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Microstructure characterization of mechanosynthesized CeO_2 stabilized nanocrystalline ZrO_2

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Abstract- In this research work, nanocrystalline cubic (c) zirconia was synthesized by mechanical alloying monoclinic (m) ZrO_2-CeO_2 powder mixture (0.9: 0.1molar ratio) using high-energy planetary ball mill. X-ray powder diffraction (XRD) patterns of ball-milled powders reveal that the mechanical alloying technology was effective to synthesize stable cubic (c) zirconia phase within a short milling time. Structural and microstructural changes of different phases and relative phase abundances have been estimated by adopting Rietveld analysis of XRD data. Output results of Rietveld analysis are used to explain the formation mechanism. The average crystallite sizes of cubic zirconia are between 5 to 8 nm. After 8h of ball milling, c- ZrO_2 becomes the major phase with some minor contribution of m-ZrO2 phase so that the final ball-milled product is recognized as nano-dimensional partially stabilized zirconia (PSZ) ceramic. Finally, HRTEM study of 8h ball-milled powder mixture corroborates with the results as obtained by the Rietveld analysis of XRD data.

Index Terms- Ball milling; Rietveld analysis; cubic ZrO_2; Nanoparticles.

1. INTRODUCTION

In recent years, the high-energy ball milling method has received considerable attention basically for (i) producing nanoparticles with enhanced surface reactivity (ii) amorphization of powder sample (iii) polymorphic and other types of phase transitions, (iv) producing metal–metal, metal–ceramic or ceramic–ceramic nanocomposites [1-5]. The materials transfer by diffusion of components during ball milling provides the way to new phase formation. This solid-state technique is especially useful for synthesizing those compounds that are difficult to prepare in the conventional process due to the requirement of high pressure or temperature. In the present study, the ball-milling method has been employed for stabilization of Zirconia phase by CeO_2 doping. Rietveld's whole profile fitting method is adopted for microstructure characterization of the prepared nanocrystalline PSZ powders. Rietveld refinement method based on pseudo-Voigt analytical function can successfully be applied for phase quantification as well as microstructure characterization of a multiphase material.

Pure, undoped zirconia exists in three polymorphs: monoclinic (space group: P21/c) from room temperature to 1440K, tetragonal (space group: P42/nmc) between 1440 and 2650K and cubic (space group: $Fm\bar{3}m$) up to the melting point of 2950K. Being stabilized in the cubic phase, zirconia has a wide range of technological applications as structural ceramics [6, 7]. These materials exhibit a high ionic conductivity at high temperatures allowing their use in fuel cells, oxygen sensors, oxygen pumps etc [8].

The purpose of the present research work is (i) to prepare nanocrystalline PSZ at room temperature by high energy ball milling, adding CeO_2 as a dopant and (ii) to characterize prepared materials in terms of several microstructural defect parameters by analyzing X-ray diffraction profiles with Rietveld's powder structure refinement method. (iii) to find out direct supportive evidence of XRD pattern analysis method by HRTEM study.

2. EXPERIMENTAL

Mechanical alloying was executed by a high-energy planetary ball mill (Model-P5, M/s FRITSCH, GmbH, Germany). Monoclinic ZrO_2 and CeO_2 powders were mixed in a required molar ratio (0.9:0.1) and the starting ingredients were sealed in a chrome steel vial containing chrome steel balls. The ball-to-powder weight ratio (BPWR) was kept at 40:1. Milled powder was collected from the vial after a selected milling time interval varying from 1h to 8h. Step-scan XRD data (step size 0.02^o 2θ) of unmilled and all ball milled powders were recorded from an X-ray powder diffractometer (Panalytical; Model PW1830) with Ni-filtered CuK_α radiation. The 8h ball milled powder was finely dispersed in alcohol and a tiny drop of the solution then taken on a carbon-coated Cu-grid of TEM. The TEM was operated at 200KV (Model HR-TEM, JEOL JEM 2100) for obtaining well-resolved TEM micrographs of nanocrystalline ZrO_2 particles.

3. EVOLUTION OF MICROSTRUCTURE BY X-RAY POWDER DIFFRACTION

In the present study, Rietveld's whole profile fitting method has been successfully adopted employing

Rietveld software MAUD 2.79 [9] for microstructure characterization of the ball-milled materials. The simulated powder diffraction pattern contains necessary structural and microstructural information of the individual phases, m-ZrO_2 (ICSD # 1522143; monoclinic, Space Group (S.G.): P21/c, a = 5.1462Å, b=5.2082 Å , c= 5.3155 Å , β = 99.03), CeO_2 (ICSD # 9009008; Cubic, S.G.: Fm$\bar{3}$m, a= 5.411 Å), c-ZrO2 (ICSD # 1521753; cubic, S.G.: Fm$\bar{3}$m, a= 5.0900 Å). Simulated XRD pattern of respective milled samples are refined to fit the experimental XRD data and refined structural and microstructural parameters reveal the measure of crystallite size, r.m.s. lattice strain, lattice parameters and relative abundance of individual phases in the milled powder samples.
Refinement continues for minimizing the difference between the observed (I_o) and simulated (I_c) powder diffraction patterns till convergence is reached. Value of the quality factor, GoF ~1.0, confirms the goodness of refinement [10-14].

The Rietveld analysis has been successfully applied for the phase quantification of the composite materials [15-19] and also has been adopted in the present work for accurate phase quantification of the ball-milled m-ZrO_2-CeO_2 powder mixture.

4. RESULTS AND DISCUSSION

Fig. 1(a) illustrates the X-ray powder diffraction patterns of unmilled and all ball-milled (1, 3, 5 and 8h) m-ZrO_2 –CeO_2 powders. The XRD powder pattern of unmilled (0h) homogeneous powder mixture contains only the reflections of m-ZrO_2 and CeO_2 phases. With increasing milling time the intensity of CeO_2 reflections decrease rapidly and all the reflections of CeO_2 vanish completely in XRD pattern of 8h ball-milled sample. For Rietveld analysis, all the experimental patterns (I_0) are fitted with the theoretically simulated patterns (I_c) and are shown in Fig. 1(a). Nearly linear residual fitting plot (I_0–I_c) gives evidence of the good quality of fitting. The GoF values (1.1–1.4) as obtained from the Rietveld analysis of XRD data reveal theoretically that the simulated powder patterns are properly refined to fit the experimental powder patterns [10-12]. Microstructure characterization by Rietveld method reveals that the c-ZrO_2 phase has been grown just after 1h of ball milling and becomes the major

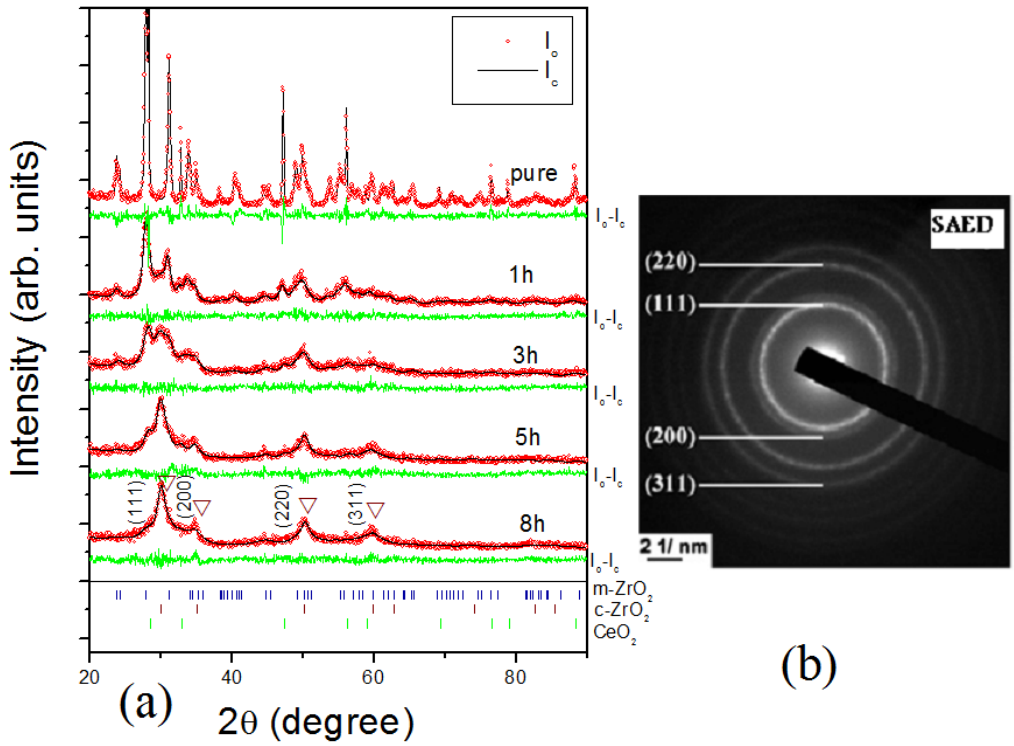

Fig. 1(a) X-ray powder diffraction patterns of ZrO_2-CeO_2 ball-milled powder mixtures. Experimental data points are shown as hollow circles, while refined simulated patterns are shown as continuous lines. The difference between the experimental data (I_o) and the fitted simulated pattern (I_c) is shown as a continuous line (I_o- I_c) under respective diffraction pattern. **(b)** Indexed selected area electron diffraction (SAED) pattern of 8h ball-milled homogeneous mixture of ZrO_2-CeO_2 powders.

Table 1. Microstructure parameters of unmilled and ball milled CeO_2- ZrO_2 powder mixture revealed by Rietveld's X-ray powder structure refinement analysis.

Milling time	Phase present	Mol fraction $\pm[10^{-3}$ to $10^{-2}]^*$	Lattice Parameter $\pm[10^{-5}$ to $10^{-3}]^*$ a (Å)	b (Å)	c (Å)	β (degree)	Crystallite Size (nm) $\pm[10^{-2}$ to $10^{-1}]^*$	R.m.s strain $\langle\langle\varepsilon_L^2\rangle^{1/2}\rangle \times 10^3$ $\pm[10^{-3}$ to $10^{-2}]^*$
0 min	CeO_2	0.10	5.409	5.409	5.409		174.2	0.55
	m-ZrO_2	0.90	5.148	5.204	5.315	99.162	37.1	2.16
1h	CeO_2	0.18	5.426	5.426	5.426		10.7	0.20
	m-ZrO_2	0.42	5.131	5.186	5.294	99.218	16.8	1.33
	c-ZrO_2	0.40	5.119	5.119	5.119		5.0	3.57
3h	CeO_2	0.07	5.396	5.396	5.396		10.7	0.62
	m-ZrO_2	0.33	5.153	5.168	5.343	99.066	7.5	0.23
	c-ZrO_2	0.60	5.119	5.119	5.119		4.6	1.40
5h	CeO_2	0.04	5.391	5.391	5.391		9.5	3.60
	m-ZrO_2	0.23	5.182	5.082	5.459	98.225	6.9	3.11
	c-ZrO_2	0.73	5.110	5.110	5.110		7.3	0.35
8h	m-ZrO_2	0.17	5.198	5.067	5.449	98.052	5.2	6.14
	c-ZrO_2	0.83	5.100	5.100	5.100		8.4	1.06

*Error limits

phase after 8h of ball milling. Fig. 1(b) is depicting HRTEM image of the indexed selected area electron diffraction (SAED) pattern of 8h ball-milled sample that clearly reveals the presence of c-ZrO_2 phase in that sample.

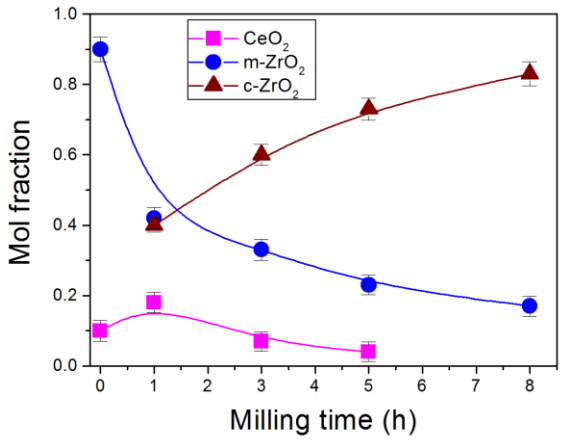

Fig. 2. Variation of mol fractions of different phases obtained by ball milling ZrO_2-CeO_2 mixture powders with increasing milling time.

Results of the Rietveld analysis are plotted in Figs. 2, 4-6 and tabulated in Table 1. The nature of variation of mol fractions of different phases with increasing milling time for m-ZrO_2-CeO_2 ball-milled mixtures is shown in Fig. 2. In relatively lower milling time, cold-welding and fracturing of the component powders result in phase transformation of m-ZrO_2 to c-ZrO_2 [3]. The mol fraction of m-ZrO_2 initially, up to 1h of milling decreases and that of CeO_2 insignificantly increases with increasing milling time. A certain drop in mol fraction of CeO_2 is noticed within the milling time of 1-5h due to the growth of c-ZrO_2 phase from CeO_2-ZrO_2-base solid solution. The solid solution phase tends towards the complete formation and the phase content of c-ZrO_2 increases slowly in the expanse of m-ZrO_2 till the end of ball milling. Final 8h ball-milled powder mixture contains 83% c-ZrO_2 and 17% m- ZrO_2 phase. The atomic model unit cell of m-ZrO_2, CeO_2 and c-ZrO_2 are shown in Fig. 3.

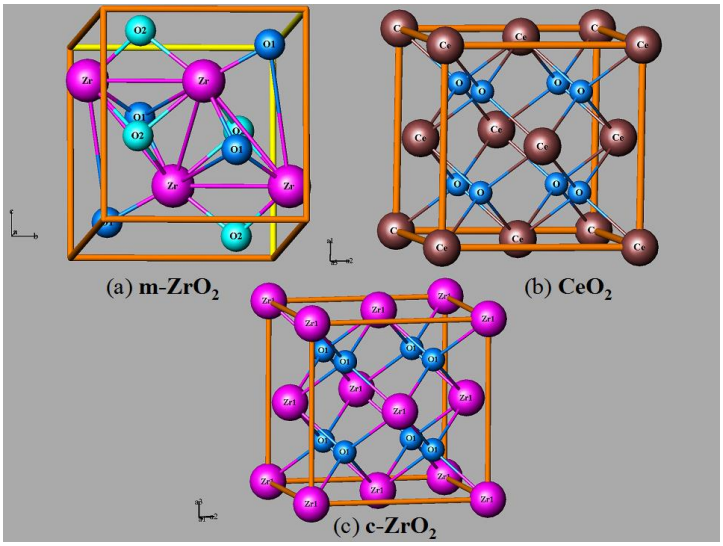

Fig. 3. Proposed atomic model of **(a)** m- ZrO_2 **(b)** CeO_2 and **(c)** c- ZrO_2 phase (unit cell).

After 1h of milling, the c-ZrO_2 phase starts to grow with a lattice parameter (5.119 Å), very close to a-axis length of m-ZrO_2 lattice (5.131 Å) and results in initiating the change of lattice parameters of all the phases (Fig. 4). A significant change in lattice parameter of m-ZrO_2 has been observed between 1h and 5h of milling time when the CeO_2-m-ZrO_2 solid solution grows towards the complete formation. As particularly the 'a' and insignificantly 'b' values of m-ZrO_2 phase approaches toward the lattice parameter of c-ZrO_2 phase with increasing milling time, it may be visualized that the growth of the densest (111) plane of c-ZrO2 phase has been started on the 'ab' (001) plane of m-ZrO_2 phase.

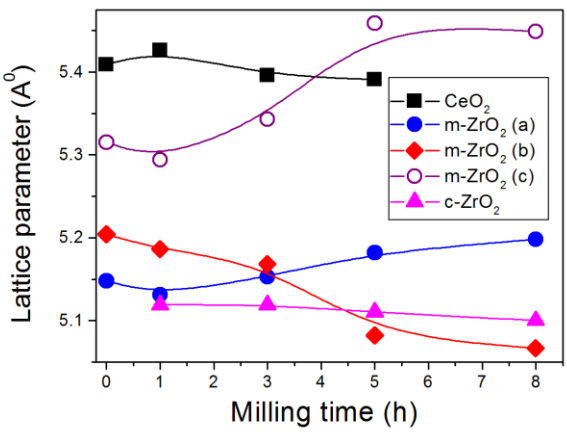

Fig. 4. Variation of lattice parameters of m- ZrO_2, CeO_2 and c- ZrO_2 phases with increasing milling time.

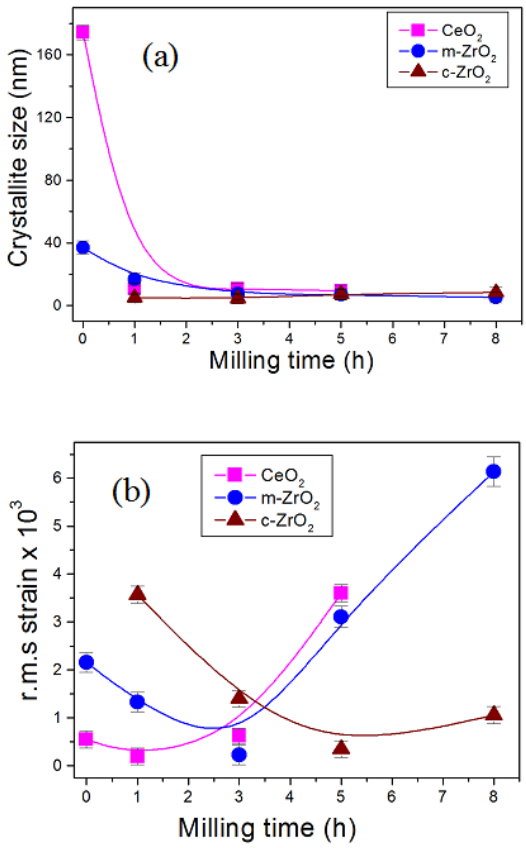

Fig. 5. Variation of **(a)** crystallite sizes **(b)** r.m.s. strains of m- ZrO_2, CeO_2 and c- ZrO_2 phases with increasing milling time.

Figures 5(a) & (b) illustrate the variations of crystallite size (coherently diffracting domain) and r.m.s lattice strain values of different phases with increasing milling time. Within 1h of milling, the crystallite size of CeO_2 suddenly drops from ~174 nm to ~10 nm and approaches the value of that of m-ZrO_2. Nature of variation shows that the crystallite size of CeO_2 plays an important role in the formation of CeO_2-ZrO_2 solid solution. After formation c-ZrO_2 is noticed to appear with a small crystallite size value ~5nm due to high impact energy produced during mechanical alloying which remains almost unchanged till the end of ball-milling. Fig. 5(b) shows that an increase in milling time is manifested in increasing the r.m.s strain only as crystallite size of all phases almost reached saturation value after just 1h milling. HRTEM image (Fig. 6) for 8h ball-milled powder mixture directly gives evidence that the particle size of c-ZrO_2 phase is below 10 nm.

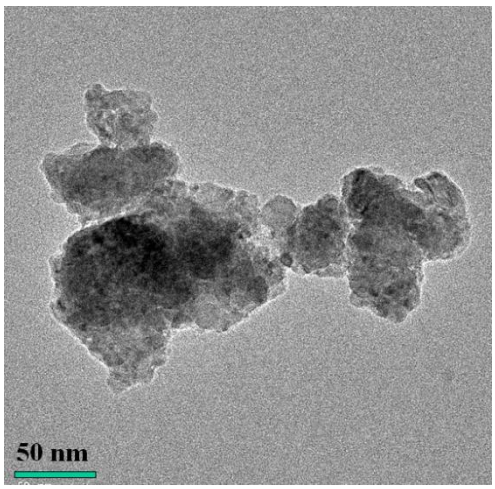

Fig. 6. Brightfield TEM image of 8h ball-milled powder containing ZrO_2-CeO_2 nanoparticles.

5. CONCLUSIONS

Microstructure characterization of unmilled and ball milled samples clearly reveals nanocrystalline PSZ can be prepared at room temperature by ball milling the mixture of m-ZrO_2 - CeO2 (0.9:0.1 molar ratio). Phase transformation kinetics follows the route: ball milled m-ZrO_2 – CeO_2 mixture produces nanocrystalline m-ZrO_2-based solid solution and c-ZrO_2 phase grows from the solid solution with a small crystallite size. HRTEM study supports the results as obtained from XRD data analysis by Rietveld method.

6. ACKNOWLEDGEMENT

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