Synthesis and Characterization of Nanocrystalline RuO₂–ZrO₂

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The nanocrystalline samples of zirconium oxide doped with ruthenium oxide (RuO₂) have been synthesized from chlorides as precursors by chemical precipitation method. The as-prepared and annealed powder samples were studied by XRD, TEM and Impedance Spectroscopy. With 7.5 mol% of RuO₂, only a small percentage of ZrO₂ stabilizes in tetragonal form without stabilization in cubic form. With 9 mol% and above, ZrO₂ stabilizes in mixed phases having both tetragonal and cubic structure. On annealing, up to 1273 K the proportion of the cubic phase increases; however annealing at temperatures above 1273 K makes the sample to become monoclinic. Average grain size, as determined by Scherrer’s formula using X-ray linewidth, increases with increase of annealing temperature. The same trend is observed in TEM studies. TEM studies show the agglomeration of grains. X-ray diffraction for various concentrations of RuO₂ shows the presence of small amount of RuO₂ as impurity. This implies that Ru⁴⁺ goes to the interstitial position also in addition to its occupation of substitutional position of Zr⁴⁺ due to its smaller ionic radius (0.062 nm) compared to that of Zr⁴⁺ (0.084 nm). The impedance spectroscopy measurement shows that the conductivity decreases with an increase of grain size. The phase changes in the stabilization process with different concentrations and annealing temperatures, and growth of grain size in RuO₂ stabilized ZrO₂ will be presented. One of the salient points in this study is stabilization of ZrO₂ with RuO₂ alone without Y₂O₃ as reported in the literature.

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1. Introduction

Many research works on synthesis, structure and properties of the nanocrystalline materials, e.g. nanocrystalline ceramics have demonstrated that the high interfacial and grain boundary energies of the nanocrystalline solids lead to the formation of diffusion induced solid solutions and new compounds.¹⁻³ Zirconia (ZrO₂) is a technologically important material which occurs in three polymorphic phases, monoclinic, tetragonal and cubic at different temperature ranges.⁴ The tetragonal or cubic phases of ZrO₂ can be stabilized by doping ZrO₂ with CaO, MgO, Y₂O₃, Sc₂O₃, CeO₂ etc. Zirconia doped with different dopants find different applications.

Ruthenium oxide (RuO₂) can be effectively used as electrodes for oxygen evaluation⁵ and as a high-catalytic in Fischer-Tropsch reactions.⁵ The use of ruthenium electrodes, if the electrolyte is found to be ruthenia stabilized zirconia, the thermodynamic equilibrium can be maintained at the electrode-electrolyte interface even after many cycles of operation. In the present study, the grain size effect has been utilized to dope RuO₂ into ZrO₂ and hence to stabilize the tetragonal or cubic phase of ZrO₂. The results of synthesis and structural characterisation of nanocrystalline zirconia doped with different concentrations of ruthenium are reported in this paper.

2. Experimental Procedure

Nanocrystalline zirconia powders doped with 5, 7.5, 9, 10 and 15 mol%RuO₂ were prepared by chemical precipitation method. Zirconium oxy chloride (ZrOCl₂·8H₂O) and ruthenium chloride (RuCl₃·3H₂O) were taken in appropriate ratios in aqueous medium in a flask fitted with a reflux condenser.

The aqueous solution was hydrolyzed for 72 h. The pH value during hydrolysis was measured to be 1 and it does not change during hydrolysis. The resultant sol was neutralized with ammonium solution and a precipitate was obtained. The precipitate was washed with distilled water and then dried. The as-prepared powder was annealed at different temperatures. The powder X-ray diffraction was carried out on all the samples using a Sievert X-ray diffractometer using Cu-Kα₁ radiation and a quartz monochromatometer in the two theta range 20°–70° in steps of 0.02°. The instrumental broadening was estimated with a standard silicon sample and accounted properly in the particle size estimation using the Scherrer’s formula.⁷ The microstructure of the powder samples was characterized using a transmission electron microscope-TEM (JEOL 2000FX).

The nanocrystalline powders were annealed at 873 K and 1073 K for 1 h. The 8 nm dia and 1.2 nm thickness pellets of these samples were made applying an uniaxial pressure of 0.57 GPa. The relative density of the pellet was measured by Archimedes principle and found to be 72% of the bulk density. The impedance measurements were done on the pellets made from as-prepared and annealed powders, using Solartron SI 1260 impedance/gain phase analyzer in the frequency range 10 Hz to 1 MHz, from room temperature to 873 K. Platinum paint was used as electrodes. The paint was applied on both surfaces of the pellet.

3. Results and Discussion

Figure 1 shows the TEM pictures of the 10% RuO₂ doped ZrO₂ (10RuSZ) as-prepared powder and the one annealed at 1273 K for 1 h. The average particle size of the as-prepared as well as the annealed samples is found to be in the range of 50 nm. The fine particles are more or less spherical and
each particle is found to be an aggregate of very small crystals of size 8 nm in the as-prepared sample and 20 nm in the 1273 K annealed samples respectively. Similar morphology is found in all the samples with different concentrations of the dopant.

It is observed from the X-ray diffraction analysis that there is an optimum level of the RuO₂ content for the formation of cubic solid solution with ZrO₂ nanoparticles. With 5% RuO₂, the zirconia powder exhibited only monoclinic phase for different annealing temperatures. As the ruthenia content is increased via 7.5, 9, 10 and 15 mol%, the volume fraction of the tetragonal phase increases up to 9 mol% and no signature of cubic phase is seen. However, at 10 mol% of ruthenia cubic phase is stabilized from 873 to 1173 K annealing. But, beyond 10 mol% of ruthenia, there is a decomposition of the tetragonal solid solution at a lesser temperature of annealing. Figure 2 shows the XRD spectra of 9.0 mol%RuO₂ doped ZrO₂ (9.0RuSZ) nanocrystalline powder annealed at different temperatures along with the as-prepared one. The XRD spectrum of the as-prepared powder revealed large line broadening; may be due to small crystallites with strain. The differential thermal analysis (DTA) on the as-prepared powder also did not show any crystallization phenomenon. Thus, the powder seems to be already crystallized during synthesis itself; however the extent of the crystallinity is less. When the powder is annealed at 873, 1073 and 1173 K, the tetragonal phase is found to appear. And again the powder becomes completely monoclinic when annealed at 1273 K. But in the case of 10RuSZ, the main phase of the powder is cubic with a small fraction (%) of the RuO₂ phase till the annealing temperature of 1173 K. Figure 3 shows the XRD spectra of 10RuSZ powder annealed at different temperatures. There is no splitting of lines due to reflections by the planes 002 and 200, 311 and 113 which will indicate the formation of tetragonal phase. After annealing at 1273 K, a small splitting is observed for both the reflections by 002 and 311 planes. This splitting is clearly seen after annealing at 1473 K. Hence from 1173 to 1473 K the sample remains in tetragonal form. When the annealing temperature is increased to 1673 K, the sample starts transforming into the monoclinic phase. XRD measurements around 72°–76° have been suggested to have a clear observation of peaks of cubic, tetragonal and monoclinic phases. In future measurements with close scanning around
this region will be done.

From Figs. 2 and 3, it is clear that the cubic phase stabilization is better achieved in 10RuSZ. On the other hand, if the ruthenium content is increased to 15%, the tetragonal phase disappears even for the annealing temperature of 1273 K. For the same treatment, 10RuSZ exhibits mainly cubic phase. Figure 4 shows the XRD spectra of 15% RuO₂ doped ZrO₂ nanocrystalline powder heat treated at different temperatures. It is inferred from the XRD analysis of these samples that there is an optimum level of the dopant concentration to stabilize the cubic phase at room temperature. The formation of tetragonal solid solution starts at the regime of 7.5% RuO₂ and the cubic phase fraction is maximum with 10% of the RuO₂. For the higher content of ruthenium (15%), it seems that the tetragonal solid solution decomposes relatively at a lower temperature (1273 K) into the monoclinic ZrO₂ and the segregated RuO₂. This decomposition starts only after 1673 K in 10RuSZ. Thus in the nanocrystalline state of the zirconia powder, ruthenium finds a limited solubility and the resultant phase is a metastable one. Higher concentration of ruthenium destabilizes the tetragonal phase and cubic phase. This may be due to the fact that the increased driving force by the excess ruthenium on the surface of the zirconia particles may cancel out the particles surface energy thus resulting into a thermodynamically stable monoclinic phase. The details of the annealing temperature and average grain size for the three compositions of RuO₂–ZrO₂ are given in Table 1.

The complex impedance spectra (Z’’ plotted against Z’) for the pellets of the as-prepared 10RuSZ samples and 873 K and 1073 K annealed samples, measured at room temperature are shown in Fig. 5. For the as-prepared sample at room temperature the grain and grain boundary components are obtained as two depressed semicircles. However, for the samples annealed at 873 K and 1073 K, the contributions due
to the grains and grain boundaries seem to become equal, may be due to grain growth and hence only one semicircle is seen along with the electrode effects. When the annealing temperature increases, the resistance of the material also increases. Moreover the magnitude of conductivity in the as-prepared pellet is higher than that in the annealed one. It may be mainly due to grain boundary effect and partly due to the porosity of the material. In addition to this, the average grain size also increases with increase of annealing temperatures. The values of R from the high frequency depressed semicircle reveals that the conductivity decreases with grain size (with increase of annealing temperature).

Figure 6 shows the complex impedance (CI) spectra obtained from 573 to 873 K for 10 RuSZ (873 K annealed powder) sample. The impedance spectra show typical depressed single semi-circle arc behaviour. The single semi-circle is observed corresponding to the grain and grain boundary implying identical time constants. Moreover the arcs are found to be highly depressed which is due to the distribution of relaxation times. Hence the semi-circle in the spectra is the combination of constant phase elements (CPE) in series with the parallel combinations of the overlapped, unresolved grain and grain boundary part. However, as the temperature is increased, the grain boundary and the electrode-electrolyte polarization effects dominate than the bulk. In principle, the grains should show only resistance without any polarization effect. Thus the overall impedance behavior is mainly due to the contribution from the grain boundaries. As the measuring temperature is increased, the conductivity is also increased.

The conductivity variation with temperature for 10 RuSZ is plotted as Arrhenius plots in Fig. 7, for the as-prepared and 873 K annealed and compacted pellets. The activation energy is (1.35 eV) higher for the as-prepared sample compared to the value of 0.5 eV for annealed sample. The decrease in the activation energy may be attributed to the cubic phase stabilization state of Zirconia and the presence of small amount of impurity phase present in the 10RuSZ, 873 K annealed powder.

4. Conclusion

Zirconia nanoparticles doped with ruthenium in different concentrations were prepared by chemical precipitation. The particles are found to be aggregates of very fine crystallites. A metastable cubic phase stabilization is observed till the an-
nealing temperature of 1173 K in 10 mol% RuO₂ doped ZrO₂, 10 mol% being the optimum value of the dopant to stabilize the cubic phase. Above 1173 K, the cubic phase decomposes to tetragonal phase and finally to monoclinic phase at 1673 K. The conductivity at higher temperatures is due to grain boundary contributions. The decrease in the activation energy for the high temperature annealed sample is attributed to the cubic phase stabilization state of zirconia and small amount of impurity phase (RuO₂) present in the system.

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