PHASE TRANSITION AND CRYSTAL GROWTH
OF YSZ NANOPARTICLES WITH VARIOUS Y₂O₃ CONTENTS
PREPARED BY SOL-GEL PROCESS

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ABSTRACT

The phase transition and growth of yttria-stabilized zirconia (YSZ) nanocrystallites prepared by a sol-gel process with various amounts of ZrOCl₂·8H₂O and Y(NO₃)₃·6H₂O in ethanol-water solutions at low temperatures were studied. DTA/TGA, XRD, and TEM were used to characterize the YSZ nanocrystallites. The crystallization temperature of 3YSZ, in which Y₂O₃/(Y₂O₃+ZrO₂) = 0.03 gel powders, estimated by DTA/TG is about 427°C. When 3YSZ and 5YSZ gels were calcined at 500°C, their crystal structures were composed of coexisting tetragonal and monoclinic ZrO₂. Cubic ZrO₂ was obtained when added Y₂O₃ was greater than 8 mol%. A nanocrystallite size distribution between 10 and 20 nm was obtained from TEM observations.

INTRODUCTION

Zirconia-based ceramics are very important for electrochemical and structural applications. These materials exhibit desired mechanical strength and electrical properties (1-3). When doped with yttria, fine-grained tetragonal zirconia polycrystals (Y-TZP) and partially stabilized zirconia (Y-PSZ) exhibit excellent strength and fracture toughness because of the stress-induced martensitic transformation of tetragonal precipitates to monoclinic symmetry (4).

Stabilized ZrO₂ solid solution has been used widely in several commercial fields. In these stabilized systems, yttria stabilized zirconia (YSZ) is the most common system. YSZ has high ionic conductivity and thermal stability, for which it is used in oxygen sensors and solid oxide fuel cells (SOFCs) (5,6). Due to high strength and toughness compared with others, tetragonal YSZ is regarded as an important engineering ceramic.

To obtain dense and pure YSZ with fine grains, it is necessary to prepare nanoparticles with excellent sintering ability. Various methods for the synthesis of YSZ nanoparticles have been reported, such as coprecipitation (7), hydrothermal process (8-10), and...
hydrolysis of metal alkoxides (11,12). However, these methods are difficult to control and are expensive.

In recent years, a sol-gel process has been widely used in the fabrication of oxides because of its inherent advantages over other conventional processes (13-15). For example, high surface area of dried gels can result in the formation of fine powder with high reactivity that permits a low process temperature. By starting with well-mixed solutions of sols, high purity, low sintering temperature, and a high degree of homogeneity in a molecular scaled product can be obtained with this method.

Using a sol-gel process to prepare monodispersed and spherical zirconia powders from heating ethanol-water salt solutions has been reported by Moon et al. (16,17). Li et al. (18-20) have also demonstrated a similar way to synthesize YSZ nanoparticles. However, the effect of Y₂O₃ addition on the phase transition and growth of YSZ nanocrystallites has not been discussed in detail.

In the present study, ZrOCl₂·8H₂O and Y(NO₃)₃·6H₂O were used for the synthesis of YSZ nanocrystallites by a sol-gel process. The main objective of the investigation was to examine the effect of Y₂O₃ addition on the phase transition and growth of Y₂O₃-ZrO₂ gel-dried nanoparticles.

**EXPERIMENTAL PROCEDURE**

**Gel Preparation**

The starting materials were zirconyl chloride octahydrate (ZrOCl₂·8H₂O) and yttrium nitrate [Y(NO₃)₃·6H₂O] supplied from Alfa Aesar and Riedel-deHaën, respectively. Zirconyl chloride octahydrate and yttrium nitrate were dissolved in a deionized water-ethanol solution in a volume ratio of 1:5. Solutions of various Y₂O₃ to (Y₂O₃ + ZrO₂) ratios varying from 3, 5, 8, and 10 mol% were prepared and labeled as 3YSZ, 5YSZ, 8YSZ, and 10YSZ, respectively. The mixture solution was then added with a certain amount of polyethylenglycol (PEG) as a dispersant. The mixture solution was stirred and heated to 75°C in a thermostatic bath to obtain white gel-like precipitates. NH₄OH was then added into the gel until a pH of 9 was attained. During precipitation, the gel was repeatedly rinsed with a large amount of deionized water and tested with AgNO₃ solution to make sure no AgCl precipitates remained, and then the powders were freeze-dried at -55°C in vacuum.

**Sample Characterization**

Differential thermal and thermogravimetric analyses (DTA/TGA) (Setsys evolution, Setaram, France) were conducted on a 50 mg powder sample at a heating rate of 5°C/min in air with Al₂O₃ powders as the reference material. The calcination temperature was determined from the result of DTA. The crystalline phase was identified by X-ray diffraction (XRD) and electron diffraction (ED) analyses. XRD was performed using an X-ray diffractometer (Model Rα II A, Rigaku, Tokyo) with CuKα radiation and a Ni filter operated at 30 kV, 20 mA, and a scanning rate of 0.25°/min. The morphology of
the YSZ gel powders and calcined nanocrystallites was examined by scanning electron microscopy (SEM, Philips, XL-40FEG), and transmission electron microscopy (TEM, H700H, Hitachi) operating at 200 kV.

RESULTS AND DISCUSSION

Thermal Behavior of the YSZ Gels with Varying Y$_2$O$_3$ Content

The (DTA/TG) curves (not shown) of the 3YSZ gel powders measured at a heating rate of 5°C/min indicated an endothermic peak at about 80°C accompanied with a weight loss of 7% caused by the evaporation of an ethanol-water solution. Apparently, the weight loss at 100 ~ 430 °C is attributed to the dehydration of precursors. An exothermic peak at 427°C is due to the formation of the tetragonal to monoclinic phase transformation for 3YSZ gel powders.

The DTA curves of the YSZ gels with various Y$_2$O$_3$ contents at a heating rate of 5°C/min are shown in Figure 1. When the Y$_2$O$_3$ content increases, the exothermic peak temperature of the YSZ gel powders shifts to high temperature. Figure 1 also indicates that the tetragonal to monoclinic phase transformation is 429°C for 5YSZ gel powders. When the exothermic peak temperature is greater than 456°C, only pure cubic ZrO$_2$ forms with 8YSZ and 10YSZ.

![Figure 1. Exothermic peak temperature of various YSZ gel powders at a heating rate of 5°C/min.](image)

Phase Characterization of the YSZ Gel Powders

XRD results for the four precipitates with various Y$_2$O$_3$ contents when calcined at 500°C for 2 hours are shown in Figure 2. The XRD patterns of the 3YSZ gel powder calcined at 500°C for 2 hours are shown in Figure 2 (a). The (101), (110), (112), (211), (202), and (220) reflections correspond to tetragonal ZrO$_2$, and the (011), (111), (111), (021), (211), (211), (202), (013), and (222) reflections correspond to the monoclinic ZrO$_2$. 

988 Electrochemical Society Proceedings Volume 2005-07
Figure 2. XRD patterns of YSZ gel powders with various Y$_2$O$_3$ contents and calcined at 500°C for 2 hrs; (a) 3YSZ, (b) 5YSZ, (c) 8YSZ, and (d) 10YSZ.

Figure 2 (b) shows the XRD patterns of the YSZ gel powders with 5 mol% Y$_2$O$_3$. It demonstrates that in the crystalline phase in the 5YSZ monoclinic and tetragonal ZrO$_2$ coexist. The major (111), (200), (220), (311), (222) and (400) reflections of the cubic ZrO$_2$ that appear in the YSZ gel powders with 8 and 10 mol% Y$_2$O$_3$ are shown in Figure 2 (c) and (d), respectively. The result of Figure 3 confirms that the exothermic reaction at 427°C is the phase transformation of YSZ. The crystal structure varies from the tetragonal and monoclinic dual phase to the pure cubic phase when the Y$_2$O$_3$/ (Y$_2$O$_3$ + ZrO$_2$) ratio is greater than 8 mol%.

Figure 3. TEM images of 3YSZ nanoparticles calcined at 500°C for 2 hrs; (a) BF image (b) lattice image showing d-spacing of (101) of tetragonal ZrO$_2$ is 2.89 Å and (111) of monoclinic ZrO$_2$ is 3.21 Å.

**Morphology of the YSZ Nanocrystallites**

The TEM bright-field (BF) micrograph and corresponding lattice image of the 3YSZ gels calcined at 500°C for 2 hours are shown in Figure 3. ZrO$_2$ nanocrystallites appear as dark
particles with diameters from 10 to 20 nm (Figure 3 a). The lattice image (Figure 3 b) provides evidence for the presence of tetragonal and monoclinic ZrO$_2$ in the system. Figure 4 is a TEM micrograph and lattice image of the 8YSZ gel powders calcined at 500°C for 2 hours. Figure 4 (a) is the TEM-BF micrographs of the 8YSZ nanocrystallites. The diameter is measured directly from the BF image, which indicates that the nanocrystalline 8YSZ with average diameter from 10 to 20 nm has a round morphology and good crystallinity. Figure 4 (b) reveals lattice images of the 8YSZ nanocrystallites, which provide evidence of the presence of cubic ZrO$_2$ in this system.

![Figure 4](image_url)

Figure 4. TEM images of 8YSZ nanoparticles calcined at 500°C for 2 hr, (a) BF image (b) lattice image showing the d-spacing of (111) of cubic ZrO$_2$ is 2.93 Å.

CONCLUSIONS

The phase transition and growth of YSZ nanocrystallites has been investigated using DTA/TGA, XRD, and TEM. The following conclusions may be drawn from this study:

- As the Y$_2$O$_3$ content increases, the exothermic peak in the DTA of the YSZ gel powders shifts to high temperature from 427°C to 460°C.
- The tetragonal and monoclinic ZrO$_2$ coexists in both 3YSZ and 5YSZ gel powders calcined at 500°C for 2 hours. However, when the Y$_2$O$_3$ content is higher than 8 mol%, only cubic YSZ nanocrystallites exist.
- It was found from calculations and direct observations that the particle size of the YSZ nanocrystallites ranges from 10 to 20 nm.

ACKNOWLEDGMENTS

The authors wish to thank the National Science Council of Taiwan, ROC for the financial support under contract NSC 93-2120-M-006-004. Prof. M. P. Hung, Prof. M. H. Hon, and Mr. S. Y. Yau offered advice and suggestions on the experiments and analyses for which we are very grateful.
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Electrochemical Society Proceedings Volume 2005-07 991