

Nanocrystalline Growth Activation Energy of Zirconia Polymorphs Synthesized by Mechanochemical Technique

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[Manuscript received March 17, 2012, in revised form February 7, 2013, Available online 18 October 2013]

The synthesis of ZrO_2 by mechanochemical reaction using $ZrCl_4$ and CaO as raw materials and subsequent annealing of the products were investigated. The effect of thermal treatment on the structural evolution and morphological characteristics of the nanopowders was studied by X-ray diffractometry, Raman spectroscopy, transmission electron microscopy, scanning electron microscopy, differential thermal analysis and Rietveld refinement. The results showed that the average crystallite size of ZrO_2 was less than 100 nm up to around 1100 °C. The activation energy for ZrO_2 nanocrystallite growth during calcination was calculated to be about 13,715 and 27,333 J/mol for tetragonal (t- ZrO_2) and monoclinic (m- ZrO_2) polymorphs, respectively. Mechanism of the nanocrystallite growth of the ZrO_2 polymorphs during annealing is primarily investigated.

KEY WORDS: Zirconia nanoparticles; Mechanochemical synthesis; Characterization methods; Activation energy; Phase transformation

1. Introduction

Refractory transition-metal oxides such as zirconia are an industrially important class of ceramic materials^[1,2]. Zirconia and zirconia-based ceramics are of both scientific and technological interest as structural and functional materials due to the superior properties of zirconia. Zirconia (ZrO_2) is hard with good mechanical properties and has a high fracture toughness and hardness, possesses a high melting point (2710 °C), and is resistant to chemical attack by strong acids^[3] along with excellent refractance. Zirconia is also stable in oxidizing environments, allows oxygen diffusion through its bulk^[4], exhibits low thermal conductivity at high temperature, good thermal stability and resistance to thermal shock, large ionic conductivity, and is electrically insulating. These properties enable zirconia to be widely used, e.g. as an abrasive, as a hard resistant coating for cutting tools, in oxygen electrodes and sensors, and in high temperature engine components^[1,2,5–7]. Few materials show as much potential as ZrO_2 and ZrO_2 -based ceramics, because of such a wide range of advanced engineering ceramic applications.

To produce these ceramics, high-purity powders with uniform particles of submicron size and good sintering properties are required^[8,9].

Zirconia has four well-defined polymorphic forms at atmospheric pressure: the monoclinic, tetragonal, orthorhombic and cubic phases^[10]. Only the monoclinic form is stable at room temperature. During the last decades an active research has been undertaken in different laboratories, in order to obtain zirconia and zirconia-based ceramic powders with the required characteristics of size, purity, uniformity, crystallinity and etc. As a result of the intensive work done, a wide variety of physical and chemical preparation techniques were found^[11].

Conventionally, ZrO_2 is synthesized from the high temperature decomposition of zirconium compounds such as nitrates, carbonates, or silicates^[2,3,12–14]. In recent years low temperature synthetic methods have been developed. Nowadays due to the need for high performance products in ceramic industry there has been an increasing interest in the synthesis of nanopowders. The nanostructured zirconia-based ceramic powders are gaining increasing importance and various routes have been employed for the production of nanocrystalline zirconia-based particles, such as co-precipitation^[15], sol–gel preparation method^[16], hydrothermal synthesis^[17,18], polymerized complex processes^[19] and gel-combustion process^[15,20–25].

One of the most powerful techniques for the synthesis of a wide range of materials such as zirconia is a solid-state process named mechanochemical treatment. This technique is a non-equilibrium solid-state process in which the final product

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<http://dx.doi.org/10.1016/j.jmst.2013.10.012>

retains a very fine amorphous or nanocrystalline structure. This process is versatile, simple and cost effective and can be used to synthesize a wide variety of materials with a high yield rate on a commercial scale. This process can also be designed in such a way to synthesize nanocrystalline particles dispersed within a soluble matrix. In other words, chemical precursors react, either during milling or at the subsequent heat treatment stage, to form a nanocrystalline powder embedded within a soluble salt matrix phase. The ultrafine powder is subsequently recovered by selective removal of the matrix phase through washing with an appropriate solvent. The ability to decrease time and temperature of the chemical reaction at low energy consumption is another advantage of this technique^[26–28].

The aim of the present work was to investigate on the mechanochemical treatment of anhydrous ZrCl_4 and CaO to obtain more information on the nature of this process and to determine the effect of thermal treatment on the structural evolutions and morphological characteristics of the nanopowder and also to obtain the activation energies of crystallite growth for the different polymorphs of the zirconia phase. The mechanism of the nanocrystallite growth is also discussed.

2. Experimental Procedure

Zirconia was prepared according to the previously published work^[29]. The starting materials were anhydrous ZrCl_4 (Acros) and CaO (Alfa Aesar). Stoichiometric amounts of ZrCl_4 and CaO were used according to reaction (1) without any process control agent. The starting materials were weighed and prepared in a glovebox under inert atmosphere and after sealing the milling jar, it was transferred to the milling machine. Mechanical treatment of reactant mixtures was carried out in a FRITSCH planetary mill (planetary micro mill pulverisette7) at 5000 r/min under inert atmosphere using 12 and 4 alumina balls of 10 and 15 mm in diameter respectively and an alumina jar of 80 ml. The ball to powder mass ratio of 10:1 and 5 h milling time was used in this study. All of the samples were prepared in a glovebox before the milling procedure to avoid moisture adsorption.

The heat treatment of the prepared powders was carried out at a rate of $100\text{ }^\circ\text{C/h}$, under air atmosphere with 1 h holding time at the maximum temperature. The milled powders were annealed at $250\text{ }^\circ\text{C}$, where all the starting powders had reacted. The reaction produced $\text{CaCl}_2(2\text{H}_2\text{O})$ and $\text{Zr}(\text{OH})_4$ phases^[29]. The removal of the salt-by product ($\text{CaCl}_2(2\text{H}_2\text{O})$) was performed by washing the powder with distilled water several times using a sonifier and centrifuge. The washed powder was dried in an oven and all of the subsequent heat treatments were carried out in air at temperatures between 400 and $1700\text{ }^\circ\text{C}$. The phase composition and crystal structures of the prepared powders were investigated at room temperature using X-ray powder diffraction measurements. X-ray powder diffraction data were recorded under ambient conditions on a high resolution laboratory X-ray powder diffractometer (Bruker D8 ADVANCE, $\text{MoK}\alpha_1$ radiation from primary $\text{Ge}(220)$ -Johannsson type monochromator, Lynx-Eye position sensitive detector (PSD) in Debye-Scherrer geometry) at 50 kV and 40 mA. All the X-ray samples were filled in low absorbing glass capillaries of 0.3 mm diameter (Hilgenberg glass No. 14) and sealed in a glovebox under argon atmosphere using a hot wire. Data were taken in steps of $0.007^\circ 2\theta$ from 2° to 55° of 2θ at a rate of $0.06^\circ/\text{min}$. The samples were spun during measurement for better particle statistics. A quantitative phase analysis of the measured powder diffraction patterns using the

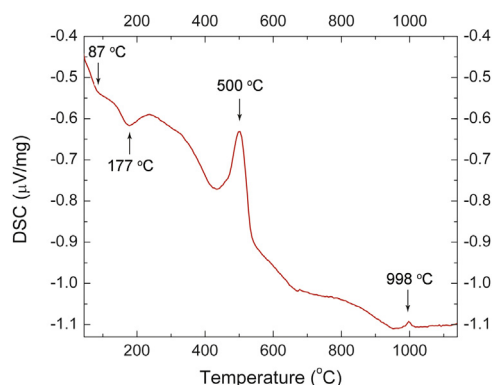
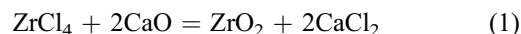


Fig. 1 DSC curve of the zirconium hydroxide powder heat treated up to around $1200\text{ }^\circ\text{C}$ (heating rate 10 K/min).

PDF-2 database (ICCD, 2007) in combination with the program MATCH^[30] was used to identify the phases. For Rietveld refinement the Topas4-2 program^[31] was used. To overcome difficulties and limitations of other methods of microstructural analysis and to consider all the benefits of the whole profile fitting methodology, Rietveld's powder structure refinement procedure based on pseudo-Voigt (pV) profile fitting function has been adopted in the present study. The thermal behavior of the washed calcined as-milled powder was investigated using a DSC analyzer under air atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and a sample size of about 10 mg per run. The microstructures of the samples were analyzed using a transmission electron microscope (JEOL 4000 FX) and a scanning electron microscope. Raman spectroscopy was used for further verification of the presence of tetragonal zirconia.

3. Results and Discussion

The starting powder mixture of ZrCl_4 and CaO in stoichiometric molar ratio was milled with the aim of inducing the mechanical reaction according to reaction (1).



According to our previous work^[29], the synthesis mechanisms maybe described by the following reactions. After milling the ZrCl_4 and CaO mixture for 5 h at ball to powder ratio (BPR) = 10, ZrCl_4 is partially amorphous while the crystallite size of CaO is slightly decreased (according to the XRD results not shown here). The formation of zirconium hydroxide occurred after the heat treatment of the milled powder which completed at $250\text{ }^\circ\text{C}$ ^[29]. Based on thermodynamic calculations the amount of H_2O present in air is about 285 times more than needed. Finally the washed heat treated powder containing amorphous $\text{Zr}(\text{OH})_4$ converts into ZrO_2 with removing the hydroxyl groups during the second heat treatment stage as shown in reaction (2).

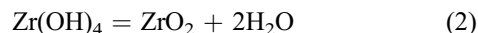


Fig. 1 presents the differential scanning analysis (DSC) curve of the dried zirconium hydroxide powder. After heating the sample from room temperature up to $1100\text{ }^\circ\text{C}$, two endothermic peaks at around $87\text{ }^\circ\text{C}$ and $177\text{ }^\circ\text{C}$ are present due to the release

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