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Mechanochemical Synthesis and Sintering of $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$

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Abstract—The $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ tetragonal solid solution was prepared by solid-state reaction from mechanically activated powder mixtures. The effects of the activation medium and particle size on the sintering behavior of the material was examined.

INTRODUCTION

Zirconia-based ceramics, exhibiting a unique combination of high melting temperature, chemical durability, corrosion resistance, hardness, strength, and thermal-shock resistance and low thermal conductivity, are promising structural materials. In view of this, a great deal of attention is focused on the development of commercially viable techniques for producing these ceramics.

At present, ultrafine zirconia powders are commonly produced by chemical methods: coprecipitation [1–5], solution evaporation [4, 6, 7], and sol–gel processing [6, 8, 9].

The inherent drawbacks of the first two methods—broad particle-size distributions, aggregation of particles, and formation of micropores—impede densification of the resulting powders at low temperature.

Sol–gel processing is the most effective chemical method for preparing fine-particle zirconia, offering the ability to produce high-purity, monodisperse powders. This method, however, also suffers from a number of drawbacks, such as high shrinkage during drying and long processing durations.

Fine-particle oxide powders can also be prepared through mechanical activation of the raw materials—grinding the starting mixture in mills and disintegrators. This procedure creates additional active centers on freshly prepared surfaces and activates the diffusion processes, thereby enhancing the reactivity of the powder mixture and accelerating solid-state reactions [10, 11].

The purpose of this work was to prepare ultrafine $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ powders via mechanical activation and to examine their sintering behavior.

EXPERIMENTAL

As starting chemicals, we used hydrated nitrates, analytical-grade $ZrO(NO_3)_2 \cdot nH_2O$ and reagent-grade $Y(NO_3)_3 \cdot 6H_2O$, because their hardness is a few times lower than that of anhydrous salts and oxides, which allows one to reduce the specific energy and avoid contamination from grinding media.

Mechanical activation was carried out for 4 h in air or with water or acetone (10% of the sample weight) in a FRITSCH planetary mill (electrocorundum jars, Al_2O_3 balls), where impacts and friction during milling resulted in size reduction. The specific energy supplied to the powder ranged from 5 to 20 kJ/mol.

As found by chemical analysis, the reaction mixtures milled for 4 h were contaminated with no more than 0.1 mol % Al_2O_3.

RESULTS AND DISCUSSION

According to x-ray diffraction (XRD) data (Siemens D-500/HS diffractometer), milling broke down the structure of the nitrates, resulting in an x-ray amorphous phase (Fig. 1).

The average particle size in the mechanically activated powder mixtures was evaluated by electron microscopy (BS-300 instrument):

Medium	Particle size, nm
air	140
water	70
acetone	100

It is well known that, during milling in the presence of a surfactant, the kinetics of strength loss depends on the rate of surfactant adsorption on fractured surfaces [10].

The adsorption of water or acetone, employed as surfactants in this work, on freshly fractured surfaces weakens chemical bonds between surface atoms, induces a surface charge, and gives rise to the formation of various surface species. These processes facilitate crack nucleation and growth, to the point of fracture, thereby reducing the strength of solids and promoting

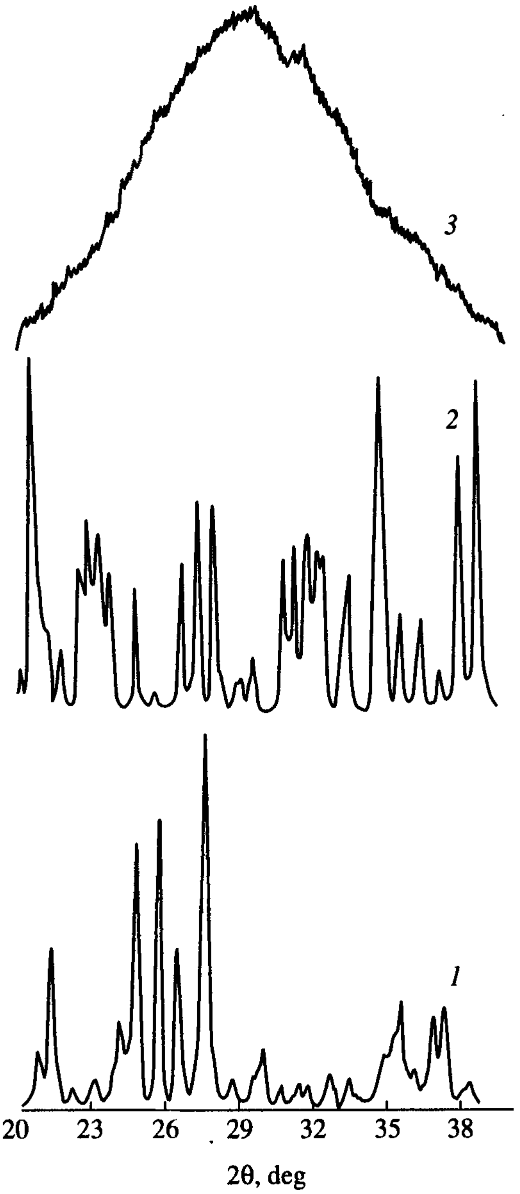

Fig. 1. XRD patterns of (*1*) $ZrO(NO_3)_2 \cdot nH_2O$, (*2*) $Y(NO_3)_3 \cdot 6H_2O$, and (*3*) their MA mixture ($ZrO_2 : Y_2O_3 = 97 : 3$).

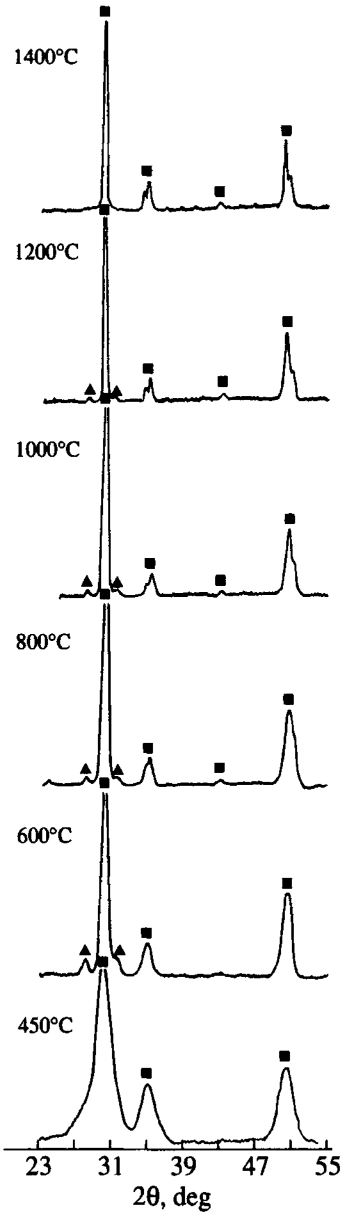

Fig. 2. XRD patterns of tetragonal $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ prepared from mechanically activated mixtures by firing between 450 and 1400°C.

migration of the liquid into the bulk. As a result, the material disintegrates into small particles.

Comparison of the enthalpies of vaporization of water ($\Delta_v H^0$(60°C) = 42.5 kJ/mol) and acetone ($\Delta_v H^0$(56.1°C) = 29.1 kJ/mol) [12] suggests that water is a more active adsorptive than acetone and, hence, milling with water must result in a faster rate of size reduction, in agreement with our electron-microscopic data.

Since the amount of air adsorption is smaller compared to water and acetone, mechanical activation in air is less efficient and requires higher specific energies.

XRD data indicate that firing the mechanically activated mixtures at temperatures between 280 and 450°C yields the $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ tetragonal solid solution (Fig. 2). The broad peaks in the XRD patterns testify to a small particle size (≤150 nm according to electron-microscopic examination).

After firing at 600°C, the material consists of tetragonal $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ and a small amount of monoclinic ZrO_2 (≈9–10%). The content of monoclinic ZrO_2 gradually decreases as the firing temperature rises from 600 to 1300°C and reaches zero by 1400°C (Fig. 2).

Concurrently, the XRD peaks from $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ become sharper, suggesting an increase in average particle size D. To evaluate the particle size of $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ in the range 600–1300°C, we used the formula $D = 0.89\lambda/(\beta\cos\theta)$ [1], where λ is the

Shrinkage (Δ, %) and open porosity (P, %) for $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ materials prepared by sintering for 2 h between 900 and 1400°C

Activation medium	Δ	P	Δ	P	Δ	P	Δ	P	Δ	P	Δ	P
	900		1000		1100		1200		1300		1400	
Air	3	32	5	27	6	24	7	20	11	11	15	6
Water	7	28	13	18	18	1	18	1	–	–	–	–
Acetone	4	30	7	27	11	20	15	7	17	1	–	–

wavelength of x-rays (CuK_α) and β is the peak width at half maximum. The results (Fig. 3) demonstrate that D increases rapidly at firing temperatures above 1000°C. The smallest particle size was found in the materials prepared from starting mixtures mechanically activated in water.

The sintering behavior of mechanically activated powders was studied on green compacts prepared by uniaxial compression at 150 GPa. The compacts were sintered isothermally between 800 and 1400°C for 2 h in a Silit furnace. Heating to the sintering temperature was performed at a high rate of 500°C/h to avoid annealing of activation-induced structural defects, which are known to accelerate diffusion processes and, hence, sintering [13].

The shrinkage and open porosity data for the resultant $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ materials are summarized in the table.

It can be seen that the mechanical-activation medium has a significant effect on the sintering behavior of the powders.

It is well known that sintering is accompanied by grain growth (Fig. 3). It seems likely that the active recrystallization of the ZrO_2-based solid solution studied does not impede—and even promotes to a certain extent—densification, reducing the porosity of the samples.

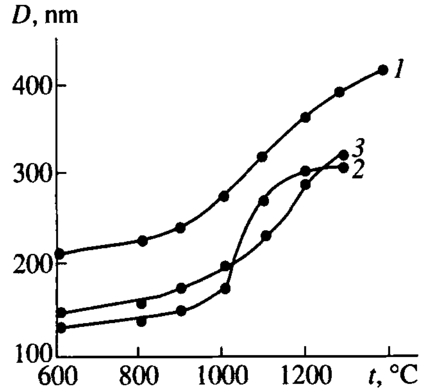

Fig. 3. Average particle size as a function of firing temperature for $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ materials prepared from starting mixtures mechanically activated in (*1*) air, (*2*) water, and (*3*) acetone.

According to our data, mechanical activation of the hydrated zirconium and yttrium nitrates used as starting materials allows the sintering temperature to be reduced by 300–400°C owing to the higher reactivity and smaller particle size of the mechanically activated reagents.

CONCLUSION

Mechanical activation of the hydrated salts used as starting reagents in the preparation of the $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ solid solution allowed us to obtain ultrafine (≈100 nm) powders, lower the sintering temperature by 1100–1300°C, and reduce the heat-treatment duration.

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