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# Dolomite Stabilized Zirconia for Refractory Application : Part-I Phase Analysis, Densification behavior and Microstructure of Partial Stabilized Zirconia

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## Abstract

In the continuous casting of steel, Zircon and Zirconia based products are used due to its high thermal stability, excellent erosion resistance, self-opening, consistent casting speed and resistance to oxygen lancing during casting for removal of inclusion clogging and to streamline the flow. Higher casting sequences of molten steel CaO or MgO stabilized zirconia nozzles were being used and for industrial application point of view, dolomite stabilized zirconia (DSZ) could be a better substitute for the stabilization of zirconia. DSZ samples were prepared having 3,4,5,6 and 7 mole % of dolomite by solid state route using high purity monoclinic zirconia and dolomite. The decomposition behaviour, phase stability and densification behavior of co-grounded zirconia-dolomite mixer were studied. It was observed that finer dolomite particle size (-63μm) resulted in higher amount of t/c $ZrO_2$ phase stabilization as a function of temperature. The effect of pre-calcination temperature on phase formation and densification was optimized. Higher t-phases were achieved with 3, 4 and 5 mol% dolomite whereas 6 and 7 mol% dolomite had more of cubic phases. The non-isothermal densification of the pre calcination compact showed two stage sintering behavior. Effect of sintering schedule on densification and phase formation of DSZ was co-related. Substructure grain was observed in cubic grain for 5mole% dolomite addition in SEM micrograph. Tetragonal zirconia precipitates in cubic zirconia with increasing dolomite content in the partial stabilized zirconia.

**Keywords** : Dolomite stabilization, Calcination, Partial Stabilized Zirconia, Microstructure

## Introduction

Zirconia is an important structural ceramics having high melting point (2680°C), corrosion resistance and proper combination of strength, toughness and hardness(1). When monoclinic zirconia is heated around 1160°C, it transforms to tetragonal zirconia associated with volume shrinkage. The tetragonal phase is stable between 1160 and 2360°C. Above 2360°C, cubic zirconia is stable(2). Several works have been carried on the stabilization of m-$ZrO_2$ with the addition of stabilizing agents like $Y_2O_3$, $Ce_2O_3$, CaO and MgO. Yttria stabilized Zirconia is very costly whereas calcia stabilized zirconia forms calcium zirconate(3). Although MgO stabilized zirconia has good thermal shock resistance it forms solid solution which destabilizes zirconia(4). However, it is difficult to prepare high density stabilized zirconia bodies when calcia is used as the stabilizer whilst bodies containing magnesia destabilize on thermal cycling in the temperature range 1000-1500°C. Nozzle clogging is the accumulation of alumina or alumina with other refractory compounds in the nozzle bore, which subsequently restricts the flow of steel through the nozzle during the casting of molten iron or steel.

The reaction between molten steel and component of slag ($SiO_2$, FeO, and MnO) reacts with refractory and alumina inclusions build up in the nozzle surface. In the continuous casting of steel, nozzle clogging is one of the most disruptive phenomena in the operation of the tundish mold system. The flow pattern of molten steel gets disturbed and if any clog chips entrapped in stream on solidification forms crack and lowers the strength and toughness(5). In the presence of calcia, alumina reacts to form a calcium-aluminate, which can be liquid below steel casting temperatures but the melting temperature depends on the calcia content. The density of alumina is lower than steel and alumina will tend to be driven towards the nozzle wall and there is a possibility of diffusion of CaO from the nozzle refractory to the surface and reacts with alumina. The excessive amount of calcia in the nozzle lead to erosion as the calcia in the refractory matrix is depleted(6). The lime is

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being treated for anti-clogging which form calcium-aluminate and for CaO-stabilized zirconia based might be de-stabilized due to depletion of CaO by reacting with alumina. So it will increase the erosion and reduce the hot strength on cooling as t→m transformation. Pure $ZrO_2$ is being avoided to use in refractory due to the t→m transformation associated with 3-4% volume expansion and stress leads to crack and failure. Either cubic or partial stabilized $ZrO_2$ is suitable for refractory grade as increase the thermal expansion along with low thermal conductivity limits the thermal gradient. The amount of stabilizer CaO/MgO required for refractory grade cubic/PSZ $ZrO_2$ is dependent on the design of microstructure and subsequently the phases. The careful controlling processing influences the cubic and monoclinic/meta stable tetragonal zirconia in the final PSZ which can limit the thermal and transformation stresses. PSZ with better thermal shock resistance is being done by the controlled stabilization of zirconia with addition of MgO or CaO. In this work attempts have been made to stabilize monoclinic zirconia with the addition of dolomite and to optimize the processing parameter for industrial application.

## Experimental Procedure

High purity commercial available Zirconia Lian Hai Resources Ltd., China and dolomite Jigme Mining Corporation Ltd., Bhutan were taken as the starting raw materials. The chemical analysis of the raw material is given in the Table1.

**Table 1**. Chemical analysis of raw materials

| *Raw Materials* | *$ZrO_2$* | *CaO* | *MgO* | *$Al_2O_3$* | *$Fe_2O_3$* | *$SiO_2$* | *$TiO_2$* | *LOI* |
|---|---|---|---|---|---|---|---|---|
| Zirconia | 99.05 | - | - | 0.10 | 0.06 | 0.50 | 0.15 | - |
| Raw Dolomite | | 30.12 | 21.41 | 0.39 | 0.23 | 0.44 | | 47.41 |

Dolomite was grounded to fine powder (63 and 100μm) and a mixer of zirconia and fine dolomite (3, 4, 5, 6 and 7 mole %) was prepared by solid state route. The weighted amount of zirconia and fine grounded dolomite powder was wet milled with zirconia grinding media in a pot mill. The resultant slurry was dried, grounded and calcined at different temperatures (1000, 1100, 1200 and 1300°C) and was subjected for phase analysis for optimization of calcined temperature. The dried co-grounded powder was subjected to DSC/TG analysis conducted in air on NETZSCH STA 409 using alumina crucible at a heating rate of 10°C/min. The calcined powder was mixed with 3% PVA and uniaxially compacted to cylindrical pellets of 12.5 mm dia. The non-isothermal densification behaviour of the compact was studied by dilatometry firing at 1500°C @ 10°C/min. Sintering the compacts was studied at 1550°C and 1600°C for 4 hours with a heating rate of 4°C/min. The bulk density of the samples was measured by Archimedes principle. The polished samples were chemically and thermally itched and the microstructure was observed by SEM (JEOL- JSM 6480 LV) in SE mode at 15KV.

## Results and discussion

### 3.1 Effect of particle size on phase evolution in the calcined powder

The study on the stabilization of zirconia by dolomite has been carried out by solid state route using monoclinic zirconia powder and dolomite (63,100μm). Figure 1 shows XRD pattern of co-grounded zirconia-dolomite powder calcined at 1300°C for 2 hours with different dolomite particle size (63,100μm).

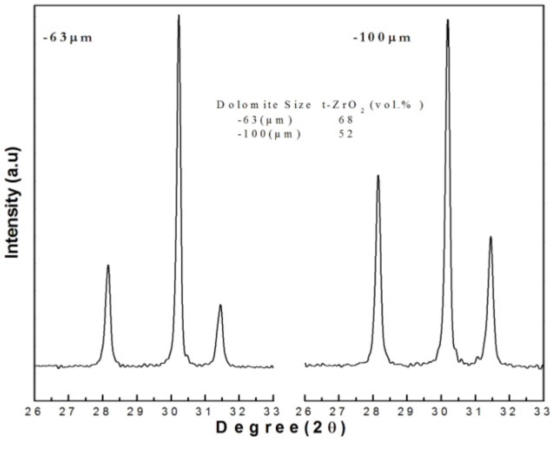


**Figure 1**. X-ray diffraction pattern of calcined zirconia-6mole% dolomite powder

The degree of tetragonal/cubic $ZrO_2$ phase stabilization was measured by XRD phase analysis at low angle scan ($2\theta = 26°-36°$). It is seen that the fraction of t/c $ZrO_2$ retention is higher (t/c =0.68) in the batches having fine dolomite (63µm) in comparison to coarser dolomite (100µm) for which the t/c =0.52. Thus for all further studies ahead, fine dolomite (<-63µm) was chosen.

### 3.2 DSC /TG

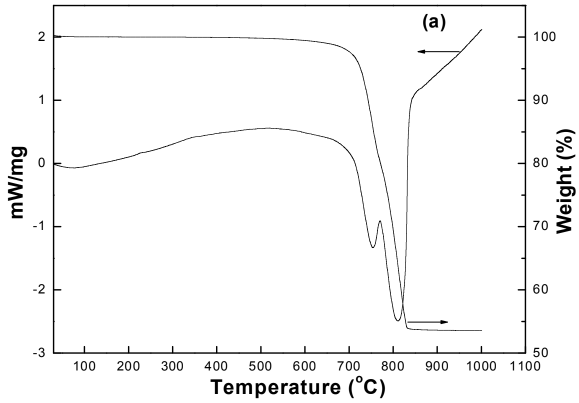
Figure 2 (a) shows that DSC/TG plot for dolomite, the first endothermic peak at 750°C is due to the decomposition of dolomite which is associated with a weight loss of 29.3% according to reaction : The weight losses are consistent with a two-step decomposition reaction of dolomite :

$$CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2 \qquad (1)$$

The second one is due to decomposition of $CaCO_3$ according to the reaction:

$$CaCO_3 = CaO + CO_2 \qquad (2)$$

Figure 2 (b) shows the DSC/TG plot for zirconia-6 mol% dolomite mixture. The addition of zirconia shifts the dolomite decomposition from 750ºC, 805°C to 380°C, 600°C temperature as well as separates the two closely spaced decomposition peaks. The endothermic peak at 380°C (associated with a weight loss 0.4%) corresponds to the decomposition of dolomite and the broad endothermic peak at 600°C is due to decomposition of $CaCO_3$. The reasons for the above conclusions are as follows : Equation (1) states that the weight loss is 23.90%. 6mole% dolomite-zirconia corresponds to 8.65 wt% dolomite and the weight loss for this amount is 0.44% which exactly matches with the theoretical weight loss. Thus addition of zirconia shifts the dolomite decomposition to a lower temperature as well as separates the two closely spaced decomposition peaks. This is due to lowering the partial pressure of $CO_2$ in the system, which promotes earlier decomposition.(7,8)



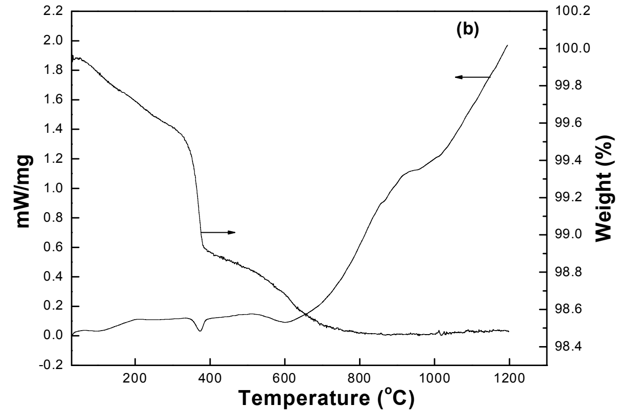


**Figure 2.** (a) DSC/TG behavior of dolomite and (b) DSC/TG behavior of zirconia-6mole% dolomite powder

### 3.3 XRD of calcined powder

Figure 3 shows the XRD pattern of the calcined zirconia-6 mol% dolomite composition as function of temperature. It is seen that the t(111) peak intensity increases with the increase in calcination temperature while the intensity of m(111) and m(111) peak reduces. During calcination, reaction between $ZrO_2$ and dolomite take place and dolomite is incorporated in the $ZrO_2$ lattice.

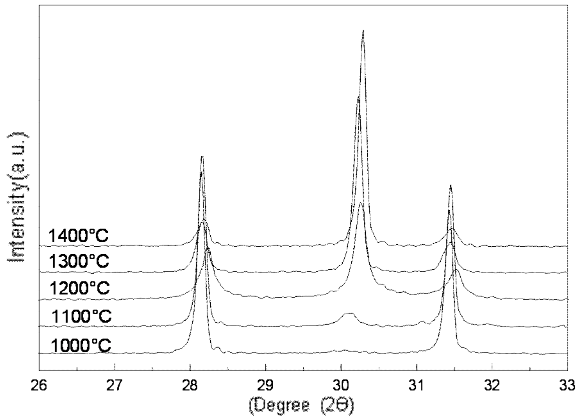


**Figure 3**. XRD pattern of the calcined zirconia-6 mol% dolomite composition as function of temperature

Therefore, higher is the calcination temperature for $ZrO_2$-dolomite mixture, higher will be the fraction of stabililized $ZrO_2$ phase. From Table 2 it is observed that (t+c) increases with increasing the calcinations temperature and it increases rapidly in the temperature 1000-1300°C, the increase is relatively small from 1300°C and 1400°C. However, increasing the calcination also increases in the crystallite size and the material also partially sinters. When such phenomenon takes place, it becomes difficult to densify these high temperature calcined products during sintering process$^{(9)}$. It was observed that powders calcined at higher temperature (i.e.1400°C) had very low sintered density (< 70% relative density). Therefore, it was decided to fix the calcination temperature at 1300°C.

**Table 2.** t/c-$ZrO_2$ phase in calcined zirconia-6 mol% dolomite composition as function of temperature

| *Calcination temperature (°C)* | *1000* | *1100* | *1200* | *1300* | *1400* |
|---|---|---|---|---|---|
| t/c Phase (vol%) | 1.13 | 4.20 | 54.52 | 67.79 | 82.07 |

### 3.4 Densification behavior of $ZrO_2$-dolomite compacts

The shrinkage curve (Figure 4) shows two steps sintering for $ZrO_2$-dolomite. The first step start at about 1080°C and finishes at about 1280°C and is immediately followed by second step which finishes at about 1450°C. The first stage is due to particle rearrangement leading to the neck formation by surface diffusion mechanism as well as the dissolution of dolomite into the $ZrO_2$ lattice.$^{(10,11)}$

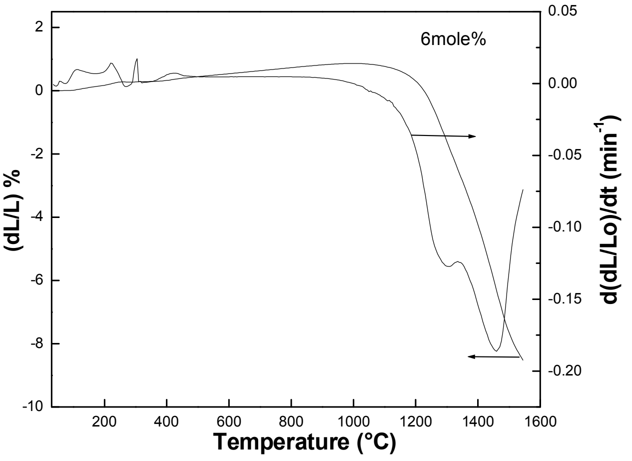


**Figure 4**. Non-isothermal densification behavior of zirconia-6 mole% dolomite powder

The second stage is due to sintering of zirconia-dolomite by lattice diffusion mechanism. Major shrinkage takes place during second stage of sintering. The calcined $ZrO_2$-dolomite compacts (calcination temperature 1300°C) were sintered at 1550°C and 1600°C with holding time 1 hour, 2 hours and 4 hours at the peak temperature. The dolomite content was varied from 3 to 7 mole%.

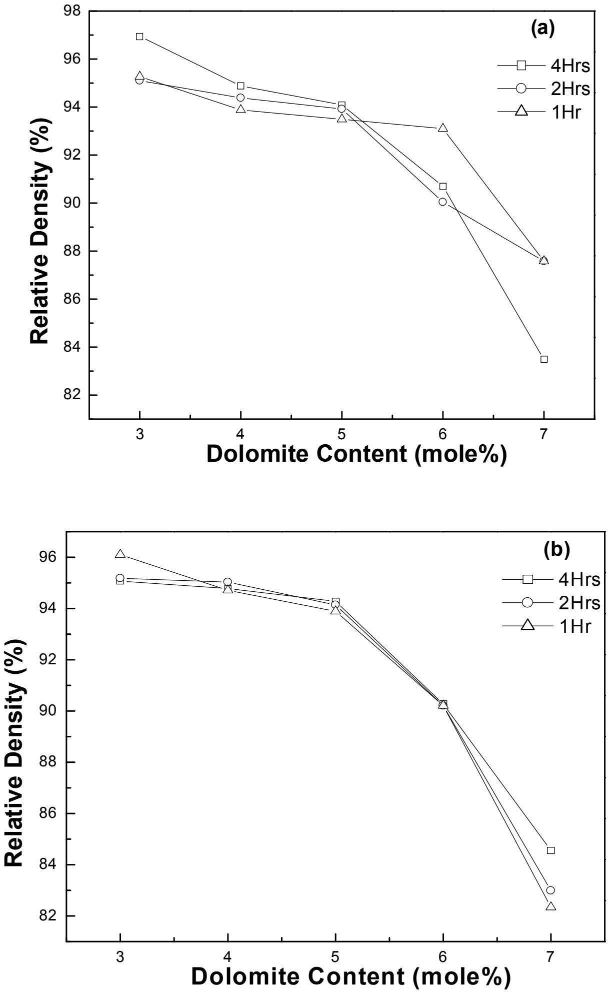


**Figure 5.** Relative density of dolomite-$ZrO_2$ as a function of dolomite content (a) at 1550°C, (b) at1600°C

The relative density as a function of dolomite content in plotted Figure 5 (a) for sintering temperature 1550°C and Figure 5 (b) for sintering temperature 1600°C. Both the graphs show that at either of the sintering temperature, the relative density of $ZrO_2$-dolomite decrease with increase in dolomite content. This is due to the reason that an increase in the dolomite content increases the amount of cubic $ZrO_2$ in the sintered sample given in the Figure 5 (c). Increase in dolomite content increases the defects in the crystal lattice and reinforcement of the diffusion process as CaO content increased which in further retards the process of densification.$^{(12)}$ It was observed at 6 mole% dolomite addition m-$ZrO_2$ disappears, however both c and t-$ZrO_2$ presents as equal proportion. Since cubic $ZrO_2$ has poor sinterability, the relative density reduces at higher dolomite content. The theoretical density of the dolomite stabilized zirconia decrease from 5.77 gm/cc for 3 mole% to 5.66 gm/cc for 7 mole% dolomite. Thus, at the 3 mole% dolomite addition, where the fraction of t-$ZrO_2$ phase is higher it has highest sintered density (95-96% relative density), whereas in 7 mol% dolomite the relative density is only 83-84% due to higher fraction of cubic $ZrO_2$ in that composition.

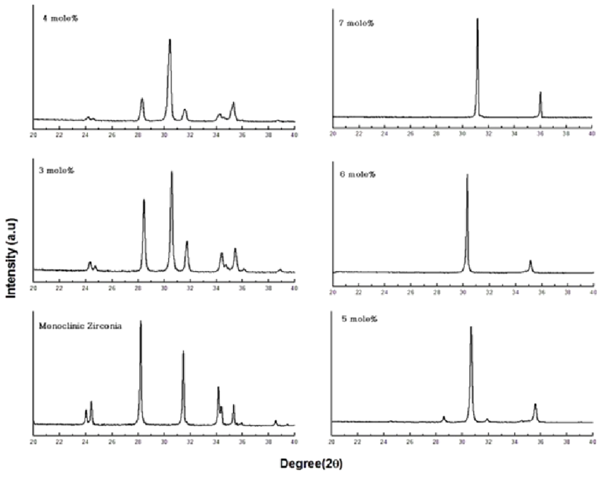
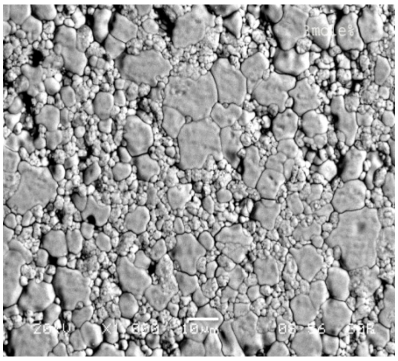


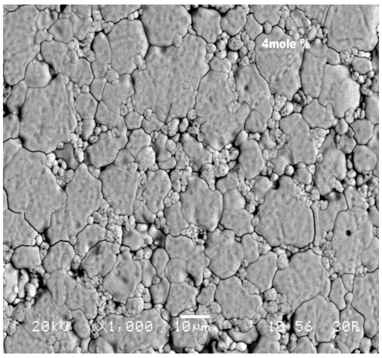
**Figure 5**. (c) Phase analysis of dolomite-$ZrO_2$ sample fired at1600°C

### 3.5 Microstructure of sintered zirconia-dolomite samples

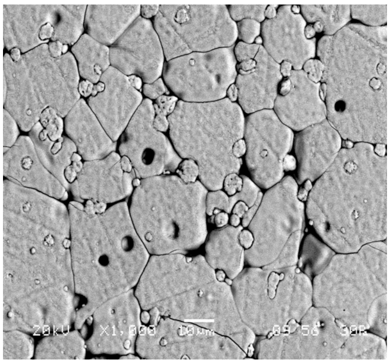
The SEM microstructures of the sintered $ZrO_2$-dolomite samples are shown in Figure 6 (A-E). $ZrO_2$-3 mole% dolomite has a duplex microstructure with small grains (2-5 µm) dispersed in large grains (8-25µm). XRD analysis has shown that this material has nearly 37% tetragonal, 45% monoclinic and 18% cubic zirconia. It is well known that m-$ZrO_2$ and t-$ZrO_2$ have smaller grain sizes. Thus the small grains are either m or t-$ZrO_2$ and large grains are cubic $ZrO_2$. For $ZrO_2$-4 mole% dolomite shows bimodal grain size distribution due to the coexistence of m, t and c-$ZrO_2$ phases, the size of the large grains are larger (10-30 µm) than the 3 mole% dolomite.



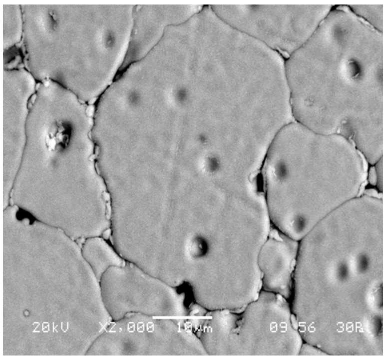
(a)



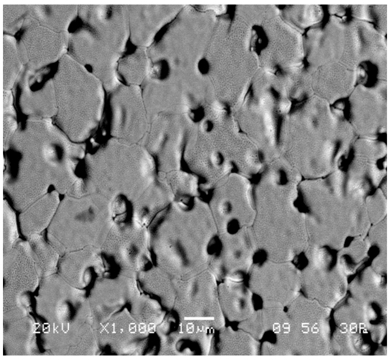
(b)



(c)



(d)



(e)

**Figure 6.** Microstructure $ZrO_2$-dolomite sample sintered at 1600°C (a) 3 mol%, (b) 4 mol%, (c) 5 mol%, (d) 6 mol% and (e) 7 mol% dolomite respectively

**Table 3.** Average grain size of sintered zirconia-dolomite samples (1600ºC)

| *Dolomite Composition (mole %)* | *Grain Size (μm)* |
|---|---|
| 3 | 10.289 |
| 4 | 13.84 |
| 5 | 22.65 |
| 6 | 23.96 |
| 7 | 20 |

Increasing in the dolomite amount in PSZ forms a substructure grains inside the large cube grains, which has become prominent in 5 mole% dolomite samples. Similar kind of substructure or colony formation has reported by Mustafa et.al(13) and they attributed it to the formation of t-$ZrO_2$ precipitates inside the cubic grain.Finally, at 6 and 7 mol% dolomite samples (Figure 6 (D) and (E) respectively), large grains with both intergranular and intragranular porosity have been observed. The 7 mol% dolomite composition show very porous microstructure with grain size 25-40μm. The average grain sizes for all the composition have been listed in Table 3.

## Conclusions

Co-grinding of zirconia and dolomite forms partial stabilized zirconia and at 1100°C t-$ZrO_2$ appears after the complete decomposition of dolomite and followed by reaction with zirconia. However for 3, 4 and 5 mole% dolomite compositions had a mixture of monoclinic, tetragonal and cubic $ZrO_2$, 6 and 7 mole% dolomite compositions had predominantly cubic $ZrO_2$. The densification of the PSZ decreases with addition of dolomite amount as higher cubic phase formation. Higher calcination lowers the densification of the compact as higher (t\c) ratio has higher crystallite size to fully sinter at 1600°C. The SEM microstructure show bimodal grain size distribution having both small and large grains for 3, 4 and 5 mole% dolomite compositions and predominantly large grains for 6 and 7 mole% dolomite compositions. Dolomite contents above 4mole% in the compositions show the colony structure in which small grains develop inside large cubic grains along with intergranular and intragranular porosity.

## References

1. Stevens, R. (1986). *An Introduction to Zirconia*. Magnesium Elektron Ltd., Twickenham : UK.
2. Subbarao, E. C., Maiti, H. S. and Srivastava, K. K. (1974). Martensitic transformation in zirconia. *Phys. Status Solidi A*. **21** : 9-40.
3. Durrani, S.K., Akhtar, J., Ahmad, M. and Hussain, M.A. (2006). Synthesis and characterization of low density calcia stabilized zirconia ceramic for high temperature furnace application. *Mater. Chem. Phys.* **100** : 324-328.
4. Jensen, D.G. (1996). Enhanced Toughness of a Partially Stabilised Zirconia at Elevated Temperatures. *J. Eur. Ceram. Soc.* **16(8)** : 825-831.
5. Rackers, K.G. and Thomas, B.G. (1995). Clogging in continuous casting tundish nozzles. *In 78th Steelmaking Conference. Nashville, TN, April 2. ISS, Warrendale, PA.* **78** : 723-734.
6. Moulden, G.T. and Sabol, R. (2000). Development of doloma tundish nozzles to reduce alumina clogging. *Ironmaking Steelmaking.* **27(6)** : 35-38.
7. Sahu, J. K., Chaudhuri, S. K. and Prasad, B. (1997). Development of alumina clogging resistance nozzles for continuous casting of steel. *Proceedings of the Unified International Technical Conference on Refractories*. 1435-1440.
8. Otsuka, R. (1986). Recent studies on the decomposition of the dolomite group by thermal analysis. *Thermochim. Acta.* **100(1)** : 69-80.
9. Engler, P., Santana, M.W., Mittleman, M.L. and Balazs, D. (1988). Non-isothermal in situ XRD analysis of dolomite decomposition. *Rigaku J.* **5(2)** : 3-8.
10. Bhattacharyya, S., Pratihar, S.K., Sinha, R.K., Behera, R.C. and Ganguly, R.I. (2002). Preparation of alumina–high zirconia microcomposite by combined gel-precipitation. *Mater. Lett.* **53(6)** : 425-431.
11. Coble, R.L. (1961). Sintering crystalline solids. I. intermediate and final state diffusion. *J. Appl. Phys.* **32(5)** : 787-792.

12. Kingery, W.D. and Berg, M. (1955). Study of Initial Stages of Sintering Solids by Viscous Flow, Evaporation-Condensation, and Self-Diffusion. *J. Appl. Phys.* **26(10)** : 1205–12.

13. Rudyak, I. N. and Karaulov, A. G. (1972). Sintering of zirconia as a function of the stabilizer concentration. *Ogneupory.* **10** : 41-44.

14. Mustafa, E., Wilhelm, M. and Wruss, W. (2002). Microstructure and phase stability of Y-PSZ co-doped with MgO or CaO prepared via polymeric route. *Br. Ceram. Trans.* **101(2)** : 78-83.