Facile Synthesis of Highly-dispersed Yttria-doped Zirconia Nanoparticles

Shaoyan Wang,*[1,2] Xiaoan Li,[2] Yuchun Zhai,*[1] Yang Li,[2] and Kaiming Wang[2]
[1]*School of Materials and Metallurgy, Northeastern University, Shenyang 110006, P. R. China*
[2]*School of Chemical Engineering, Anshan University of Science & Technology, Anshan 114044, P. R. China*

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By dissolving starting materials $ZrOCl_2 \cdot 8H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ in ethanol and adding concd $NH_3 \cdot H_2O$ diluted with ethanol, the coprecipitation is easily brought about to generate hydroxide precursor. The precursor is filtrated, washed with ethanol, dried, and calcined to form highly dispersed uniform yttria-doped zirconia nanoparticles ready for good YSZ powder compacts.

Nanocrystalline yttria-stabilized zirconia (YSZ) powder is a promising material for advanced ceramic applications. In order to obtain good sinterability of the calcined powders, highly dispersed powders with uniform size are necessary.

Aqueous coprecipitation method is the most commonly used for the synthesis of mixed oxides, but powders with a small particle size obtained by this processing are often heavily agglomerated. The main reason for the agglomeration is the absorbed water and surface hydroxy group on the precipitated hydroxide precursors, besides the particle agglomeration occurs when the precipitated precursors or gels are dried and milled, and also calcined. This effect reduces the sintering behavior of the calcined powder, hence, greatly compromises their usefulness. In order to overcome this disadvantage in aqueous solution, YSZ nanoparticles have been synthesized by chelate[1] or oxalate[2,3] processing to avoid formation of hydroxide precursors, and could also be obtained by hydroxide processing when necessary measures to solve the problem of heavy agglomeration caused by hydroxide precursors were taken as follows: During the process of hydroxide precipitate formation, sonication[4] or use of urea as precipitating agent and polyacrylic acid as dispersing agent[5] were adopted to alleviate the agglomeration between the hydroxide particles. After hydroxide precipitate formation, washing the precipitate with ethanol[6,7] and accompanying with ultrasonication,[8] or making the precipitate react with hexamethyldisilazane vapor[9] were utilized to remove hydrogen bonding which would cause the agglomeration. The hydroxide precursors could be transformed to oxide directly at low temperature by hydrothermal method[10–12] to avoid the fast grown-up of the particles during calcination.

In order to obtain dispersed YSZ nanoparticles, ethanol was commonly used as a washing solvent in precipitation method[4–8,10] and as a reaction solvent in solvothermal method[13] or sol–gel method.[14] Ethanol played an important role to suppress the formation of agglomerates and aggregates. In this paper, ethanol was used as a medium in which the coprecipitation was carried out, and highly dispersed uniform Y_2O_3-doped ZrO_2 nanoparticles with good sinterability were synthesized.

The starting materials $ZrOCl_2 \cdot 8H_2O$ and 3 mol % $Y(NO_3)_3 \cdot 6H_2O$ were dissolved simultaneously in C_2H_5OH (95%) to form 0.5 mol/L solution, and a little deionized water was needed to assist to dissolve these starting materials. Concd $NH_3 \cdot H_2O$ was diluted to 2 mol/L solution with C_2H_5OH (95%) also. The $NH_3 \cdot H_2O$ solution was then added dropwise to the vigorously stirred $Y(NO_3)_3$-doped $ZrOCl_2$ solution to produce a white, gelatinous $Y(OH)_3$-doped $ZrO(OH)_2$ precipitate. After filtrated, washed with C_2H_5OH (95%), dried at 100 °C for 2 h and calcined at 600, 700, and 800 °C for 2 h, respectively, $Y(OH)_3$-doped $ZrO(OH)_2$ gel was transformed into Y_2O_3-doped ZrO_2 ready for sintering studies.

Because water is a medium or a main component of the medium in the traditional precipitation method for the preparation of nanosized metal oxides, the formation of agglomerates is unavoidable. Figure 1a is a TEM micrograph of yttria-doped zirconia powders produced by hydroxide precipitation method in water. In this case, uneven heavy agglomerates generated from primary fine particles of an about 10 nm in diameter. The agglomeration cannot be alleviated under the condition that there exists a large amount of water. This is illustrated by Figure 1b that shows a TEM micrograph of the powders obtained by using mixture of ethanol and water (the volume ratio is 1:1) as solvents for precipitating and washing.

Although washing with ethanol is a widely adopted procedure to suppress the formation of agglomerates and aggregates, we cannot overcome agglomeration thoroughly only by washing hydroxide precipitate with C_2H_5OH. Figure 1c shows this result. Figures 1d, 1e, and 1f are the TEM micrographs of Y_2O_3-doped ZrO_2 powders synthesized in C_2H_5OH, and washed with C_2H_5OH, and calcined at different temperature. These nanoparticles in Figures 1d–1f had good dispersity and were uniform in size and shape. Their average diameter was 11 nm when calcination temperature was controlled at 600 °C, 17 nm at 700 °C, and 19 nm at 800 °C, respectively. The particles did not grow up ob-

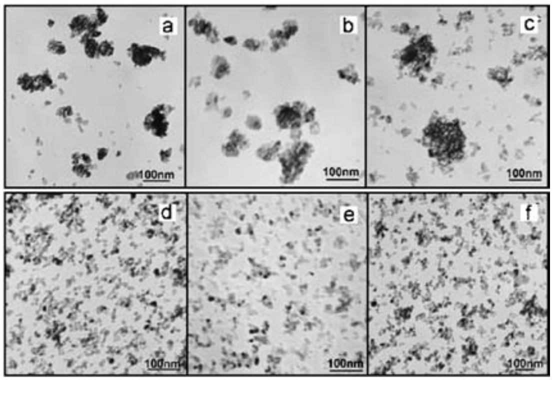

Figure 1. TEM micrographs of Y_2O_3-doped ZrO_2 powders: a, Synthesized and washed in water, calcined at 600 °C; b, synthesized and washed in the mixture of water and C_2H_5OH (1:1 vol.), calcined at 600 °C; c, synthesized in water and washed in C_2H_5OH, calcined at 600 °C; d, synthesized and washed in C_2H_5OH, calcined at 600 °C; e, 700 °C; f, 800 °C.

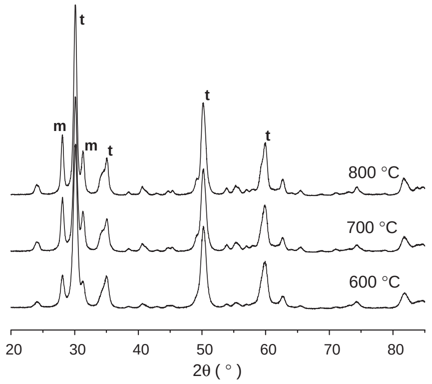

Figure 2. XRD patterns of YSZ powder synthesized in ethanol at various temperatures (t, tetragonal phase; m, monoclinic phase).

viously when calcination temperature stepped up. Our experiment proved that the agglomeration mentioned above could be solved by C_2H_5OH used as medium instead of water because C_2H_5OH weakened hydrogen bonds that lead to hard agglomerates at the first stage where the precipitation had just formed. This is the crucial step to obtain the target powders.

As shown in Figure 2, XRD patterns of YSZ powders synthesized in ethanol and calcined at 600, 700, and 800 °C reveal that a large amount of the tetragonal phase together with the monoclinic phase were formed and that the amount of the monoclinic phase increased slightly with increasing calcining temperature.

The sintering behavior of ceramic powder compacts depends on various factors such as the initial particle size, dispersity, composition, phase, sintering temperature, time, etc. Under the same preparing conditions except for the coprecipitation medium, the initial particles different in the dispersity to a great degree lead to the powder compacts much different in sintering behavior.

In this letter, the compacts without any additive were prepared in a hardened steel die to form pellets with a diameter of 13 mm. The pellets were sintered in air. When the initial particles were prepared in water or in a mixture of water and ethanol with a volume ratio 1:1, the fractured surfaces of the sintered pellets had heavy cracks and uneven agglomerates as shown in Figures 3a and 3b because of localized densification. Whereas the initial particles were prepared in ethanol, the fractured surface was flat with evenly sintered grains of about 600 nm in diameter as shown in Figure 3c. Although the sintered pellet had some residual pores because of the small preparing pressure of 7 MPa, its density estimated from the mass and dimension of the sintered body was 5.97 g/cm^3. When the pressure used for the green compact was 10 MPa and sintering temperature was 1500 °C, the density of sintered body reached 6.16 g/cm^3. From Figure 3d, we can see that the grain diameter became larger (about 800 nm) and the amount of pore became smaller than those of the former, and there existed fracture across crystals as well as along crystals on the surface of the sintered body. If we optimize the system of sintering process using the initial particles prepared in ethanol, the ceramic with good property should be produced.

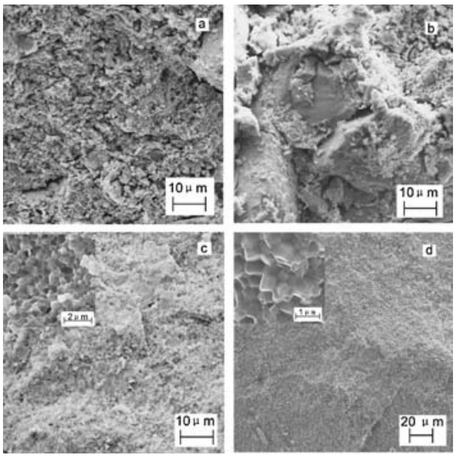

Figure 3. SEM micrographs of the fractured surface of Y_2O_3–ZrO_2 sintered compacts: The initial YSZ powders synthesized under the conditions of a, water; b, mixture of water and ethanol (1:1 vol.); c, ethanol as precipitating and washing solvents, calcined at 600 °C, compacted at 7 MPa, and sintered at 1400 °C for 4 h; d, ethanol as solvents, calcined at 600 °C, compacted at 10 MPa, and sintered at 1500 °C for 2 h.

In conclusion, we have shown that homodispersed nano-Y_2O_3–ZrO_2 can be readily synthesized by a coprecipitation method and the crucial is using ethanol as reacting and washing media. This is a simple green processing without pollution. The sintered ceramic with a homogeneous microstructure, uniform grain size distribution, and high density can be obtained when the highly dispersed nano-yttria-doped zirconia is used.

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