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Structural and microstructural changes in monoclinic ZrO_2 during the ball-milling with stainless steel assembly

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Abstract

High-energy ball-milling of monoclinic ZrO_2 was performed in air using the planetary ball mill with a stainless steel milling assembly. Structural and microstructural changes during the ball-milling were monitored using X-ray powder diffraction, Raman spectroscopy, Mössbauer spectroscopy, field emission scanning electron microscopy and energy dispersive X-ray spectrometry. The results of line broadening analysis indicated a decrease in the crystallite size and an increase in the microstrains with the ball-milling time increased up to ~150 min. The results of quantitative phase analysis indicated the presence of a very small amount of tetragonal ZrO_2 phase in this early stage of ball-milling. The onset of m-$ZrO_2 \rightarrow t$-ZrO_2 transition occurred between 10 and 15 h of ball-milling, which resulted in a complete transition after 20 h of ball-milling. Further ball-milling caused a decrease of the t-ZrO_2 lattice parameters followed by a probable transition into c-ZrO_2. It was concluded that the stabilization of t- and c-ZrO_2 polymorphs at RT can be attributed to the incorporation of aliovalent cations (Fe^{2+}, Fe^{3+} and Cr^{3+}) introduced into the sample due to the wear and oxidation of the milling media.

Keywords: A. Oxides; C. Raman spectroscopy; C. Mössauer spectroscopy; C. X-ray diffraction

1. Introduction

In dependence on temperature, ZrO_2 appears in three different polymorphs: monoclinic ($P2_1/a$), tetragonal ($P4_2/nmc$) and cubic ($Fm3m$). At room temperature (RT), pure zirconia is monoclinic (m-ZrO_2 having a distorted fluorite-type (CaF_2) structure, with the Zr atom in the coordination seven. At high temperature, the following phase transitions occur:

$$m\text{-}ZrO_2 \xrightarrow{1170\,^\circ C} t\text{-}ZrO_2 \xrightarrow{2370\,^\circ C} c\text{-}ZrO_2 \xrightarrow{2680\,^\circ C} \text{melt}$$

High-temperature t-ZrO_2 often appeared at RT as a metastable phase in the crystallization products of its amorphous precursors. The reason(s) for the appearance of this high-temperature polymorph at RT has been investigated intensively. There are several proposed models that emphasize the stabilizing influence of the crystallite size [1–3], lattice strains [4,5], impurities [6], structural similarities between the starting material and t-ZrO_2 product [7–9], lattice defects (oxygen vacancies) [10,11], etc. A critical review of the subject has been prepared by Štefanić and Musić [12].

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The first report about a partial-phase transition from *m*-ZrO_2 to *t*-ZrO_2 caused by ball-milling was given by Bailey et al. [13]. The formation of a high-temperature polymorph of ZrO_2 was attributed to the surface energy effect in accordance with the model proposed by Garvie [1–3]. The authors also observed that the presence of impurities significantly influenced the stability of the *t*-ZrO_2 product. However, most of the later investigations neglected the effect of impurities and explained the observed transition simply in terms of surface energy changes [14–20]. Murase and Kato [21] examined the *t*-ZrO_2 → *m*-ZrO_2 transition during the ball-milling in different atmospheres and found out that the absence of oxygen or water significantly increases the stability of a metastable *t*-ZrO_2.

Our recent investigation has shown that the ball-milling has little or no influence on the *m*-ZrO_2 → *t*-ZrO_2 transition when the ZrO_2 ball-milling assembly, which reduces the influence of an additional material, was used [22]. It was concluded that a partial transition from the monoclinic to tetragonal ZrO_2 polymorph, observed in earlier ball-milling experiments, can be attributed to the stabilizing influence of impurities due to the wear of the milling media rather than the effect of particle size (surface energy). A small possibility of direct *m*-ZrO_2 → *c*-ZrO_2 transition could not be discounted [19,20]. However, such a transition without an intermediate appearance of *t*-ZrO_2 phase is highly unlikely.

In the present work, structural and microstructural changes in *m*-ZrO_2 during the ball-milling with stainless steel assembly were examined from the results of X-ray powder diffraction combined with the results of Raman spectroscopy, ^{57}Fe Mössbauer spectroscopy and FE SEM/EDS analysis.

2. Experimental

The starting material was a monoclinic ZrO_2, Puratronic®, 99.978% (metal basis), produced by Alfa Aesar. Milling was performed in air using the Fritsch planetary ball mill ‘‘Pulverisette 6’’ with a stainless steel (18% Cr + 8% Ni) milling assembly. The rotation speed was 500 rpm and the powder-to-ball weight ratios 1:10. Milling time varied from 10 min to 30 h. For thermal stability study, the product ball-milled for 30 h was subjected to temperature treatment at 500, 600, 800 and 1000 °C for 2 h.

Structural and microstructural changes in the ball-milled products were investigated at RT using X-ray powder diffraction, Raman spectroscopy, ^{57}Fe Mössbauer spectroscopy, field emission scanning electron microscopy (FE SEM) and energy dispersive X-ray spectrometry (EDS).

XRD measurements were performed using a Philips counter diffractometer MPD1880 with monochromatized Cu Kα radiation (graphite monochromator). Silicon, α-Si (space group $m\bar{3}m$, $a = 5.43088$ Å [23]) was used as a standard for the approximation of instrumental profile and a precise determination of lattice parameters.

Raman spectra were recorded using a computerized DILOR Z24 triple monochromator with Coherent INNOVA 100 argon ion laser, operating at 514.5 and 488 nm line for excitation. An Anaspec's doublepass prism premonochromator was used to reduce parasite laser plasma lines. Laser power of 60 mW was applied. To reduce the heating of the samples during recording of the spectra, the incident beam was focused in the line shape.

Mössbauer spectra were recorded in the transmission mode using a spectrometer manufactured by Wissenschaftliche Elektronik GmbH (Starnberg, Germany). ^{57}Co in a rhodium matrix was used as the Mössbauer source. The spectrometer was calibrated with α-Fe. Mössbauer spectra were fitted using the MOSSWINN program.

FE SEM/EDS analyses of uncoated samples were made using the field emission scanning electron microscope JSM-7000F (JEOL) equipped with an energy dispersive X-ray spectrometer INCA-350EDS Microanalysis System (Oxford Instruments).

3. Powder-pattern fitting methods

The crystallite size and microstrain of the ball-milled *m*-ZrO_2 products were estimated from the results of whole-powder-pattern profile refinements (program GSAS [24] with graphical user interface EXPGUI [25]) following the procedure proposed in the Size/Strain Round Robin [26]. Due to the presence of contaminations and amorphous phase, the refinements were performed using combined Rietveld [27] and Le Bail et al. [28] methods. After Rietveld refinement, R_{wp} (weighted residual error) index were between 0.10 and 0.12. The obtained values of profile parameters were used as an input data for Le Bail refinement (refinement without structural constraints [28]), after which R_{wp} index significantly decrease. XRD patterns were scanned in 0.05° steps (2θ), in the 2θ range from 20° to 80°, with a fixed counting time (8 s). In the refinement, we used a modified pseudo-Voigt function