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Effect of Heating Mode on Sinterability of YSZ+CeO_2 Ceramics

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Abstract: In the current research work, a comparative study on densification and microstructural evolution of CeO_2 particle reinforced 8 mol % yttria stabilized zirconia (YSZ) sintered ceramics has been carried out. The ceramic compacts were fabricated via microwave and conventional sintering methods. The sintering conditions that were used for microwave and conventional methods are 1400 °C for 20 min and 1400 °C for 5 h, respectively. The sintered samples were characterized for densification, microstructural behavior, and hardness. Microwave sintering method of sintering resulted in high sintered densities as compared to the conventional counter parts. Microwave sintered samples exhibited finer grains as compared to conventionally sintered specimens. The grain size of the 8YSZ+CeO_2 sintered ceramics was found to decrease with CeO_2 addition. The X-ray diffraction (XRD) results showed no phase change because of CeO_2 addition. The Vickers hardness was found to increase with increasing amount of CeO_2.

Keywords: yttria stabilized zirconia; microwave sintering; CeO_2-YSZ ceramics

1. Introduction

It is well recognized that microwave sintering (MW) process enhances material diffusion kinetics in ceramics [1]. In MW, electromagnetic waves couples with ceramics via its dielectric loss and generate heat in the material. Depending upon the dielectric loss the material will experience very high or low heating rates. Due to microwaves and continuous material interaction and high heating rate, higher densities are achieved within minutes, whereas, conventional sintering requires many hours to obtain relatively higher sintered densities [2]. Additionally, as reported by several researchers [3,4], the electromagnetic field enhances the driving force for diffusion, and hence, densification rate increases in microwave sintering. Therefore, through microwave sintering we can achieve high densities at much shorter soak times and lower sintering temperatures. Major advantages of using MW are discussed in detailed by Xie et al. [5]. Microwave sintering of zirconia based ceramics, has been studied by previous researchers [2,5–7]. Previously, microwave sintered zirconia based ceramics, such as CeO_2 stabilized ZrO_2 and Al_2O_3 reinforced ZrO_2, were investigated. Among those ceria + 8 mol % YSZ is considered as a candidate material for thermal barrier coatings. Ceria + 8 mol % YSZ has superior toughness and thermal shock resistance, and high insulation capability. Moreover, thermal shock tolerance and corrosion resistance of YSZ were improved by the addition of CeO_2 [8,9]. In a previous study, CeO_2-YSZ ceramics processed through microwave sintering, achieved higher density values and better mechanical properties [5,10] than the conventional sintering (CS) methods. Earlier work [11,12] reports that CeO_2/Y_2O_3 has the greater impact on stabilizing the tetragonal and cubic phases in the Ce-TZP (tetragonal zirconia polycrystals) ceramics, leading to improved mechanical properties. It was also suggested that addition of CeO_2 to YSZ enhances the thermal insulation properties and had the

impact on crystal structural change [13,14]. Mechanical and thermal properties of YSZ composite improved by the addition of CeO_2 as the coefficient of thermal expansion is very high and thermal conductivity of CeO_2 is lower than YSZ. The current research aims to study the effect of ceria addition on the microstructural behavior and mechanical properties of CeO_2 + 8 mol % YSZ ceramics fabricated by microwave sintering. 8 mol % YSZ ceramics with different (10, 12, and 14 wt %) amounts of CeO_2 were compacted and sintered in microwave and conventional furnaces. The densification behavior, XRD analysis, microstructure characteristics, and hardness were studied and compared.

2. Experimental Details

The starting materials used were commercially available 8 mol % yttria stabilized, cubic phase zirconia (8YSZ) powder (particle size 20–50 μm), and high-quality ceria powder (particle size of 20–60 μm), and acquired from Sigma Aldrich India Pvt Ltd., Bangalore, India. The powder morphology is shown in Figure 1. CeO_2 and 8YSZ powders were mixed in a ratio of 10:90, 12:88 and 14:86 by weight by ball milling (VB Ceramic Consultants, Chennai, India) for about 15 min at 300 rev·min^{-1} to ensure uniform mixing. Tungsten carbide balls (60 mm diameter) were used for ball milling. Green cylindrical compacts (8 mm in radius and 5 mm height) were made by pressing the blended powders in a 50 ton hydraulic press with a uniaxial pressure of 5 ton. The pressed compacts were sintered in the microwave furnace operating at 2.45 GHz frequency. The SiC susceptor was used in the MW furnace (VB Ceramic Consultants, Chennai, India). In order to obtain an accurate value of density, hardness, etc., three samples of each composition were sintered in the same run. The MW sintering conditions used were temperature of 1400 °C for 20 min. For comparison, in parallel another set of samples was sintered in the conventional furnace at 1400 °C with dwell time of 5 h with a heating rate of 5 °C per minute. The sintered densities of the ceramics were measured using the Archimedes method. The phase composition of the sintered ceramics was identified using XRD (BRUKER D8 Advanced, Yokohama, Japan, Cu Kα, λ = 1.5405 Å) with an exciting potential of 40 kV, and the current of 30 mA. XRD performed on all of the specimens in 2θ range of 20–90°. Scanning electron microscope (Zeiss Penta FET precision, Model: 51-ADD0048, Carl Zeiss Pvt Ltd, Bangalore, India) with working distance of 11.5 mm and 20 kV voltage was used to examine the microstructure of the sintered samples. Prior to SEM analysis, the surfaces of the specimens were well polished using diamond paste, and were thermally etched by holding in a furnace at 100 °C below the sintering temperature for 1 h. The grain sizes of the samples were calculated by the linear grain intercept method using SEM micrographs. The hardness of the samples was measured by using semi-automatic Vickers's micro hardness tester (Chennai Metco Private Limited, Chennai, India) at 500 kgf load with the diamond pyramid indenter with a dwell time of 10 s. The reported hardness values are an average of ten indentations made on random spots throughout the surface.

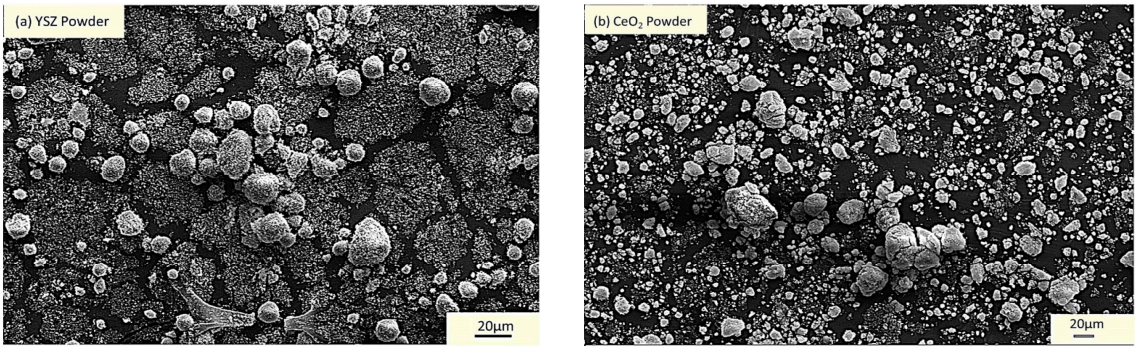


Figure 1. Scanning electron microscope (SEM) images of as received (**a**) yttria stabilized zirconia (YSZ) and (**b**) CeO_2 powders.

3. Results and Discussion

3.1. Densification and Hardness

Table 1 compares the densities of YSZ ceramics doped with 10, 12, and 14 wt % of CeO_2 sintered in conventional and microwave furnaces at 1400 °C/5 h and 1400 °C/20 min, respectively. In general, microwave sintered samples exhibited higher sintered density values than the conventionally processed specimens, due to uniform heating and microwave non-thermal effect. A notable density variation can be seen in YSZ samples (without any ceria addition) that are processed in the microwave and conventional sintering techniques. The microwave sintered YSZ sample exhibited 92.2% relative density, while the conventionally sintered YSZ pellet showed 85% relative density. However, the relative density of MW sintered 8YSZ that was obtained in this work is less when compared to the work of Janney et al. [1], who reported 99% relative density for 8YSZ samples sintered in microwave furnace at 1195 °C for 1 h. Samuels and Brandon [15] reported lower relative density of 85% at 1300 °C for 12 mol % YSZ for microwave sintered sample. Nightingale et al. [4] reported a relative density of microwave sintered YSZ as 89% at 1300 °C. Meek et al. [16] reported highest relative density of 97.6% for microwave sintered Y_2O_3-ZrO_2 samples. 10, 12 and 14 wt % addition of CeO_2 resulted into 1.08%, 3.14%, 4.33% increment in the densities of MW sintered 8YSZ ceramics, respectively. A relative density of 96.2% of the microwave processed YSZ with 14% CeO_2 was found to be the highest among all compositions. It is obvious that the ceria addition to 8YSZ increases the sintered density using microwave sintering method. Microwave energy absorption is associated with the material's dielectric loss factor. At low temperatures, YSZ cannot absorb microwaves effectively because of its low dielectric loss factor. However, in the presence of SiC as a susceptor, YSZ gets heated initially from the heat generated in SiC. After reaching a critical temperature, YSZ strongly couples with electromagnetic field and a higher heating rate is obtained due to increased dielectric loss factor. Additionally, there is non-thermal microwave effect that enhances the material diffusion. These are the possible reasons for higher densities in microwave sintered ceramic samples.

Table 1. Density, grain size and hardness of CeO_2+YSZ ceramics processed through microwave (MS) and conventional (CS) sintering.

Composition	Sintering Mode	Relative Density	Theoretical Density (g/cc)	Grain Size (μm)	Vickers Hardness (Hv_{500})
8 mol % YSZ	CS 1400—5 h MW 1400—20 min	85 ± 1.81 92.2 ± 0.41	6.09	10 ± 2 0.27 ± 0.01	1136 ± 8 1312 ± 15
10CeO_2 + 8 mol % YSZ	CS 1400—5 h MW 1400—20 min	85.44 ± 1.86 93.2 ± 0.32	6.194	6.25 ± 1.03 0.24 ± 0.1	1188 ± 20 1349 ± 21
12CeO_2 + 8 mol % YSZ	CS 1400—5 h MW 1400—20 min	86.33 ± 2.42 95.1 ± 0.45	6.2148	5.82 ± 0.2 0.22 ± 0.02	1232 ± 8 1364 ± 16
14CeO_2 + 8 mol % YSZ	CS 1400—5 h MW 1400—20 min	88.53 ± 0.92 96.2 ± 0.42	6.2356	5.5 ± 0.55 0.19 ± 0.01	1295 ± 15 1375 ± 9

Notes: CS-Conventional sintering; MW-Microwave sintering.

Vickers hardness of ceramics is mainly affected by the microstructure and amount of second phase present [17]. Vickers hardness values with respect to the composition are listed in Table 1; a high value of 1375 MPa was achieved for MW sintered 14 wt % CeO_2+YSZ ceramics. The Vickers hardness of 8YSZ specimens increased with the addition of CeO_2 in both of the sintering methods. The hardness values obtained for conventional sintered 10 wt %, 12 wt % and 14 wt % CeO_2 doped 8YSZ ceramics are 1188, 1232, and 1294 Hv_{500}, respectively. These numbers are higher than the hardness value of conventionally sintered 8YSZ specimen of 1136 Hv_{500}. This is mainly attributed to high sintered densities, small grain sizes, and homogenous microstructure, as noted in microwave sintered samples. It is also deduced that addition of CeO_2 to 8YSZ resulted in increased resistance to deformation, resulting in higher hardness values due to grain refinement. A decrease in grain size results in an

increase in the grain boundary volume that retards the dislocation movement, thus leading to an increase in the hardness of the ceramics [18–20].

3.2. Microstructural Study and Phase Analysis

SEM micrographs of CeO_2+8YSZ ceramics that are processed through conventional and microwave sintering are shown in Figure 2. Microwave sintered ceramics exhibited fine uni-size grains and refined microstructure. Evenly distributed residual porosity was observed in microwave sintered samples throughout the surface, as compared to conventional sintered ceramics. This is due to uniform heating and a lower sintering temperature and holding time in microwave heating as compared to the conventional heating [21]. The microwave sintered specimens exhibited monotonous spherical grains throughout the surface. In contrast, irregular coarse grains were observed in conventionally sintered samples. The grain size of the conventional sintered 8YSZ is 10 μm and it decreases to 6.25, 5.82 and 5.5 μm with the addition of 10, 12, and 14 wt % CeO_2, respectively. The same decreasing trend was observed in microwave sintered counterparts with the addition of CeO_2. In general, a dopant oxide with dissimilar radius and valence than the solvent cations, always acts as a grain growth inhibitor in YSZ during the sintering process [22].

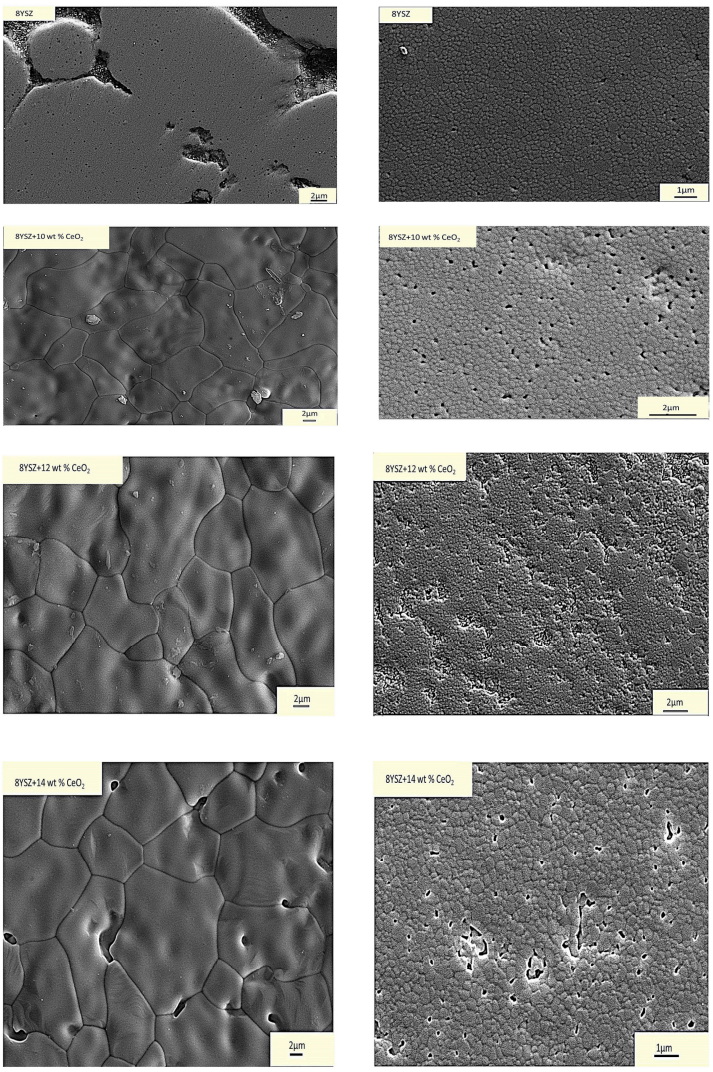


Figure 2. SEM images of CeO_2 doped YSZ sintered ceramics. (**a**) 8 mol % YSZ; (**b**) 10 wt % CeO_2+8YSZ; (**c**) 12 wt % CeO_2+8YSZ; and (**d**) 14 wt % CeO_2+8YSZ. (Left side conventional and Right side Microwave sintered samples).

The X-ray diffraction patterns of powders and sintered samples in the 2θ range from 20° to 90° are presented in Figure 3. Diffraction patterns of YSZ and the doped ceramics that are represented the cubic crystal structure. The diffraction peaks correspond to (111), (200), (220), (311), (222), (400), (331), (420) planes. The XRD patterns of sintered ceramics indicated that the ceria had formed solid solution with 8YSZ, resulted into cubic stabilized ZrO_2, and showed no difference in crystal structure formed during sintering. Also it is to be noted that no trace of undesirable monoclinic phase was detected in any sample. The crystal structure of YSZ is found to be the same in both the conventional and microwave sintering processes, and this result is similar to the reported work [23].

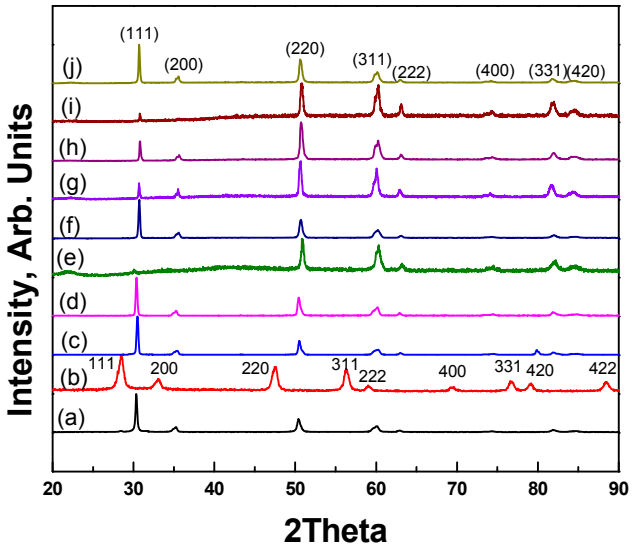


Figure 3. X-ray diffraction (XRD) patterns of the (**a**) 8YSZ Powder; (**b**) CeO_2 powder; (**c**) conventional sintering (CS) 8YSZ; (**d**) Microwave sintering (MW) 8YSZ; (**e**) CS 8YSZ + 10 wt % CeO_2; (**f**) MW 8YSZ + 10 wt % CeO_2; (**g**) CS 8YSZ + 12 wt % CeO_2; (**h**) MW 8YSZ + 12 wt % CeO_2; (**i**) CS 8YSZ + 15 wt % CeO_2; (**j**) MW 8YSZ + 15 wt % CeO_2.

4. Conclusions

In this research, 8 mol % YSZ ceramics with the addition of 10, 12, and 14 wt % of Ce_2O_3 were fabricated by microwave and conventional sintering methods. The densification, microstructure, crystal structure, and Vickers hardness of the as-sintered specimens were investigated. The main findings from the experiments are:

1. The sintered densities of 8YSZ specimens increased with the addition of CeO_2 content, irrespective of the sintering technique.
2. Additions of CeO_2 have not disturbed the stability of the cubic crystal structure of 8YSZ.
3. The CeO_2 acts as grain growth inhibitor, grain size of the 8YSZ specimens decreases with the addition of CeO_2.
4. The Vickers hardness of the 8YSZ+CeO_2 ceramics increased with the addition of CeO_2 content.
5. The enhancement in sintered densities and hardness values with the addition of ceria were more pronounced in microwave sintered samples than in the conventional method.

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Conflicts of Interest: The authors declare no conflict of interest.

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