

Zirconia stabilization assisted by high energy ball- milling

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Different zirconia (ZrO_2) – x (x = CaO, ZnO mol%) solid solutions have been produced by high energy ball-milling (HEBM). The ZrO_2 + oxide powder mixtures were milled for 15 and 25 hours, and thermal experiments were subsequently carried out. Experimental findings demonstrate a relationship of the powders' morphology and crystal structure with zirconia stabilization. After the different milling times, X-ray diffraction (XRD) studies did not show any sign of zirconia stabilization; however, after thermal experiments total cubic ZrO_2 -CaO stabilization was obtained. According to the lattice parameter measurements, solid solutions were formed with the oxides and zirconia powders during the HEBM. These results did not show zirconia stabilization in the ZnO_2 addition case. Both scanning electron microscope (SEM) and XRD structural observations indicate greater crystalline structural deformation of the ZrO_2 -ZnO high energy ball-milled powders in comparison to that of the ZrO_2 -CaO powders. Furthermore, the behaviors in the lattice parameter values of the ZrO_2 -CaO system showed a tendency toward increasing the monoclinic symmetry of the cell, which could be beneficial in obtaining total zirconia stabilization (TZS). In the dilatometer and XRD experiments monoclinic (m) $\rightarrow$ cubic (c) (CaO) or m $\rightarrow$ tetragonal (t) (ZnO) temperature changes for each oxide addition to zirconia were observed.

Key words: High energy ball-milling, Zirconia, Oxides, Stabilization, Shrinkage, Structure.

Introduction

Different synthesis methods to obtain partial (PZS) or total (TZS) zirconia stabilization have been explored in the past [1-8]. In all methods the most notable characteristics observed were the homogenous composition and the nano-sized grains. These micro-structural features produce good PZS or TZS solid solutions. The materials manufactured by mechanical milling possess both of these characteristics, and the technique improves solubility and promotes species homogeneity. The stabilization temperature in the m $\rightarrow$ t- ZrO_2 transformation depends upon these parameters, and also upon the quantity of oxide added. Few investigations have been undertaken with ZrO_2 stabilization assisted by high energy ball-milling [9-12]. In this paper we report on the results obtained from the HEBM of ZrO_2 with CaO or ZnO powder mixtures, wherein we evaluate the changes in stabilization temperature and cell volume. These evaluations were made from the results of dilatometer and XRD experiments. We analyze changes in expansion or contraction rates to determine the decomposition reactions of the additives, zirconia transitions, and sintering process.

Experimental Procedure

The mechanical milling experiments on the ZrO_2 -x (x = CaO, ZnO) powder mixtures were performed in a

vibratory ball-mill (SPEX 8000) with silicon nitride vials and balls in an argon atmosphere. The ball-to-weight ratio was 3 : 1. The starting material was a commercial powder (Merk) with the following purities: CaO (99.9%), ZnO (99%) and ZrO_2 (99.97%). The starting particle size of the powder was $< 44 \mu\text{m}$ (~ 325 mesh). The CaO additions were 4.5 and 16 mol%. The ZnO additions were 10 and 20 mol%. The samples (ZrO_2 + oxides) were milled for 15 and 25 h. The mechanically-milled powders were compacted in a steel die 5 cm in length and 1 cm in width under an applied pressure of 60 MPa to obtain rectangular samples with a depth of ~ 5 mm. The green density of the compacted material, determined from the mass and dimensions, was 55-60% of the theoretical density. The compacted material was thermally treated in air in a dilatometer (Dilatronic Theta 6548) at a constant heating rate of $10 \text{ K}\cdot\text{minute}^{-1}$ to 1,773 K. The tendency for sintering was determined from the axial shrinkage of the compacted material. Morphological and structural characteristics of the powders were observed using SEM (Jeol 6400) and XRD (Siemens D5000) techniques. Measurements obtained from the dilatometer and thermal analyses (SDT Q600) were carried out to determine the shrinkage and temperature transformation, respectively. The heating rate used in the differential scanning calorimetry (DSC) experiments was $20 \text{ K}\cdot\text{minute}^{-1}$. After thermal analysis, XRD experiments were carried out and the monoclinic-to-tetragonal zirconia ratio was estimated. The cell volume was also calculated as a function of the composition of the powder mixture. The least squares refinement method was used to obtain the lattice parameters measurements.

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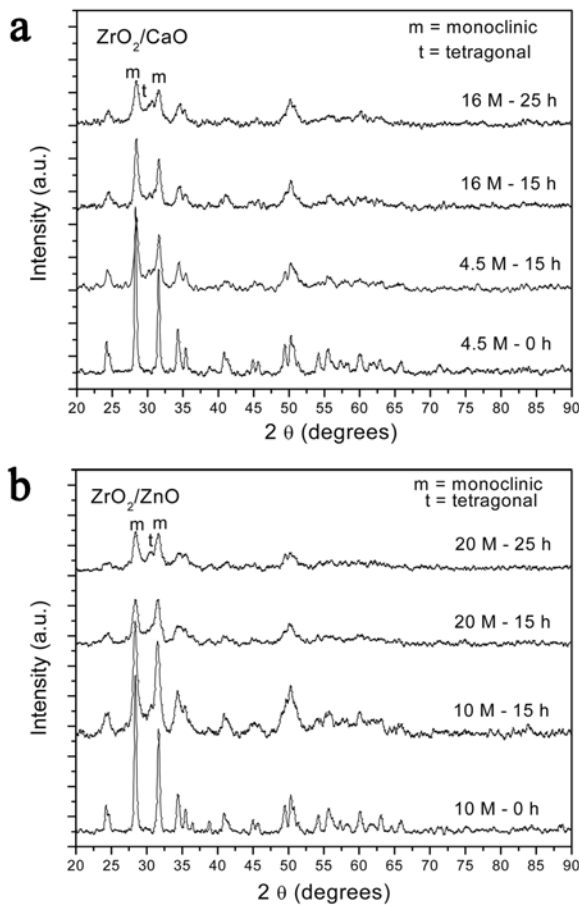


Fig. 1. XRD patterns obtained from (a) ZrO_2 -CaO and (b) ZrO_2 -ZnO powder mixtures for different HEBM times.

Experimental Results

Figs. 1(a) and (b) show the XRD patterns of the ZrO_2 -CaO (4.5, 16 mol%) and ZrO_2 -ZnO (10, 20 mol%) powder mixtures respectively for (a) 0, (b) 15 and (c) 20 hours of ball-milling. The XRD patterns show only the characteristic peaks of the ZrO_2 -monoclinic (m) phase, whose lattice parameters are: $a = 0.53129$ nm, $b = 0.52125$ nm, $c = 0.51471$ nm, $V = 0.1407$ nm³ and $\beta = 99.22^\circ$, space group P21/a, $Z = 4$. The most intense reflections correspond to the Miller indices of the planes ($\bar{1}11$) and (111). As the milling time and the oxide content were increased, the reflection intensities diminished and the peaks become wider, suggesting finer crystallite sizes and lattice micro-strains. In some XRD patterns a very small (101) reflection of the ZrO_2 tetragonal phase also appears. These results indicate that under the present

experimental milling conditions the structural transformations, for instance m-t or m-c, are far from complete.

To evaluate the oxide solubility in the monoclinic phase, lattice parameter measurements of the specimens after 25 hours of milling were carried out. Table 1 shows lattice parameter (a , b and c) and cell volume (V) values obtained for different powder mixtures. The first line values correspond to the ZrO_2 powder used as the starting material. After 25 hours of milling (line #2) the cell volume of the ZrO_2 powder exhibits a slight increase due to a heavy deformation effect and the induction of internal stresses. With the ZrO_2 -oxide samples (lines #3 and 4) the cell volumes demonstrated even larger increases. This behavior can be related to the dissolution of Ca and Zn ions in the ZrO_2 , and therefore the formation of a solid solution. The increment in the cell volume of the ZrO_2 -CaO system is greater than in the ZrO_2 -ZnO system. Hence, the Ca^{2+} ionic radius (0.099 nm), which is larger than the Zn^{2+} ionic radius (0.074), explains the increase in the ZrO_2 monoclinic phase lattice parameters. It is important to note that in the ZrO_2 -CaO system and in the pure ZrO_2 ball-milled sample, the ' a ', ' b ' and ' c ' lattice parameter values tend to reduce the symmetry of the monoclinic cell. For example, the ' a ' parameter value is decreased while the ' c ' parameter value is increased in comparison to their values obtained in tests of the prime material. This parameter behavior could be related with cell distortion and Ca dissolution after ball milling, mainly in preferential planar directions in which the monoclinic phase is stabilized.

Fig. 2 shows crystal size estimation as a function of

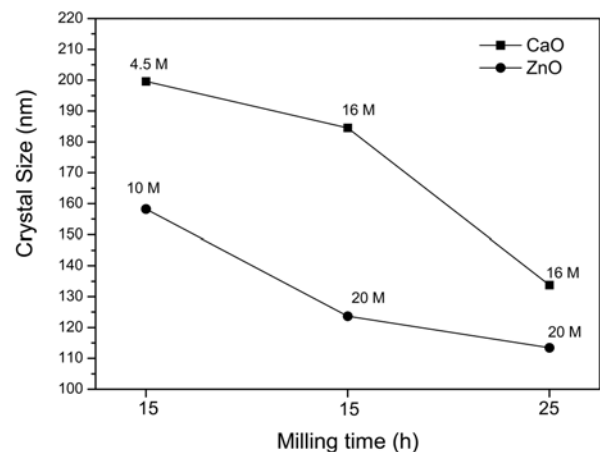


Fig. 2. Crystal size as a function of milling time for different molar concentrations in the powder mixtures.

Table 1. Lattice parameter measurements from different monoclinic- ZrO_2 powder mixtures

Experimental system	a (nm)	b (nm)	c (nm)	V (cell volume, nm ³)
ZrO_2 (starting material)	0.53154	0.52116	0.51454	0.14075
ZrO_2 (25 h. of milling)	0.53015	0.52174	0.51553	0.14083
ZrO_2 -20 %M ZnO (25 h)	0.53128	0.52154	0.51533	0.14090
ZrO_2 -16 % M CaO(25 h)	0.53038	0.52118	0.5154	0.14103

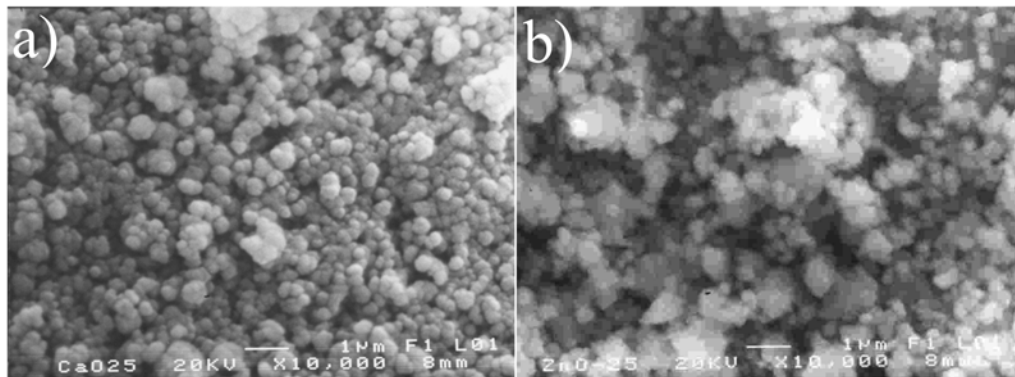


Fig. 3. SEM micrographs of the (a) ZrO_2 -16 mol% CaO and (b) ZrO_2 -20 mol% ZnO powder mixture after 25 hours of HEBM.

milling time for different oxides (CaO and ZnO) added to ZrO_2 . These measurements were carried out from the $(\bar{1}11)$ reflection using Sherrer's method. The crystal size diminishes with increased milling time and with the oxide (mol%) added to ZrO_2 . It is important to note that the crystal size is slightly larger in the ZrO_2 -CaO system than in the ZrO_2 -ZnO system. For the specimens after 25 hours of milling the crystal size is approximately 14 nm for ZrO_2 -CaO 16 mol% and 12 nm for ZrO_2 -ZnO 20 mol %.

Figs. 3(a) and (b) correspond to SEM micrographs obtained from the CaO and ZnO additions after 25 hours of milling, respectively. Fig. 3(a) illustrates a spherical morphology powder with a narrow submicrometre particle size distribution. Energy dispersive spectrometry (EDS) microanalysis showed a homogeneous chemical composition, which suggests the homogeneous distribution of the CaO in ZrO_2 as the result of the milling process. Fig. 3(b) corresponds to the ZrO_2 -ZnO 20 mol% powder mixture. This Figure demonstrates that the morphology of the ZrO_2 -ZnO powders has been highly affected by the high energy ball-milling process. There are acicular particle morphologies and a slightly larger particle size distribution with more agglomerates in comparison to those with CaO additions. These agglomerates could be related to a greater homogeneity and species distribution in the ZnO additions in comparison to the CaO additions. The greatest particle deformation obtained in this system suggests smaller crystal sizes. These results agree with crystal size XRD measurements for this system. Therefore, during the ball-milling of the ZrO_2 -ZnO powders, the considerable deformation in particle size and small crystal size are related to lessening the possibility of attaining a crystallographic system with greater symmetry (i.e tetragonal), and consequently of obtaining a PSZ or TSZ stabilization in zirconia.

Fig. 4 shows the percentage shrinkage versus temperature for the ZrO_2 -16 mol% CaO powders milled for 25 hours. The derivative of the linear shrinkage curve reaches a maximum at 1,639 K. The maximum differential shrinkage temperature is due to the transformation of m-c zirconia. The evidence of this transformation is also observed with the X-ray diffraction technique. Fig. 5(a) shows

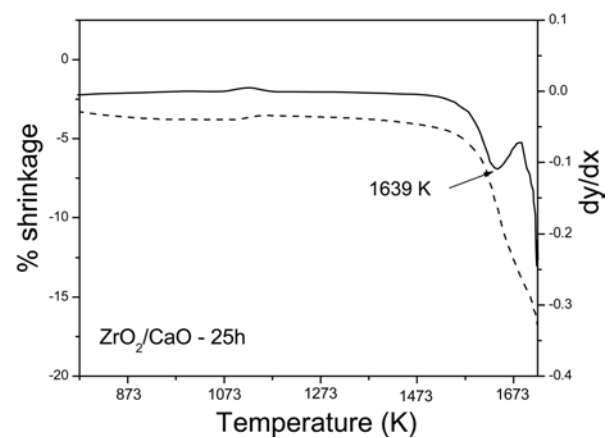


Fig. 4. Percentage shrinkage in the ZrO_2 -16 mol% CaO powder after 25 hours of milling versus temperature.

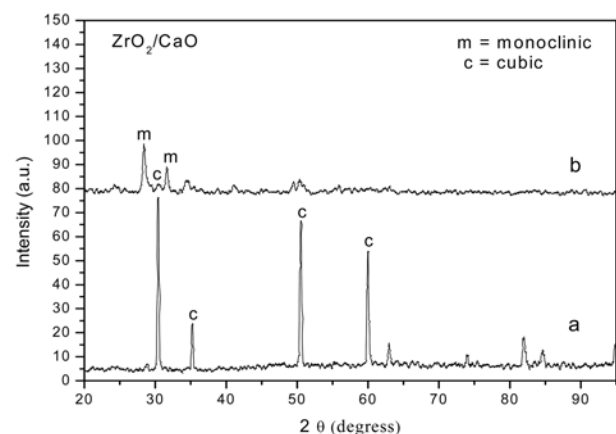


Fig. 5. XRD patterns obtained from (a) ZrO_2 -16 mol% CaO and (b) ZrO_2 -4.5 mol% CaO powder mixtures milled for 25 hours and thermally treated.

the results obtained from the ZrO_2 -16 mol% CaO specimen. The presence of a single cubic phase structure indicates that a TSZ has been obtained. On the other hand, with the 4.5 mol% CaO addition (Fig. 5(b)) a small fraction of cubic phase can be noted. This suggests that after the sintering process a PSZ has been obtained.

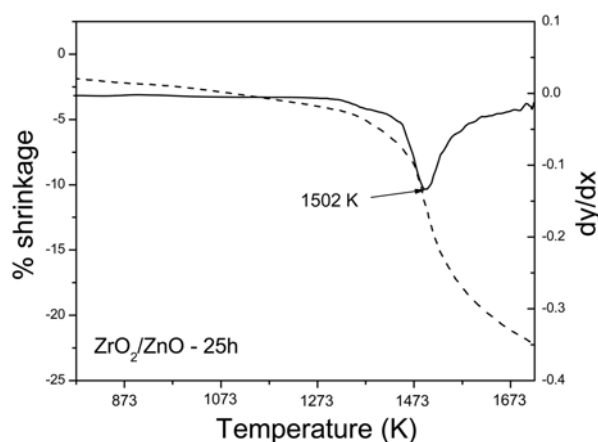


Fig. 6. Percentag shrinkage in the ZrO_2 -20 mol% ZnO powder after 25 hours of milling versus temperature.

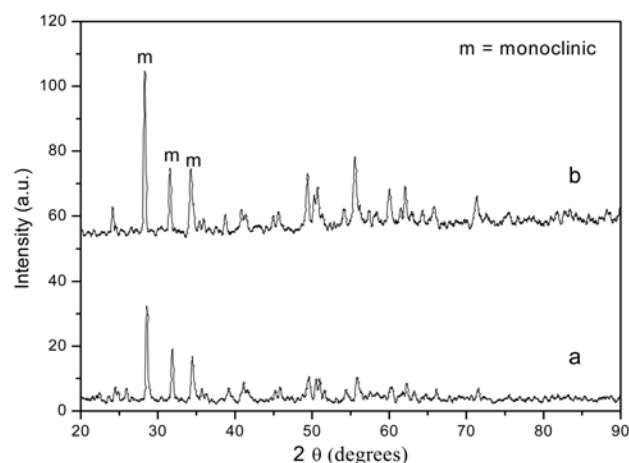


Fig. 7. XRD patterns obtained from (a) ZrO_2 -10 mol% ZnO and (b) ZrO_2 -20 mol% ZnO powder mixtures milled for 25 hours and thermally treated.

Fig. 6 shows the percentage shrinkage versus temperature for the ZrO_2 -20 %mol ZnO powders milled for 25 hours. The derivative of the linear shrinkage curve reaches a maximum at 1,502 K. A maximum differential shrinkage temperature due to the transformation of m-t zirconia is obtained. This transformation temperature coincides approximately with that of pure zirconia. Figs. 7(a) and (b) correspond to the XRD patterns of the 10% mol ZnO specimen and the 20% mol ZnO, respectively, after the sintering process. In both patterns only the presence of the monoclinic phase can be observed, or in other words, the ZnO does not show signs of zirconia stabilization.

According to these results, after the HEBM the ZrO_2 -ZnO powder mixtures observed by SEM suffered greater deformation than the ZrO_2 -CaO powder mixtures. Furthermore, the ZrO_2 -ZnO powder presented smaller

crystal sizes, as seen by XRD. These results suggest greater crystalline lattice deformation in the ZrO_2 -ZnO powder than in the ZrO_2 -CaO powder. In the CaO addition case the XRD results showed an increase in the axial 'c' lattice parameter and a decrease in the 'a' lattice parameter. This tendency in the parameter values was only in the crystallographic directions, which in the monoclinic phase increased the cell symmetry and consequently aided in the stabilization of the ZrO_2 -CaO powder during the sintering process.

Conclusions

In this study ZrO_2 -CaO (4.5, 16 mol%) and ZrO_2 -ZnO (10, 20 mol%) powder mixtures were milled using HEBM and were characterized in XRD, SEM, and dilatometer experiments. According to the lattice parameter measurements, solid solutions were formed with the oxides and zirconia powders during the HEBM. These results indicate that it is possible to obtain total ZrO_2 -CaO stabilization in the cubic phase using HEBM and sintering processes. However, these results did not show signs of zirconia stabilization in the ZnO_2 addition case. Furthermore, these powders (ZrO_2 -ZnO) presented greater particle deformation and a smaller crystal size in comparison to the ZrO_2 -CaO powders, which was possibly caused because stabilization was not obtained.

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