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Effect of CeO_2 on the sintering behaviour of zirconia–alumina composite

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Abstract

Precursor for a composite containing equimolar proportion of ZrO_2 and Al_2O_3 having higher reactivity has been synthesized by the wet interaction of inorganic salts in aqueous phase. Sintering of the compact body indicated that the densification rate increased from 1500 °C. The role of CeO_2 as a dopant was positive with respect to densification and retention of t-ZrO_2. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Powder-chemical preparation; A. Sintering; D. CeO_2; ZTA

1. Introduction

The role of CeO_2 on the transformation of Zirconia crystal had been studied by many workers. Morrell et al.[1] observed that the hardness of CeO_2–TZP falls more sharply with the increase in temperature than MgO–PSZ, and the degree of metastability increases with the increase in grain size. Yashima et al. [2] observed that reversible cubic tetragonal transformation occurred in 65 mol % CeO_2–ZrO_2. Shigematsu et al. [3] observed that martensitic transformation of CeO_2–ZrO_2 ceramics is affected by deoxidation.

Bond and Becher [4] synthesized an alumina–zirconia powder by sol–gel processing with Y_2O_3 for phase stabilization of zirconia. Fully dense composites by hot pressing with a fine grained (2 μm) alumina matrix containing dispersed 4 μm ZrO_2 particles of uniform composition were achieved [4]. Park et al. [5] studied the role of TiO_2 on the sintering behaviour and microstructure of Al_2O_3–ZrO_2 ceramics. They observed that addition of 2 wt.% TiO_2 improved sintered density to 98% of theoretical value, but sintered density decreased when more than 2 wt.% TiO_2 was added. Woltersdorf et al. [6] studied the microstructure of alumina ceramics containing zirconia. Lukin et al. [7] studied the effect of the addition of ZrO_2–Al_2O_3 on the structure and strength properties. Ranjbar et al. [8] studied the effect of chemically added zirconia and yttria on the mechanical properties of zirconia-dispersed alumina. The results of the earlier study indicated positive toughening effect by ZrO_2 in the ZrO_2–Al_2O_3 composites. Maximum toughness was achieved with 20 wt.% ZrO_2 in presence of Y_2O_3.

In the present investigation precursor powder in the Al_2O_3:ZrO_2 system having molar ratio 1:1 have been synthesized. Wet interaction of the components in aqueous medium was made to generate particles of very fine size with uniform microstructure. CeO_2 has been used as doping agent in the present investigation and sintering behaviour of CeO_2 doped, ZrO_2–Al_2O_3 composite has been studied.

2. Experimental procedure

For the synthesis of the, hydrogel $Al(NO_3)_3$ and $ZrOCl_2$ of analar quality were used. Molar solutions of each of the components were prepared in demineralized water. Required proportions of $Al(NO_3)_3$ and $ZrOCl_2$ were mixed according to molar ratio Al_2O_3:ZrO_2 = 1:1. The solution (pH = 2) was clear. Gelation was carried out by slowly adding 1:1 ammonia whereby viscosity gradually increased and ultimately set to an enblock gel at pH 8.5–9. The gel was processed properly, dried at 60 °C and milled in a pot mill.

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With the calcined powder, pellets were fabricated in a hydraulic press at a pressure of 1000 kg/cm^2 without any extra binder; only 10% uncalcined powder was used as binder.

The firing rate of the pellets was 10 °C/min up to 1000 °C and then 5 °C/min to the final temperature of heat treatment. X-ray diffraction patterns of the fired pellets were studied with a diffractometer (Philips PW-1730) using CuK$_\alpha$ radiation. SEM photographs were obtained by S-440 Leo Electron Microscope, Cambridge, UK.

Table 1
Physico-chemical characteristics of the hydrogel

Composition/properties	
ZrO_2 (wt.%)	34.00
Al_2O_3 (wt.%)	27.69
LOI (wt.%)	36.16
Al_2O_3:ZrO_2(molar ratio)	1:1
Bulk density (g/cm^3)	0.92
Sp. Surface area (m^2/g)	152.10

Table 2
Batch composition with CeO_2

Batch no.	CeO_2 (Mole%)
I	8
II	10
III	12

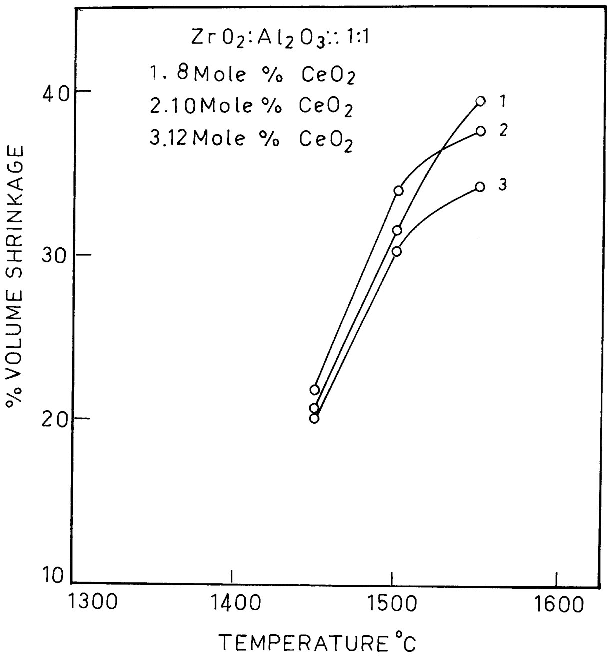


Fig. 1. Volume shrinkage–temperature curves for ZrO_2–Al_2O_3 composites.

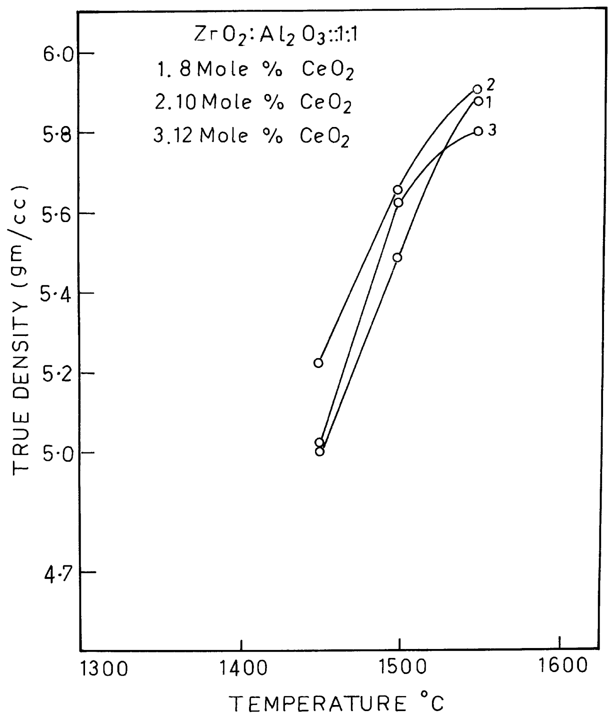


Fig. 2. True density–temperature curves for ZrO_2–Al_2O_3 composites.

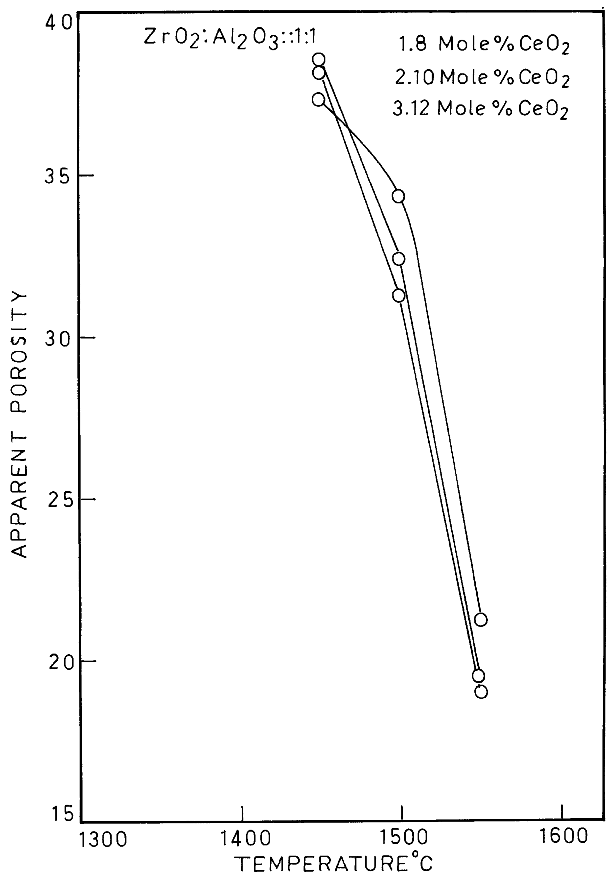


Fig. 3. Apparent porosity–temperature curves for ZrO_2–Al_2O_3 composites.

3. Results and discussion

The precursor powder for ZrO_2–Al_2O_3 composites was prepared by hydroxide hydrogel formation in aqueous medium. The complete precipitation occurred at this pH (8.5–9.0). The chemical analysis of the precursor is shown in Table 1.

The hydrogel was mixed thoroughly with requisite proportion of CeO_2 in an agate mortar as shown in Table 2.

From the chemical analysis of the product the molar ratio ZrO_2:Al_2O_3 was found to be 1:1, which was identical with that of the batch ingredients (Table 1). Thus, complete formation of hydroxide of zirconium and

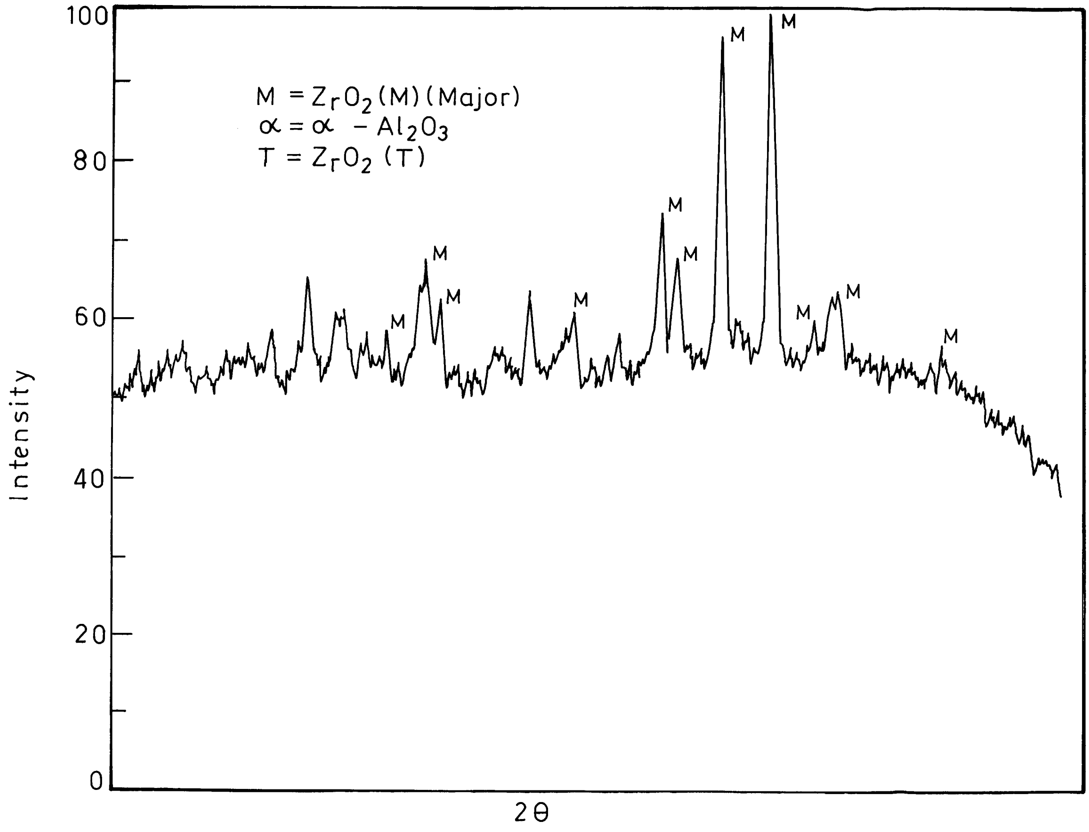


Fig. 4. X-ray diffraction pattern of zirconia–alumina composites fired at 1550 °C (Batch-I).

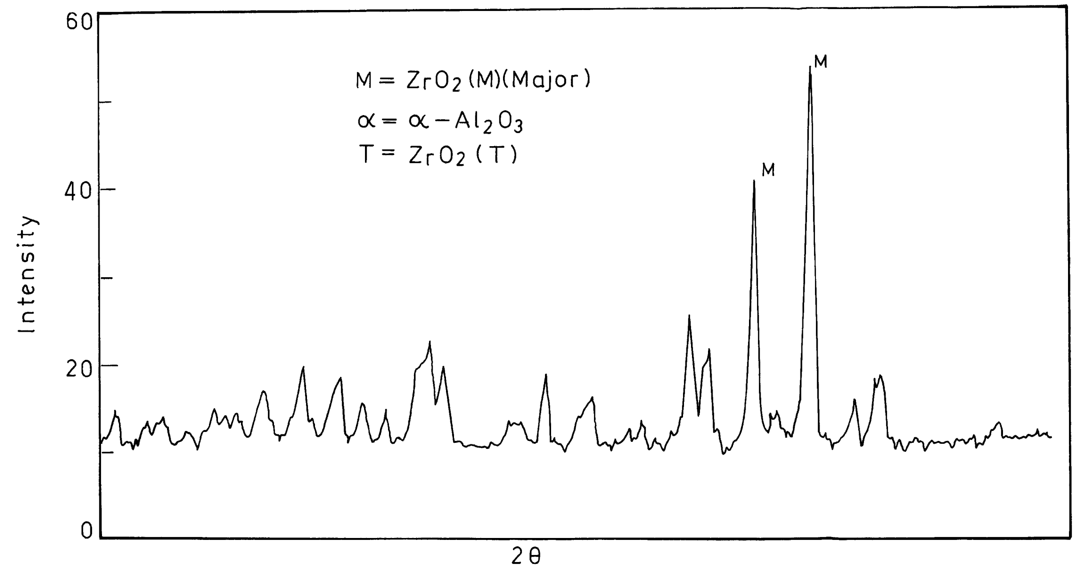


Fig. 5. X-ray diffraction pattern of zirconia–alumina composites fired at 1550 °C (Batch-II).

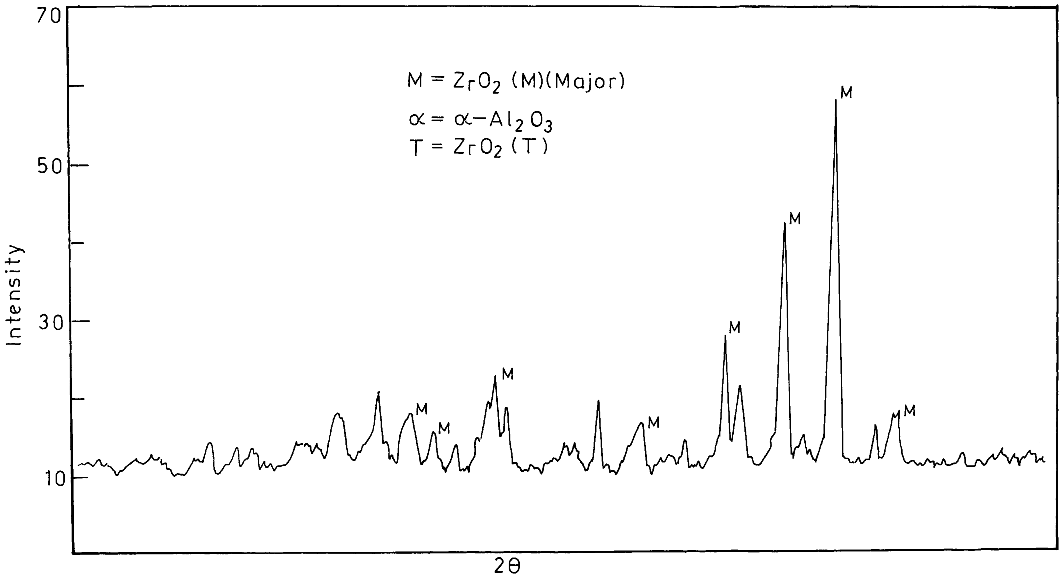
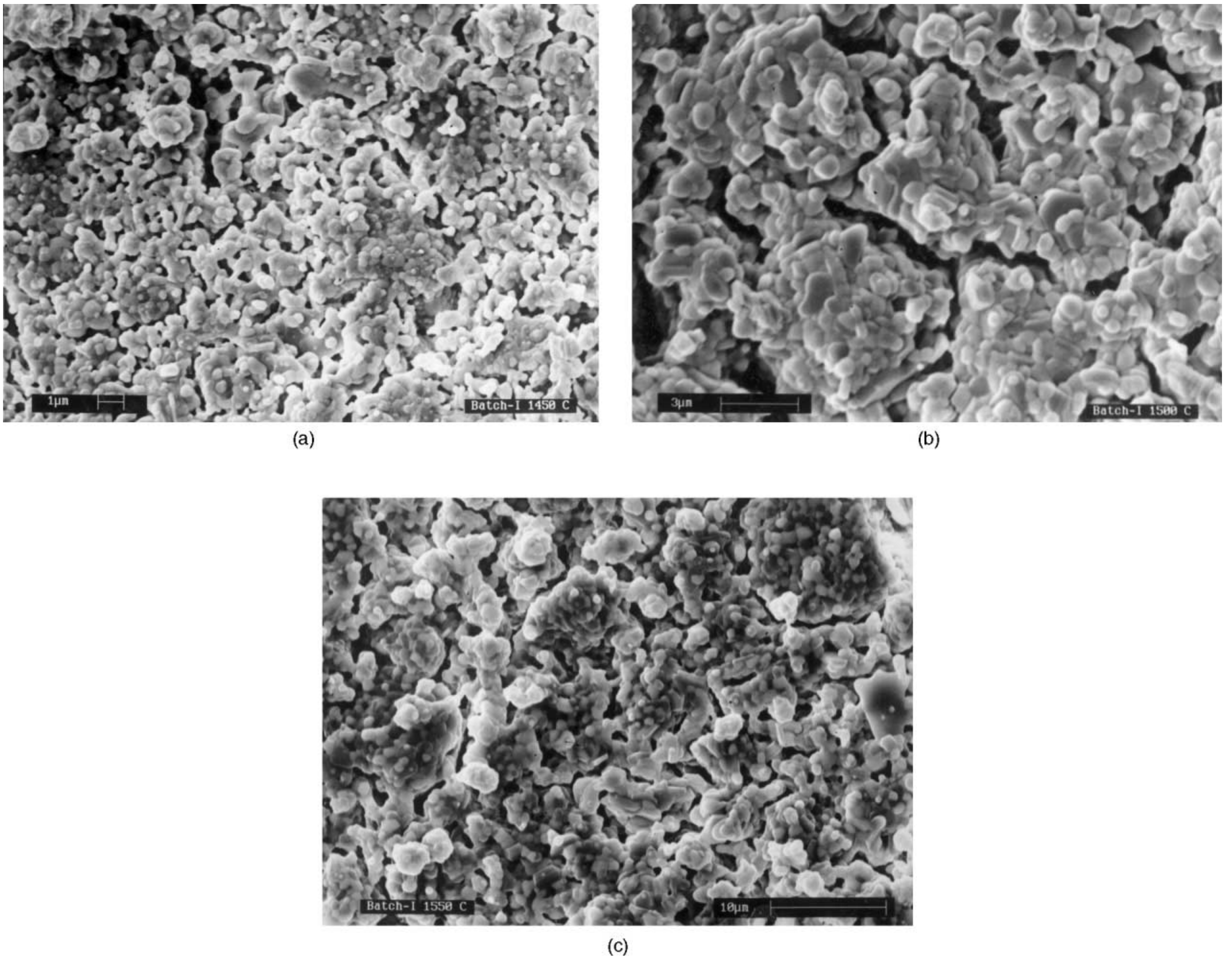


Fig. 6. X-ray diffraction pattern of zirconia–alumina composites fired at 1550 °C (Batch-III).



(a)

(b)

(c)

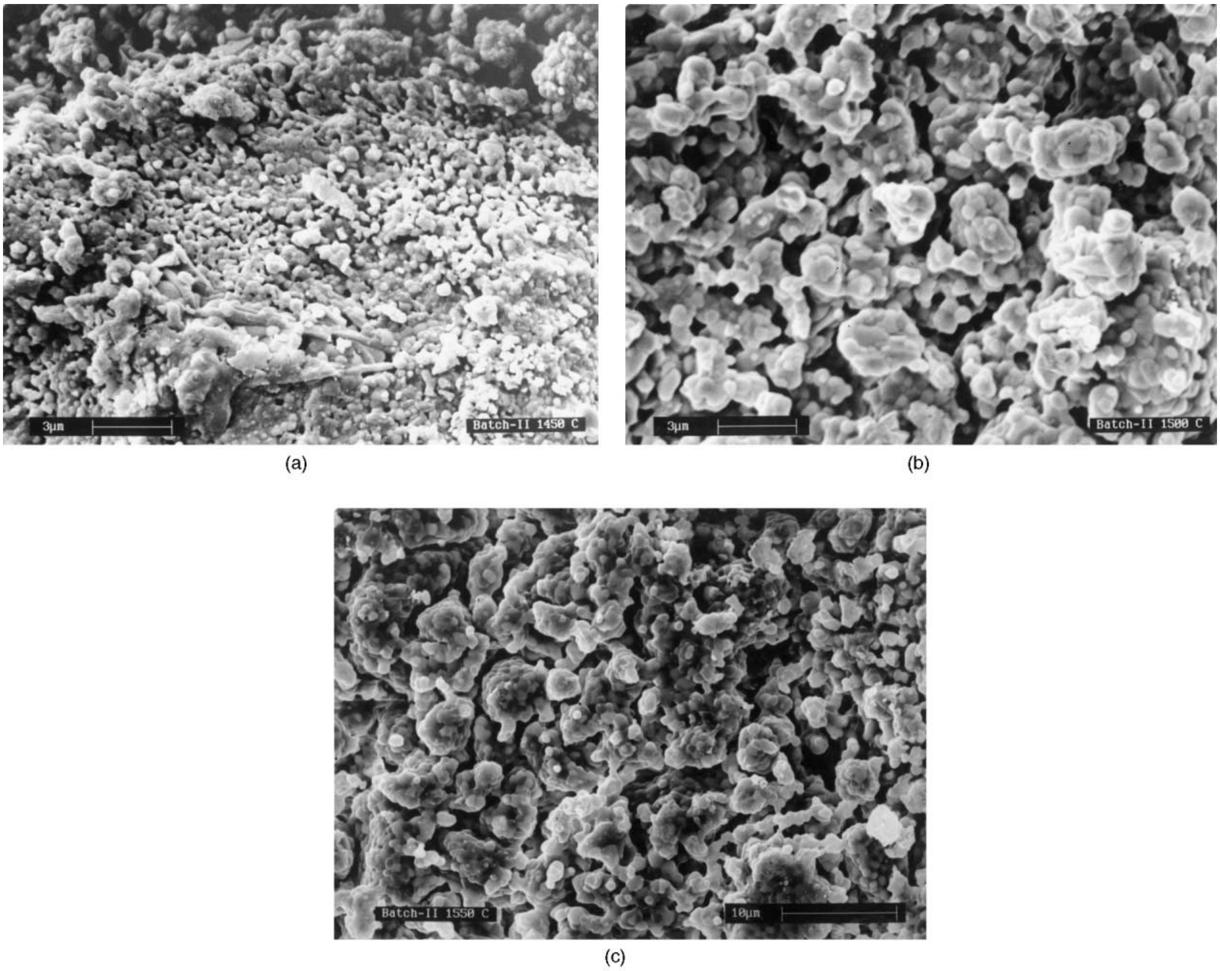
Fig. 7. SEM photomicrographs of compacts (Batch-I) sintered at: (a) 1450°C, (b) 1500°C, (c) 1550°C.

aluminium occurred in aqueous phase and this was also confirmed from the yield of the product, which was more than 95% of the theoretical value.

Again the purity of the hydrogel was ascertained by the non-existence of any oxides other than the desired constituents i.e. ZrO_2 and Al_2O_3. The opaque nature of the hydrogel was due to the non-oriented finer particles. Surface area of the powder (Table 1) was found to be significantly high compared to the naturally occurring material milled by the mechanical means. This was supported by the low bulk density of the powder.

Part of the synthesized gel powder was calcined to control the shrinkage during heat treatment of the compact mass. The fine calcined powder was mixed with about 10% non-calcined gel which acted as binder. It was further mixed with the additive in the solid state. The hydrogel was mixed thoroughly with requisite proportion of CeO_2 in an agate mortar as shown in Table 2. The pressed pellets after sintering in normal atmosphere exhibited shrinkage as shown in Fig. 1. The shrinkage of the compacts during sintering was mainly due to the expulsion of the residual water from the gel network, conversion of the hydroxides into the corresponding oxides and finally crystallization from the amorphous powder. Within the temperature range 1450–1550 °C the increase of firing shrinkage might be due to the grain growth of the respective crystalline phases. With the increase of the additives, the extent of shrinkage decreased which might be due to the more refractory nature of the rare earth oxides. The nature of the shrinkage curve did not exhibit any variation with respect to additive content. Initially a steep rise was observed up to 1500 °C followed by relatively slower rate up to the final temperature. In the later stage of sintering grain boundary diffusion was operative declining the rate of material transport. The rate of grain growth followed an inverse relationship with the amount of additive.

True density of the sintered product is related to the texture leading to densification of the materials. Initially at 1450 °C the densification was not of very high order leaving a porous microstructure. But from 1500 °C, densification rate increased. At this temperature 50% densification took place but it increased to more than 85% at 1550 °C. Comparatively maximum densification was achieved with 10 mole% CeO_2 at 1550 °C but this



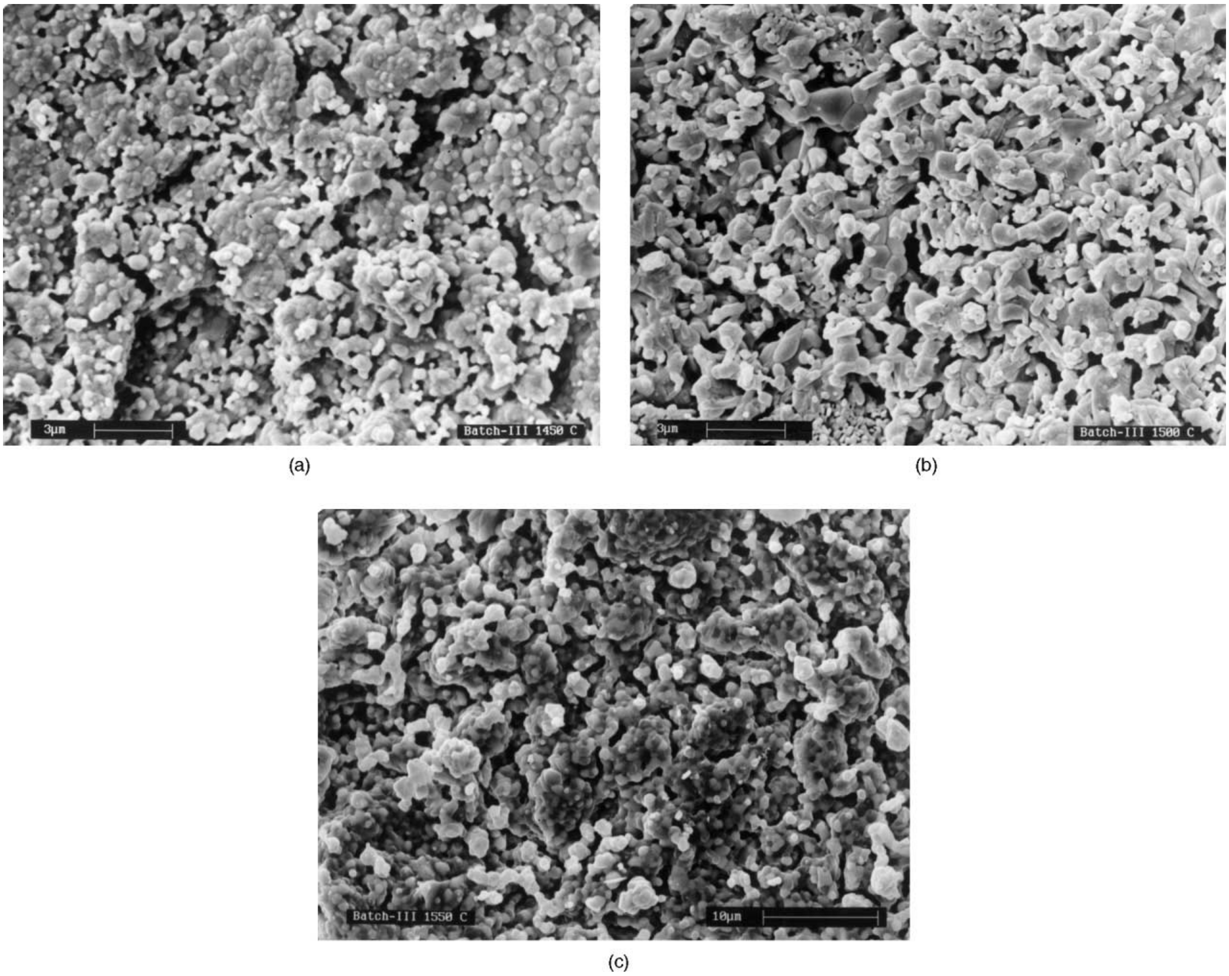
(a) (b) (c)

Fig. 8. SEM photomicrographs of compacts (Batch-II) sintered at: (a) 1450°C, (b) 1500°C, (c) 1550°C.

was quite different at 1550 °C where a direct relationship with amount of CeO_2 was observed (Fig. 2). The apparent porosity of the sintered samples was found to be a direct function of sintering temperature (Fig. 3) but from 1500 °C the rate of decrease was rather sharp. The retained porosity of the sintered sample was the maximum with 10 mole% CeO_2 and minimum with 12 mole% CeO_2. The difference was not of very high order as such the nature of the curve was similar.

XRD pattern of the samples sintered at 1550 °C have been represented in Figs. 4–6. The development of monoclinic zirconia as major phase along with Al_2O_3 and small amount of tetragonal zirconia was observed on increasing the amount of CeO_2 though the monoclinic phase was predominant and the amount of tetragonal phase increased along with Al_2O_3. In case of 12 mole% CeO_2, predominancy of monoclinic phase was observed along with the minor phase such as tetragonal zirconia and Al_2O_3. This can be attributed to the easing of the constraining matrix, which helps in the transformation of tetragonal and cubic phases. Trace amount of cubic ZrO_2 was also observed with 12 mole% of CeO_2. As the CeO_2 content in the composite increases, the tetragonal phase content goes up. This might be due to increased solid solution of CeO_2 in the zirconia matrix.

Microstructure development for the doped samples sintered at 1450, 1500 and 1550 °C was studied by SEM and the micrographs have been shown in Figs. 7–9. The sintering within the agglomerate is different from those between the agglomerate resulting in poor densification and non-uniform microstructure. The sintering rate within the agglomerate with 10 mole% CeO_2 (Fig. 8) is much higher so that they shrink from the matrix. Comparatively uniform microstructure was obtained with higher CeO_2 content and at high temperature up to 1500 °C, larger pores resembling channels were observed. But the dimension of the pores reduced with subsequent grain growth either at 1550 °C or with higher ceria content (Fig. 9). At the highest temperature of sintering, i.e. 1550 °C, pores were encircled and the grain boundaries became sharper. Ideal microstructure with homogeneous distribution of phases was obtained with 8–10 mole% CeO_2. Intragranular zirconia content



(a) (b) (c)

Fig. 9. SEM photomicrographs of compacts (Batch-III) sintered at: (a) 1450°C, (b) 1500°C, (c) 1550°C.

increased and the grain size variation was the minimum. Microstructure was characterized by cross linking, at earlier temperature with higher CeO_2 content which was minimized at 1550 °C with formation of sharp grain boundary and intragranular zirconia. It is interesting to note that in batch II and III, zirconia grains became mostly round with minimum sub rounded ones. The grain growth of intergranular zirconia appears to be due to transport of zirconia through grain boundary and that of intragranular through solid solution with dopants.

4. Conclusions

Precursor powder for sintered ZrO_2–Al_2O_3 composites having superior thermo-mechanical properties and uniform microstructure can be prepared at the desired mole ratio through hydroxide hydrogel formation.

Sintering rate increased significantly from 1500 °C. Dopant (CeO_2) reactivity for the formation of improved microstructure of this composite was found to be related to certain process parameters.

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