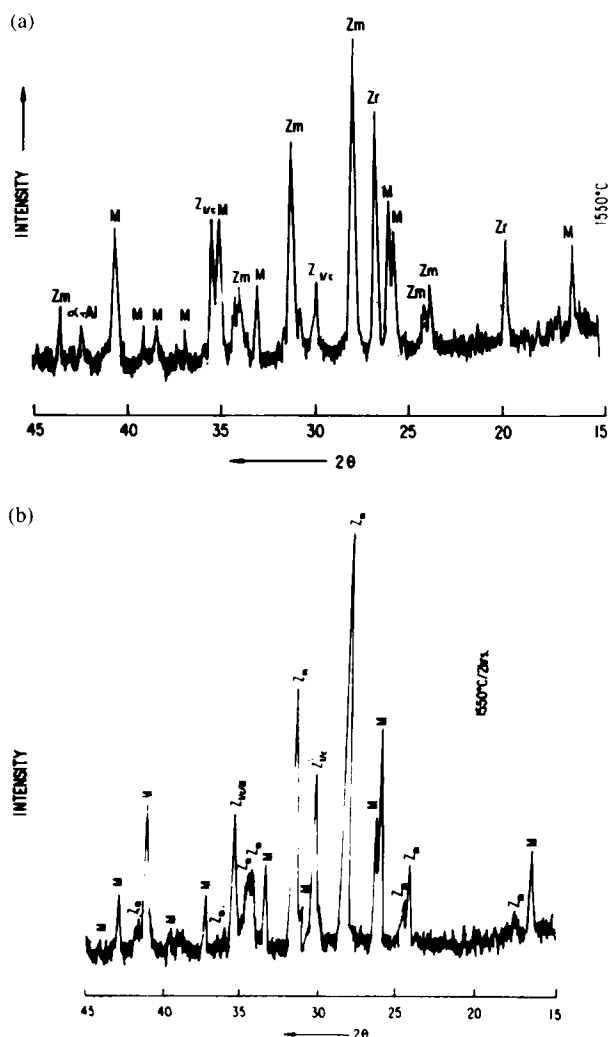


Fig. 2. XRD pattern of mullite-zirconia (MZ) composites containing yttria additive at 1550°C. (a) MZ and (b) MZY; M-mullite, Zm-m-ZrO₂, Zt/t/c-ZrO₂, Zr-zircon and α -Al₂O₃.

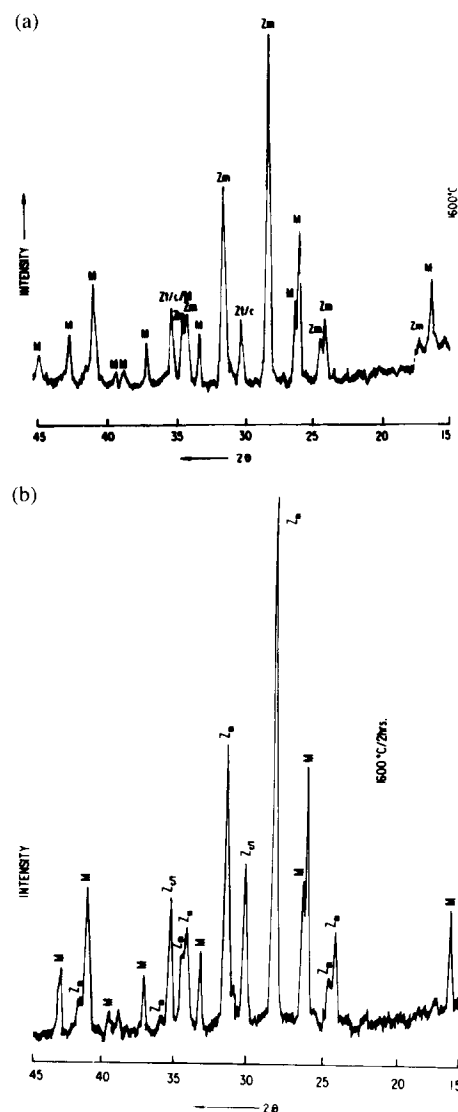


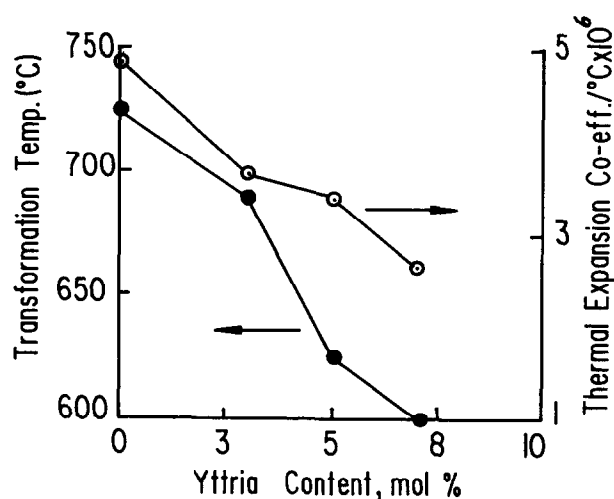
Fig. 3. XRD patterns of mullite-zirconia (MZ) composites sintered at 1600°C. (a) MZ and (b) MZY; M-mullite, Zm-m-ZrO₂, Zt/t/c-ZrO₂.

low. The addition of yttria facilitated the forward reaction by forming solid solution with zirconia and mullite. At 1600°C, the presence of higher amount of yttria led to agglomeration of zirconia particles resulting in a heterogeneous microstructure.¹⁴ Though 7MZ contains the highest amount of tetragonal zirconia at this temperature, it shows low density with porous structure (Table 3).

Composites developed from reaction sintering with and without additive showed thermal expansion coefficient values lower than that of mullite ($\alpha = 5.6 \times 10^{-6}/^{\circ}\text{C}$). Figure 4 shows the dependence of thermal expansion coefficient and martensitic start temperature (M_s) on Yttria content. The addition of yttria enhanced the reaction rate between zircon and alumina to form mullite and zirconia. A very low thermal expansion coefficient value was obtained with 7MZ sample. It was observed by EDX analysis that zirconium ions

Table 3. Relative tetragonal zirconia (%) content as a function of sintering temperature 2 h dwelling

Sample code	Tetragonal zirconia content (%) at temperature		
	1550°C	1600°C	1650°C
MZ	22.20	11.21	8.77
3MZY	25.52	16.46	10.66
5MZY	31.55	17.00	13.00
7MZY	65.76	33.00	17.31

**Fig. 4.** Thermal expansion co-efficient and transformation (M_s) temperature of the mullite-zirconia composites as a function of yttria (Y) content.

were present in mullite phase (Fig. 7). EDX analyses also show that besides zirconia, yttria also has a solubility in mullite. It was assumed that Y^{+3} occupies the AlO_6 octahedral chains by replacing Al^{+3} ions in mullite structure.¹⁸ Yttria, while going into solid solution with mullite, increases the lattice spacing thereby reducing the thermal expansion.¹⁹ A comparative statement of the ionic radii supports this observation (radii of Al^{+3} , 0.55Å; Y^{+3} , 0.93Å; Zr^{+4} , 0.80Å; and Si^{+4} , 0.41Å).

The martensitic start temperature (M_s) in case of the free zirconia occurs between 950 and 850°C.²⁰ Zirconia particles embedded in other ceramic matrices are usually retained at lower temperature due to the constraint imposed by the surrounding matrix on the transformation volume expansion and shape change. Yttria and most rare earth oxides are efficient in reducing M_s , because their solid solution with zirconia is more stable at the sintering temperature; less yttria is required to decrease M_s temperature.

The slope of the M_s versus yttria content curve is steeper when yttria content increased from 3 to 5 mol% compared to that from 5 to 7 mol%. The change in the slope of this curve is related to the solid solubility of yttria in zirconia. If we consider a zirconia (tetragonal) inclusion within an elastic

matrix and the inclusion was to transform to its monoclinic structure, classical theory indicated²¹ that the free energy change per unit volume could be written:

$$\Delta G_{t-m} = -\Delta G^c + \Delta U_{se} + \Delta U_S$$

Where ΔG^c is chemical free energy change, ΔU_{se} is the change in strain due to the constrained shape and volume change associated with the transformation and ΔU_S is the energy associated with the inclusion/matrix interface. Below 1200°C, ΔG^c is always negative for tetragonal to monoclinic zirconia conversion ΔU_S always positive. The transformation would proceed only when $\Delta G_{t-m} < 0$. Neglecting ΔU_S , with increasing amount of yttria, $|\Delta G^c|$ decreases and thereby ΔG_{t-m} for martensitic reaction increases. Decreasing chemical free energy by alloying increases the critical size required to retain the high temperature phase. Here 7MZY shows minimum M_s compared to other composites though its intergranular zirconia particle size is larger than that of other yttria containing composites (3MZY and 5MZY) but possesses highest amount of tetragonal zirconia (Table 3).

Mechanical strength of the composites is dependent on microstructure, different phases present (including pores) and their distribution. Figure 5 shows the flexural strength as a function of sintering temperature on mullite-zirconia composites with and without yttria. Strength degradation occurs in a stepwise manner. The relative density of the compact and porosity contribute significantly towards the strength improvement together with the tetragonal zirconia content. EDX analyses revealed that yttria forms solid solution with zirconia and mullite. Thus, yttria addition as a tetragonal zirconia stabiliser prevents the formation of microcracks in the matrix and yttria helps to strengthen the grain boundaries. Maximum strength was obtained from 7MZY at 1550°C which shows maximum relative density as well as relative tetragonal zirconia content. The strength degradation at 1600°C is significant with 7MZY mainly due to the heterogeneous porous microstructure which was confirmed by scanning electron micrograph (Fig. 6). At 1650°C, the yttria containing samples has lower strength compared to the control composite (MZ). At this temperature, abnormal grain growth results in higher porosity in the sample which lead to the deterioration of the strength.

The room temperature (RT) mechanical properties of the composites are described in Table 4. The control composite (MZ) has low hardness at



Fig. 6. Secondary electron image of yttria containing composite (7MZY) sintered at 1600°C after thermo-chemical etching of polished surface, showing agglomeration of zirconia phase (white) with porous microstructure.

Table 4. Hardness and fracture toughness of mullite–zirconia composites containing yttria

Sample code	Temperature of sintering (°C)	Relative density (%)	Hardness (GPa)	Strength (MPa)	Fracture toughness (MPa m ^{1/2})
MZ	1550	98.20	5.6	154	3.7
3MZY	1550	99.10	9.3	243	4.5
5MZY	1550	98.79	10.1	238	5.2
7MZY	1550	99.33	9.1	256	4.0
MZ	1600	97.58	7.5	142	2.4
3MZY	1600	98.38	6.6	160	3.8
5MZY	1600	97.73	8.0	155	4.2
7MZY	1600	95.43	5.7	100	3.3

1550°C because of incomplete solid state reaction (Fig. 2) and presence of open pores. Yttria containing samples show higher hardness at 1550°C compared to those sintered at higher temperatures. Maximum hardness was achieved in 5MZY. Increase in porosity at 1600°C compared to that at 1550°C is responsible for lower hardness values at 1600°C. The 7MZY has a higher apparent density with respect to 5MZY when sintered at 1550°C but its hardness value is low. It is anticipated that as 7MZY contains highest amount of relative tetragonal zirconia compared to 5MZY, the tetragonal zirconia particles relieve the stresses around the Vicker's indenter by transformation and twinning.²² Addition of yttria significantly increased the fracture toughness of mullite–zirconia composites. It is noticed that the fracture toughness increases from 3 to 5 mol% and then declines in 7MZY. A significant amount of zirconia solid solution with mullite at the mullite–zirconia grain boundary is assumed to be a dissipation energy region which reduced the crack propagation.²³ This was also confirmed by EDX analyses. In Table 5 it is confirmed that about 4 wt% zirconia forms solid solution with mullite, conversely 1.65

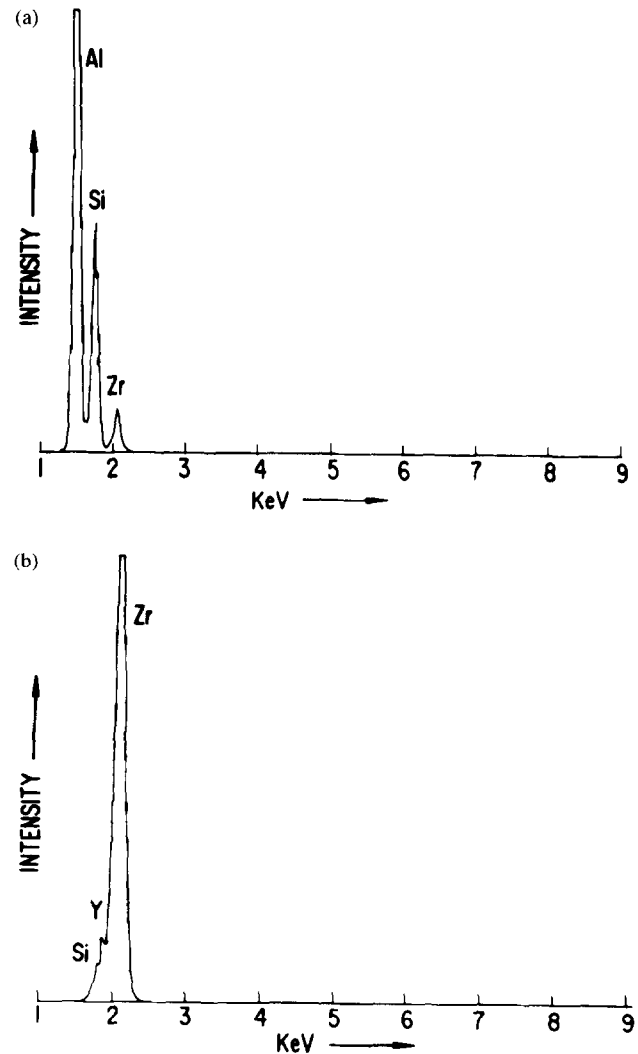


Fig. 7. EDX analyses of different phases in 7MZY. (a) Mullite grains (M). (b) Zirconia grains (Z).

Table 5. Energy dispersive X-ray analyses of different phases in mullite–zirconia composites

Phase	Alumina	Silica (wt%)	Zirconia (wt%)	Yttria (wt%)
7MZY Mullite	61.66	33.16	3.99	1.18
7MZY Zirconia	—	1.65	88.19	10.61

wt% silica is in solid solution with zirconia. The solid solution grain boundary strengthening mechanism was confirmed by transgranular type of fracture shown in an earlier publication.¹⁰ The EDX analyses of mullite and zirconia phases in yttria containing mullite–zirconia composites (7MZY) is given in Fig. 7. The mole ratio of alumina to silica was 1:1.06. No alumina was identified in zirconia phase. No free alumina was detected in both the XRD and EDX analyses of yttria containing mullite–zirconia composites.

The average intergranular zirconia particle size as a function of sintering temperature of both the control composite (MZ) and yttria containing

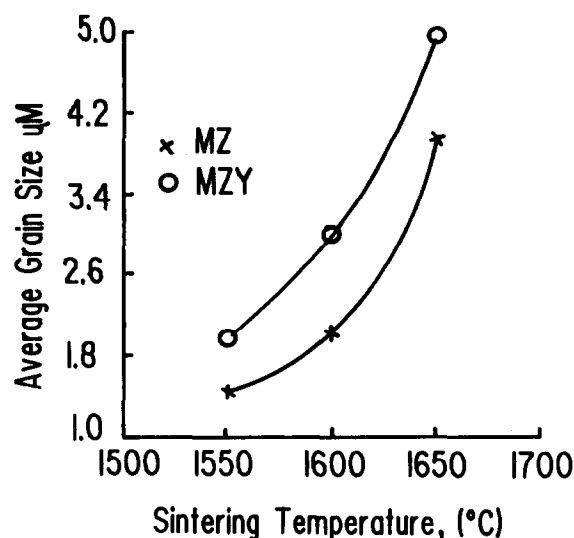


Fig. 8. Average intergranular zirconia grain size as a function of sintering temperature.

composite (3MZY) is shown in Fig. 8. The rate of change of particle size with temperature from 1600 to 1650°C is higher than that from 1500 to 1600°C. This has happened due to the fact that at 1550°C, the yttria containing composites complete reaction and achieve maximum density and at 1600°C the control composite (MZ) completes reaction and densification. So at 1650°C, the grains (both mullite and zirconia) grew by Oswald ripening with pore drag which led to porous microstructure with larger grains.

4 Conclusion

Reaction sintered mullite–zirconia composites from Indian coastal zircon flour and calcined alumina can be prepared at 1550°C in presence of yttria as an additive. The addition of yttria improves the mechanical and thermal properties of the resulting composites. The thermal expansion coefficient and martensitic transformation temperature decreases with increasing yttria content. Yttria acts as a solid solution additive. It is more effective compared to others as it does not form any detrimental low melting intergranular phase. The composites may be used as good refractory aggregate material in monolithic refractory products.

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