



Effect of CaO on the Formation of PSZ and γ -Zirconia Nanoparticles through Ball Milling

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ABSTRACT

The effect of CaO on the formation of β - and γ -zirconia nanoparticles from α -zirconia was investigated and their stability evaluated via mechanical activation. α -ZrO₂+8.5wt%CaO powder was milled for 2-150 hours with ball-to-powder weight ratios (BPWR) of 40:1 and 60:1. Structural evaluations were conducted using X-Ray diffraction and scanning electron microscope (SEM). Thermal analysis was carried out using Differential Scanning Calorimetry (DSC). Results showed that, γ -zirconia (with a cubic structure) was obtained by ball milling of α -ZrO₂+8.5wt%CaO at room temperature. It was found that α to γ phase transformation began after two hours of milling and completed after 48 hours with a BPWR of 40:1. Moreover, the Williamson-Hall equation indicated that the particle size of α -ZrO₂+8.5wt%CaO was reduced to 50 nanometers and reached its equilibrium point after 24 hours of milling and was unchanged after that. In addition, DSC analysis showed that β -zirconia and γ -zirconia were unstable in pure ZrO₂ powder, while CaO addition led to the stabilization of ZrO₂ as β -zirconia and γ -zirconia after ball milling.

1. INTRODUCTION

Mechanical deformation under shear conditions at high strain rates ($\sim 10^1$ – 10^4 s⁻¹) leads to the formation of nanostructures within powder particles in thin foils or at the surface of metals and alloys exposed to friction-induced wear conditions. For example, mechanical attrition and mechanical alloying of powder particles have been developed as versatile alternatives to other processing routes in preparing nano-scaled materials with a broad range of chemical compositions and atomic structures [1-3]. Mechanical alloying (MA) was developed by J.S. Benjamin at INCO Alloys International in the late 1960s [4] and has traditionally been used for the production of oxide-dispersion strengthened (ODS) super alloys such as ODS Fe, Ni, Al, and Ti for high-temperature applications [5–7]. This process that reduces the average grain size by a factor of 10^3 – 10^4 results from the creation and self-organization of the small and high angle grain boundaries within the powder particles during the mechanical deformation process. More recent investigations demonstrate that nanostructure formation can also occur in such unexpected cases as brittle ceramics, ceramic phase mixtures, polymer blends, and metal/ceramic nano-

composites. The deformation processes within the powder samples are important for fundamental studies of extreme mechanical deformation and the development of nanostructured states of matter with particular physical and chemical properties [8].

Zirconium dioxide is one of the most studied ceramic materials. It adopts a monoclinic crystal structure at room temperature and transitions to tetragonal and cubic structures at higher temperatures. Furthermore, some reports have revealed that β -zirconia (tetragonal structure) and γ -zirconia (cubic structure) could be achieved by 48 and 150 hours mechanical milling of α -zirconia at room temperature respectively [9].

The volume expansion caused by the cubic to tetragonal to monoclinic transformations induces large stresses that cause cracking in ZrO₂ during cooling from high temperatures. When the zirconia is doped with some other oxides, the tetragonal and/or cubic phases are stabilized. Effective dopants include magnesium oxide (MgO), yttrium oxide (Y₂O₃), calcium oxide (CaO), and cerium oxide (Ce₂O₃) [10, 11]. In some cases, the tetragonal phase can be metastable. If quantities of the metastable tetragonal phase are sufficient, then an applied stress magnified by the stress concentration at a crack tip may cause the tetragonal phase to convert to a monoclinic one with the associated expansion in volume. This phase transformation can then put the crack into compression, thereby retarding its growth and

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enhancing the fracture toughness. This mechanism is known as transformation toughening, and significantly extends the reliability and lifetime of products made from stabilized zirconia [12]. The present investigation focuses on both the formation of tetragonal and cubic zirconia from a monoclinic crystal structure via mechanical activation and the stabilization of the phases produced in the presence of CaO. The changes in structure and particle size at different milling durations will also be studied.

2. EXPERIMENTAL PROCEDURES

ZrO₂ (zirconia) and CaO powders of commercial purity (>99%) were used as the raw materials. As regarded to phase diagram of the powders, their mixture (ZrO₂-8.5 wt% CaO) was used in the experiments because of zirconia stability in this composition. Scanning electron microscopy was employed to evaluate the morphology and particle size of zirconia using the Philips XL30 scanning electron microscope (SEM). Milling was performed in a planetary ball mill at room temperature for different milling times (2, 4, 8, 16, 24, 48, 100, and 150 hours) using the tool steel cup (X210CrW12) sing bearing steel balls with BPWRs of 40:1 and 60:1 at 600 rpm. Phase analysis was carried out using an X-ray diffractometer (Philips, Cu K α , λ = 1.5218, step size= 1, time per step=2s), heat treatment was performed in a tube furnace, and thermal analysis was carried out using differential scanning calorimetry (DSC).

3. RESULT AND DISCUSSION

Figure 1. shows the SEM micrograph of the zirconia powder and the X-ray diffraction spectrum of the raw zirconia powder. Figure 1a. indicates a powder particle size of about 1 micrometer. The X-ray diffraction pattern of the powder in Figure 1b. confirms its monoclinic crystal structure. The presence of peaks related to the planes ($\bar{1}11$), (111) and (221) also indicates the monoclinic structure of the powder. Also, the sharpened peaks are indications of the particles size shown in Figure 1a. [13].

Figure 2. shows the X-ray diffraction spectrum of CaO and zirconia mixture (ZrO₂-8.5CaO) after four hours of heat treatment at 1250°C. The pattern shows that the powder has a monoclinic structure. This is probably related to the atomic rearrangement occurring during the slow cooling after heat treatment. Previous reports have indicated that the transformation point of ceramic powders depends on such variables as particle size [13]. Hence, another reason for this observation may be the inadequate temperature for a tetragonal structure to be achieved.

Figure 3. presents the X-ray diffraction spectra of the mixture of CaO and zirconia (ZrO₂-8.5CaO) powders after milling with a BPWR of 40:1.

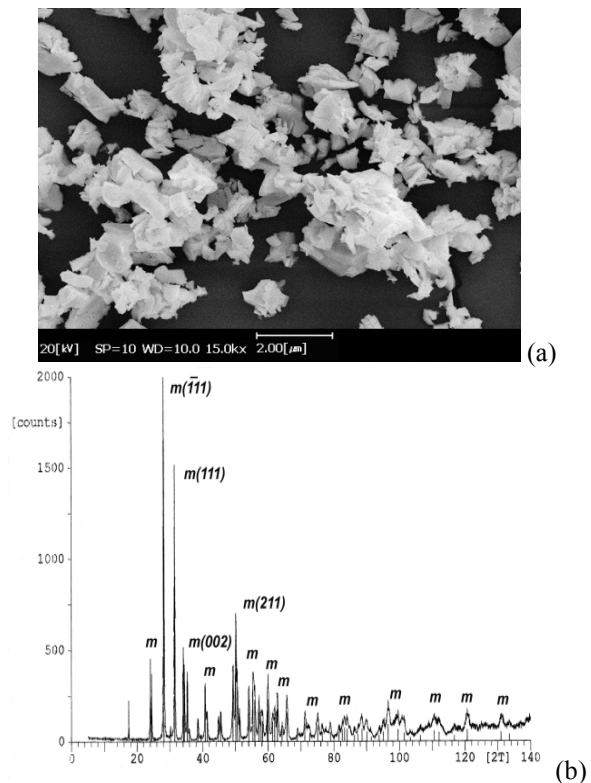


Figure. 1 (a) SEM micrograph for the pure zirconia powder, (b) X-ray diffraction spectrum of pure zirconia powder.

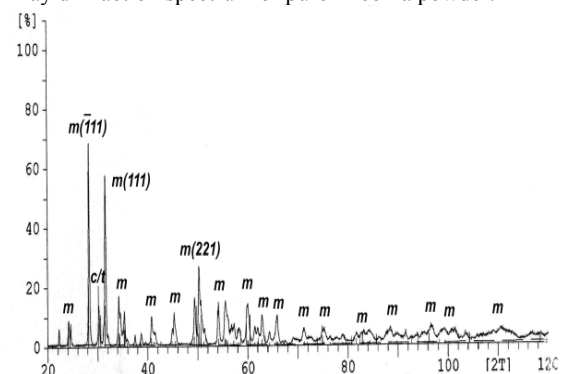
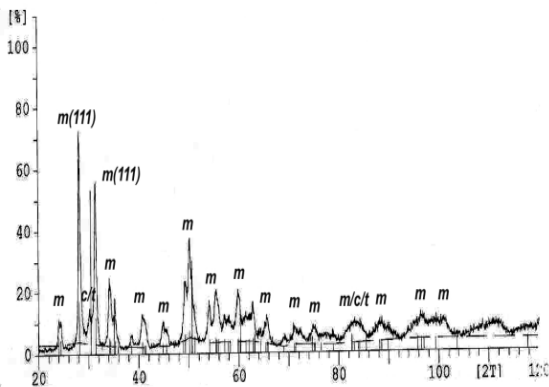


Figure 2. X-ray diffraction spectrum of ZrO₂-8.5 CaO powders after 4 hours of heat treatment.

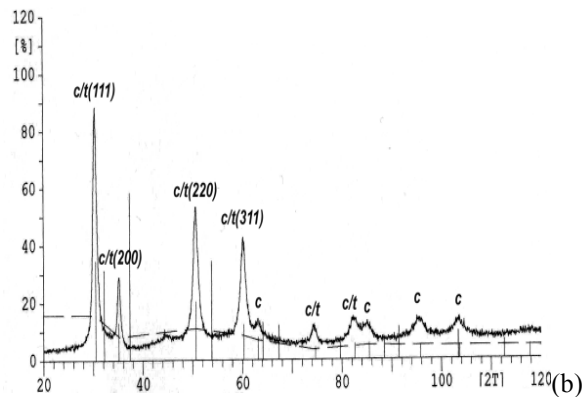
In this figure, patterns a and b are obtained after 2 and 24 hours of milling, respectively. There is in principle no significant difference between the spectrum of the milled powder (after 2 hours) and that of the un-milled one. However, the monoclinic structure (α -zirconia) peak intensity reduced and the peak width increased slightly, indicating a reduction in zirconia particle size. Also a new peak formed at $2\theta = 30$. This peak is the major one characteristic of a tetragonal structure (β -zirconia). When milling is continued up to 24 hours, the monoclinic peaks intensity reduce while that of the tetragonal or cubic peaks increases (Figure 3b). Studies have shown that phase transformation in zirconia begins from the severe plastic deformation of

the powder due to the strong collisions between steel balls and the cup against powder particles.

Consequently, plastic deformation at high strain rates occurring within the particles must lead to the crushing of laminated particles. As the powder particle is plastically deformed, most of the mechanical energies expended in the deformation process are converted into heat but the remainder is stored in the metals, thereby raising the internal energy. Similarly, these collisions lead to dislocation density increments leading to an enhanced diffusion rate. In conclusion, while the diffusion of atoms rises, the phase transformation rate increases exceedingly [8].



(a)



(b)

Figure 3. X-ray diffraction spectra of $ZrO_2-8.5CaO$ powders after: (a) 2 hours, and (b) 24 hours of milling.

Using the Williamson-Hall equation ($\beta \cos \theta = \frac{K\lambda}{d} + 2A\sqrt{\epsilon} \sin \theta$) [13], the powder particle size after 2 hours milling was estimated to be about 200 nanometers. In this equation, β is the Full Width Half Maxima (FWHM) in radian, K is the shape factor that is about 0.91, λ is the wavelength of Cu K_{α} radiation (1.5418), A is a constant, and $\sqrt{\epsilon}$ is the mean elastic deformation induced in the powder. Results indicate that after 24 hours of milling, the monoclinic structure is replaced by a tetragonal/cubic one. Moreover, the particle size of the milled powder was calculated to be about 50 nanometers using the Williamson-Hall

equation. Figure 4. presents the morphology of the milled powder after 24 hours of milling. As it can be seen in this figure, the particle size of the powder is very fine, including particles less than 50 nm in diameter. However, the mean particle size of this powder is about 50 nm. In other words, PSZ (partial stabilized zirconia) nanoparticles is formed after 24 hours milling.

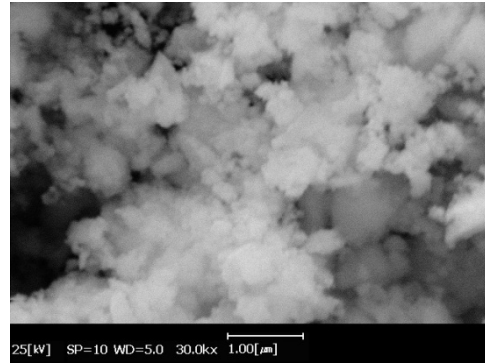


Figure 4. SEM micrograph of $ZrO_2-8.5CaO$ powder after 24 hours of milling.

The effect of CaO on the phase transformation of α -zirconia to γ -zirconia has been shown in X-ray diffraction spectra presented in Figure 5. in which the lower pattern belongs to pure zirconia powder and the upper one belongs to the mixture of CaO and zirconia ($ZrO_2-8.5CaO$) powder after 24 hours of milling. The figure also shows that α to γ phase transformation in zirconia occurred after 24 hours of milling in the presence of CaO. However, this did not happen in the absence of CaO. Phase transformation in zirconia in the presence of CaO is due to the creation of vacancies in the zirconia anion lattice which gives rise to the modified atom diffusion in zirconia that, in turn, leads to an elevated phase transformation rate [2].

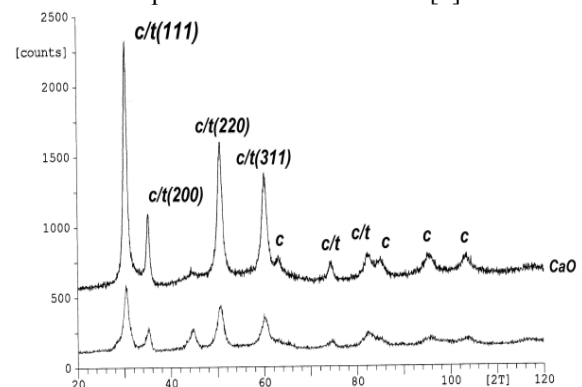


Figure 5. X-ray diffraction spectrum of $ZrO_2-8.5CaO$ powders after 24 hours of milling (up) And X-ray diffraction spectrum of pure ZrO_2 powders after 24 hours of milling (down).

To investigate the stability of the phases produced with and without CaO, DSC analysis was carried out on three powder samples. Figure 6. shows the DSC spectrum of pure ZrO_2 after 150 hours of milling (with a BPWR of 60:1).

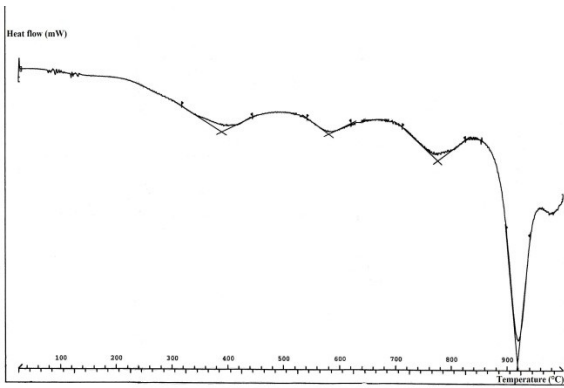


Figure 6. DSC spectrum of pure ZrO₂ after 150 hours of milling.

DSC analysis is designed to measure the amount of heat absorbed or evolved from a powder under isothermal conditions. The peak at 900°C in Figure 6. indicates that an endothermic reaction had occurred. The peaks observed at 400°C, 600°C, and 800°C might be related to the evaporation of volatile materials. As mentioned earlier, the powder structure before thermal analysis was cubic (Figure 7a). The X-ray diffraction spectrum of the powder after DSC analysis shows the monoclinic structure of the powder (Figure 7b). Therefore, the exothermic reaction at 900°C should be attributed to the phase transformation of γ to α zirconia.

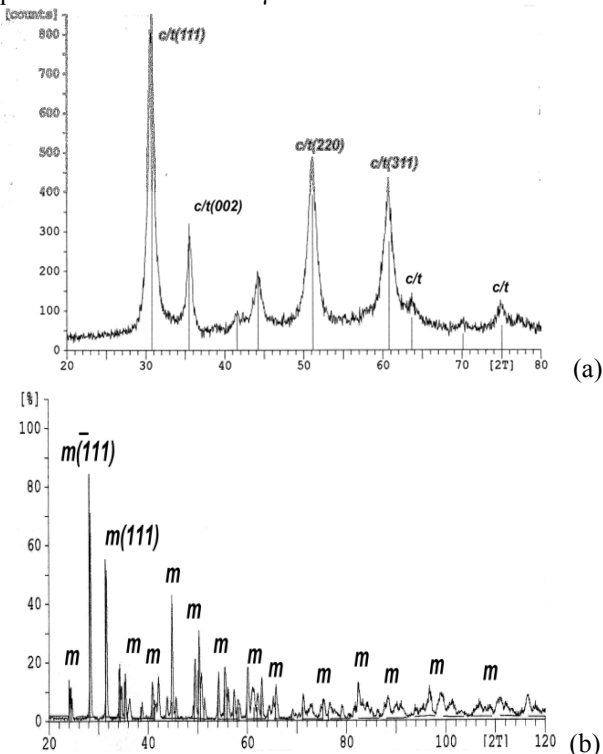


Figure 7. X-ray diffraction spectrum of pure ZrO₂ powder: (a) after 150 hours of milling, (b) after DSC Analysis.

Figure 8. shows the DSC spectrum of the mixture of CaO and zirconia (ZrO₂-8.5CaO) powder after 48 hours of milling (with a BPWR of 40:1). Experiments

revealed the completion of the phase transformation ($\alpha \rightarrow \gamma$) of the powder and its cubic structure after 48 hours of milling (Figure 9a).

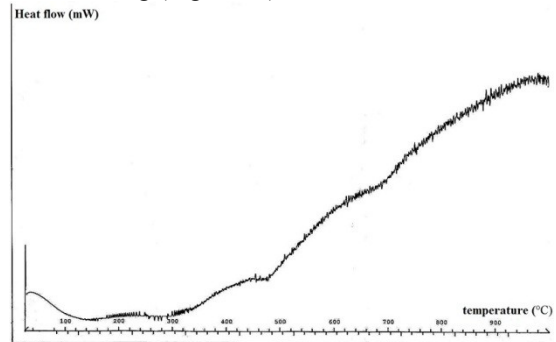


Figure 8. DSC spectrum of the CaO and Zirconia mixture (ZrO₂-8.5CaO) powder after 24 hours of milling.

seen in Figure 8. no phase transformation occurred in the powder. This is due to the phase stability of zirconia in the presence of CaO which creates vacancies in the zirconia anion lattice [11,12]. The stabilizing mechanism consists in substitution of some of the Zr⁴⁺ ions in the crystal lattice (an ionic radius of 0.80 Å which is too small for the ideal lattice of fluorite characteristic of the tetragonal zirconia) with slightly larger ions such as those of Ca²⁺ (with an ionic radius of 0.99 Å) [12]. The X-ray diffraction spectrum of the powder after DSC analysis confirms the cubic structure of the powder (Figure 9b). Moreover, the spectra indicates that the particle size of the powder became larger after heat treatment. It is clear from the thin peak of the X-ray diffraction pattern.

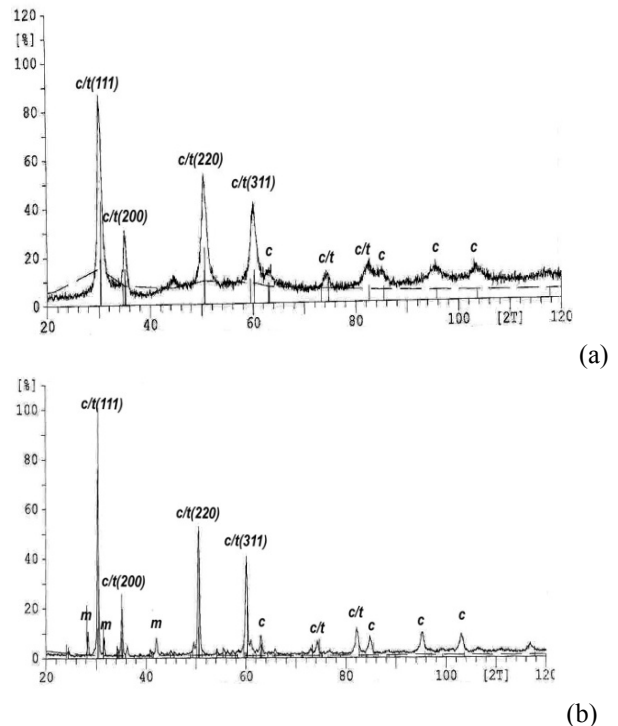


Figure 9. X-ray diffraction spectrum of ZrO₂-8.5CaO powder: (a) after 24 hrs of milling, and (b) after DSC Analysis.

4. CONCLUSIONS

Significant results of present work are as below:

α -zirconia to γ -zirconia phase transformation was began by ball milling of α -zirconia at room temperature (with a BPWR of 40:1) after two hours in the presence of CaO. After 24-hour milling with a BPWR of 40:1 in the presence of CaO, the phase transformation was continued and the intensity of the tetragonal/cubic peaks increases unlike the monoclinic peaks. The particle size of the attained powder was about 50 nm. So, PSZ nano particles was formed after 24 hours milling. Moreover, the phase transformation (α -zirconia to γ -zirconia) was completed after 48 hours milling. So, γ -zirconia nano particles could be achieved after 48 hours milling. Formation of nanoparticles (with a mean particle size of about 50 nm) led to reduction of diffusion path and increment in the phase transformation rate. Furthermore, CaO created vacancies in the zirconia anion lattice, which further enhanced the phase transformation of α -zirconia to γ -zirconia. The cubic structure was stabilized down to room temperature by adding CaO. Indeed, it was the substitution of some of the Zr^{4+} ions with Ca^{2+} that led to this stabilization.

REFERENCES

1. Edelstein, A.S. and Cammarata, R.C., "Nanomaterials; Synthesis, Properties and Applications", Institute of Physics Publications, London, (1966).
2. Koch, C.C., "Mechanical Milling and Alloying in Materials Science and Technology", (R. W. Cahn, P. Haasen, and E. J. Kramer, eds.), *Processing of Metals and Alloys*, Vol. 15, (1991).
3. Hadjipanayis, G.C., Siegel, R.w., "Nanophase Materials", Kluwer Acad. Publications, (1994).
4. Benjamin, J.S., "Mechanical alloying", *Scientific American*, Vol. 234, (1976), 40.
5. Benjamin, J.S. and Bomford, M.J., "Dispersion strengthened aluminum made by mechanical alloying", *Metallurgical Transactions A*, Vol. 8, No. 8, (1977), 1301-1305.
6. Bhagiradha Rao, E.S., "Mechanical alloying of thoria-dispersed nichrome", *Transactions of the Indian Institute of Metals*, Vol. 31, (1978), 261.
7. Naser, J., Richmann, W. and Ferkel, H., "Dispersion hardening of metals by nanoscale ceramic powders", *Material and Science Engineering*, (1997), 234– 236.
8. Bala'z', P., "Extractive Metallurgy of Activated Minerals", Elsevier, Amsterdam, (2000).
9. Koch, C.C., "Nanostructured materials: Processing, Properties and Potential", Noyes publications, New York, (2002).
10. Golzar Shahri, M., Shafiei, A., Saidi, A. and Abtahi, K., "Formation of β -zirconia and γ -zirconia nano particles from α -zirconia by mechanical activation", *Ceramics International*, Vol. 40, (2014), 13217–13221.
11. Evans, A.G. and Cannon, R.M., "Toughening of brittle solids by martensitic transformations", *Acta Metallurgica*, Vol. 34, (1986), 761-800.
12. Yanagida, H., Koumoto, K. and Miyayama, M., "The Chemistry of Ceramics", *John Wiley & Sons*, 1996.
13. Porter, D.L., Evans, A.G. and Heuer, A.H., " Transformation-toughening in partially-stabilized zirconia (PSZ)" *Acta Metallurgica*, Vol. 27, (1979), 1649-1654.
14. Williamson, G.K. and Hall, W.H., "X-ray line broadening from filed aluminium and wolfram", *Acta Metallurgica*, Vol. 1, No. 1, (1953), 22-31.
15. Habashi, F., "Hand book of extractive metallurgy", Vol. 4, Wiley-VCH Company, (1997).