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Evolution of the crystalline structure of zirconia nanoparticles during their hydrothermal synthesis and calcination: Insights into the incorporations of hydroxyls into the lattice

Fei Li [a,b], Yanhuai Li [a], Zhongxiao Song [a,*], Fei Ma [a], Kewei Xu [a], Hong Cui [b]

[a] *State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China*
[b] *Engineering Research Center for Nanomaterials & Coating, Xi'an Aerospace Composites Research Institute, Xi'an 710025, China*

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Abstract

Tetragonal and cubic zirconia nanoparticles were hydrothermally prepared and calcinated at different temperature. X-ray diffraction *via* Rietveld refinement is used to study the crystalline structure of nanoparticles. Results show that as-prepared tetragonal nanoparticles exhibit a crystalline structure with distorted lattice; the crystalline structure evolutes with the increasing calcination temperature and the distorted lattice is recovered after nanoparticles were calcinated at temperature higher than 900 °C. The cause for lattice distortion of tetragonal nanoparticles is discussed and is explained in term of the incorporations of hydroxyls into its lattice during preparation.

Keywords: Hydrothermal; Zirconia nanoparticles; Crystalline structure; Lattice hydroxyls; Rietveld

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1. Introduction

Tetragonal zirconia (TZ) has numerous promising properties and a wide range of applications, such as structural ceramics [1], sensors [2], medical implants [3,4], thermal barrier coatings [5] and so on. It is well known that nanocrystalline TZ exhibits improved properties, such as higher fracture toughness [6], higher oxygen diffusivity [7] and higher sintering resistance coupled with reduced thermal conductivity [8] as compared to the coarse-grained counterparts. Moreover, nanocrystalline TZ has attractive lower sintering temperature which is almost the half of that required for the coarse-grained counterparts [9]. Therefore, for practical use of nanocrystalline TZ, it is meaningful to synthesize TZ nanoparticles with controlled properties in commercial quantity [10,11].

Among methods to prepare TZ nanoparticles, hydrothermal synthesis is considered as an economic process to prepare TZ nanoparticles with fine grain size and narrow grain size distribution as well as weak agglomeration in large bulk quantity [12,13]. Hydrothermal synthesis of TZ nanoparticles includes a precipitation process of zirconium hydroxides from zirconium salt solution, and followed by a hydrothermal treatment of zirconium hydroxides at a temperature range of 200–300 °C and a pressure range of 2–6 MPa [12–15]. However, as is known, TZ is vulnerable to water at temperature used for hydrothermal treatment; it usually undergoes a spontaneous phase transformation from tetragonal to monoclinic [16–18]. The prevailing explanation for the phase transformation is that hydroxyls have incorporated into the lattice of TZ. The incorporated hydroxyls acted as defects and destabilized the tetragonal phase through generating tensile hydrostatic stresses in grains, or filling in the oxygen vacancies that are needed for stabilization of TZ [19,20]. Though the role of hydroxyls in the phase transformation remains uncertain, the preferable incorporations of water related species into the lattice of TZ have been experimentally confirmed by Tuan et al. [21]. Therefore, to obtain stable TZ nanoparticles, it is important to uncover whether there are hydroxyls in the lattice of the hydrothermally prepared TZ nanoparticles.

The existence of water in hydrothermally prepared nanoparticles can be directly confirmed using infrared spectroscopy (IR) and thermogravimetric analysis (TG); but, it is difficult to discern the incorporated hydroxyls, due to the coexistence of physical

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[*] Corresponding author. Tel.: +86 29 8266 8614.
E-mail address: Nanoshanxi@126.com (Z. Song).

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or chemical absorbed water as well as the lattice hydroxyls [22]. The deviation of the crystalline structure, such as the variation of the cell volume and the lattice parameters, can provide another way to study the lattice hydroxyls in nanoparticles, because the incorporations of hydroxyls into the lattice or the annealing out of hydroxyls from the lattice of nanoparticles will result in the deviation of its crystalline structure, due to the rebalance of force between atoms in cell [20,23].

In this paper, Y_2O_3 doped tetragonal and cubic zirconia nanoparticles were prepared by hydrothermal synthesis; the doping technique is used because it can stabilize tetragonal and cubic zirconia at room temperature without grain size limitation [24]; the cubic zirconia nanoparticles are used for comparison because it is stable to water according to the numerous experimental results [17,21,25]. The as-prepared nanoparticles were calcinated at different temperature. X-ray diffraction (XRD) is used to study the crystalline structure of the nanoparticles. Since it is difficult to distinguish the three closely related phases, *i.e.* the monoclinic, the tetragonal and the cubic phase of zirconia, because of the overlap between the broadening reflections resulting from small crystallites, Rietveld refinement, which is particularly useful in determining the phase composition, the lattice parameters as well as the grain size of each phase for sample with mixed phases, was used to improve the accuracy of the analysis [26,27].

2. Experiment

Hydroxides gels are co-precipitated from $ZrOCl_2{\cdot}8H_2O$ and YCl_3 mixed aqueous solution with $NH_3{\cdot}H_2O$; the ratio of Y_2O_3 to $Y_2O_3+ZrO_2$ in aqueous solution is 4 mol% (4YSZ) and 10 mol% (10YSZ) respectively to obtain pure tetragonal and cubic nanoparticles theoretically. The gels were aged for 24 h and employed for hydrothermal treatment in autoclave. The autoclave was maintained at 250 °C for 2 h with autogenously pressure of 2 MPa and then cooled naturally to room temperature. The products were washed with deionized water and alcohol to wash out Cl^- ions. The as-washed products were dried at 100 °C in air and then calcinated at different temperature from 300 to 1200 °C for 2 h in air respectively.

High-resolution transmission electron microscopy (HRTEM) images of nanoparticles were taken by JEOL 2100F. XRD patterns of samples were recorded using a powder diffractometer (Advanced D8, Bruker) with nickel-filtered and CuKα radiation; intensities were obtained in the 2θ values range between 20° and 80° with a step size of 0.02° and a measuring time of 2s per point. Grain size distributions of nanoparticles were evaluated from XRD patterns by whole powder pattern modeling (WPPM) approach (using program PM2K) [28,29]; a lognormal distribution function is used to describe the grain size distribution of nanoparticles. The phase composition, the grain size and the lattice parameters of nanoparticles were obtained through the Rietveld refinement of XRD patterns using the program MAUD [30,31].

The TG analysis for as-dried 4YSZ sample was carried out using Netzsch STA 409 from room temperature to 1200 °C, at a constant heating rate of 10 °C/min. The IR analysis for 4YSZ samples calcinated at different temperature were performed with Bruker Vertex 70 Fourier transform infrared spectrometry, using KBr disk method and recorded in the range 4000–400 cm^{-1}.

3. Results

Fig. 1a and b shows the HRTEM pictures of the as-dried 4YSZ and 10YSZ sample. In both samples, nanoparticles are highly crystalline with grain size which is approximately 10 nm as observed from the lattice fringes. Fig. 1c is the grain size distribution of nanoparticles obtained by WPPM approach; both the 4YSZ and the 10YSZ nanoparticles have narrow grain size distribution with a nearly symmetric distribution curve; in addition, the grain size and the grain size distribution width of 4YSZ nanoparticles are slight larger than that of 10YSZ.

XRD patterns of the as-dried samples and the samples calcinated at quoted temperatures are shown in Fig. 2. For the as-dried samples, the diffraction peaks were considerably broadened, indicating the formation of nanoparticles under the preparation condition used. With the increasing calcination temperature, the diffraction peaks of both 4YSZ and 10YSZ samples become sharper and sharper with increased intensity, suggesting that there is a grain-coarsening effect occurring. Qualitative analysis of XRD patterns shows that the crystalline structures of all 10YSZ samples belong to pure cubic phase, while the crystalline structures of 4YSZ samples are a mixture of tetragonal and monoclinic phase. In addition, the absence of any diffraction peak of crystalline Y_2O_3 in all samples suggests the incorporation of Y^{3+} into the lattice of zirconia and the formation of YSZ solid solution.

To study the phase composition of 4YSZ samples and the lattice parameters of nanoparticles, Rietveld refinement was used to analyze the XRD patterns in Fig. 2. The cubic structure (space group Fm-3m) is used as the starting model for refining of 10YSZ samples; the combination of tetragonal and monoclinic structures (space group P42/nmc and P21/c) is used for refining of 4YSZ samples. The agreement indices (R_p, R_wp) of all refinements are lower than 8%, which means good agreements between the line profiles obtained from experiments and the line profiles from calculated [32]. An example of the refinements is plotted in Fig. 3.

The phase fraction of 4YSZ samples, according to the results of refinements, is shown in Fig. 4 as a function of calcination temperature. Apparently, the phase fraction is dependent on the calcination temperature. The tetragonal phase fraction decreases with the increasing calcination temperature over 300–900 °C, and reaches to a minimum (90.46%) at 900 °C. When the calcination temperature is higher than 900 °C, the tetragonal phase fraction becomes to increase with the increasing calcination temperature, and reaches to 100% in sample calcinated at 1200 °C.

Fig. 5 shows the grain size of nanoparticles at different calcination temperature. Both the cubic and the tetragonal nanoparticles have same grain growth behavior with the increasing calcination temperature. Below 800 °C, nanoparticles grow slowly with the increasing calcination temperature; but when the calcination temperature is higher than 800 °C, the grain growth of nanoparticles accelerates dramatically. In addition,