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Structure Formation and Degradation of Partially Stabilized Zirconium Dioxide

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Abstract

The process of structure formation of partially stabilized zirconium dioxide powders during the heat treatment of precipitated zirconium and yttrium hydroxides and structure degradation in time depending on hydroxide precipitation method (mutual and sequential precipitation) has been investigated. During calcination, the t→m-ZrO_2 *transition takes place in sequentially precipitated hydroxides, and the m→t-*ZrO_2 *transition takes place in coprecipitated hydroxides. It was noted that soft readily destroyable aggregates are formed during the heat treatment of sequentially precipitated hydroxides. This makes it possible to produce fine* ZrO_2 *powders (*d = *50–100 nm) avoiding disaggregation and/or milling. It has been found that the zirconium dioxide degradation process, which is due to the t→m-*ZrO_2 *transformation, decreases with increasing amount of* Y_2O_3 *and cubic modification of* ZrO_2 *in heat treatment products and in the case of coprecipitation of hydroxides © 1999 Elsevier Science Limited. All rights reserved*

Keywords: powders chemical preparations, grain size, X-ray methods, Y_2O_3, ZrO_2.

1 Introduction

Yttrium oxide-stabilized zirconium dioxide is widely used as a starting material for the production of ZrO_2 ceramic.[1,2] The unique combination of high strength with high crack resistance inherent in Y_2O_3–ZrO_2-based materials is only feasible when a fine-grain and homogeneous microstructure is created.[1] The creation of such a microstructure requires fine starting materials with particles of uniform composition, size and shape, which can be synthesized from solutions under mild conditions.[2] When comparing the 'wet' methods (precipitation from solutions, cocrystallization from solutions and melts, sol–gel technology, etc.), an advantage of the method of precipitating slightly soluble compounds, especially metal hydroxides, was pointed out. It is known that Y_2O_3-ZrO_2 ceramic is prone to the low-temperature (100–500°C) degradation of structure and properties,[3] which calls for the search for and investigation of new methods of synthesis.

In view of the above, the aim of this study was to investigate the formation of the structure of partially stabilized zirconium dioxide powders during the thermal treatment of precipitated zirconium and yttrium hydroxides and its degradation in time depending on the hydroxide precipitation method (mutual and sequential precipitation).

2 Experimental

Concentrated solutions of $ZrOCl_2$ and $Y(NO_3)_3$ were chosen as starting reagents. Precipitation was performed by means of a concentrated aqueous solution of ammonia by two methods: mutual precipitation of the hydroxides $ZrO(OH)_2$ and $Y(OH)_3$ (MPH) and sequential precipitation of the hydroxides (SPH) ($Y(OH)_3$ was precipitated on precipitated $ZrO(OH)_2$) at component ratios corresponding to the formula $(1\text{-}x)ZrO_2 \cdot xY_2O_3$ (where $x = 0{\cdot}03$ and $x = 0{\cdot}04$), at which a partial stabilization of zirconium dioxide took place.

As-precipitated (after drying), as -calcined samples and samples after 1·5-and 3-year storage were investigated.

A DRON-3 M diffractometer with Cu K_α radiation was employed for the analysis. The cubic (*c*), tetragonal (*t*) and monoclinic (*m*) phase content was determined in accordance with the equation given in Ref. 3.

Photomicrographs were taken on a JEOL JEM 100 CX II electron microscope. The average powder particle size was determined from photomicrographs: $d_{av} = \Sigma d_i n_i / \Sigma n$, where n_i is the

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number of particles of d_i size and Σ_n the total number of particles.

3 Results and Discussion

XRD patterns exhibit zirconium dioxide with fluorite-type structure after calcination at 500°C. Raising the temperature causes a tetragonal deformation of the cubic lattice, as evidenced by the splitting of diffraction reflections 200 and 311. XRD patterns show the presence of three ZrO_2 modifications: c + t + m (cubic, tetragonal and monoclinic).

Figure 1 shows the variation of the average diameter of $0{\cdot}97ZrO_2{\cdot}0{\cdot}03Y_2O_3$ microparticies as a function of the hydroxide precipitation method and calcination temperature. The average particle size of stabilized zirconium dioxide is smaller than the critical size in the temperature range 500–700°C (Fig. 1, curves 1 and 2).[4] Therefore, c-ZrO_2 is formed under the given conditions. As the temperature rises, ZrO_2 particles grow and the m-ZrO_2 phase appears. Above 900°C, a rapid growth of coprecipitated-hydroxide crystals begins (Fig. 1, curve 2), which may be due to recrystallization processes, whereas the growth rate of sequentially precipitated hydroxide crystals is much lower (curve 1). Low crystal growth rate is more acceptable since it facilitates the formation of a fine-grained and homogeneous microstructure. It should be also noted that when sequentially precipitated hydroxides are heat-treated, soft readily destroyable aggregates are formed. This makes it possible to produce fine ZrO_2 powders ($d = 50$–$100\,nm$) avoiding disaggregation and milling.

Figure 2 shows the dependence of the amount of the monoclinic modification of partially stabilized ZrO_2 (composition $0{\cdot}97ZrO_2{\cdot}0{\cdot}03Y_2O_3$) on preparation conditions (precipitation method and firing temperature) and storage time (1·5–3 years). Figure 3 shows a similar dependence on calcination temperature for samples of the composition $0{\cdot}96ZrO_2{\cdot}0{\cdot}04Y_2O_3$, which was obtained by the SPH. Figure 4 shows the polymorphic composition of samples after 3-year storage.

As is evident from Fig. 2 (curve 1), during the heat treatment of sequentially precipitated hydroxides the t→m-ZrO_2 transformation takes place; this transformation is sharply speeded up as the calcination temperature is raised above 1100°C. During the storage of these samples for 1·5 and 3 years, an adequate transformation takes place (curves 2 and 3, respectively). The structure degradation process reaches practically completion within 1·5 years. During the heat treatment of coprecipitated hydroxides at over 900°C, the transitions m→t-ZrO_2 take place (Fig. 2, curve 1′). When coprecipitated calcined hydroxides are stored in the above temperature range, the opposite transition t→m-ZrO_2 takes place (curve 3′). When comparing the methods for the synthesis of partially stabilized ZrO_2 (SPH and MPH), it can be seen that in the case of MPH a higher degree of stability of the high-temperature c and t modifications of ZrO_2 and a higher degree of stabilization at over 1100°C are attained (Fig. 3, curves 3 and 3′). In contrast to the degree of ZrO_2 stabilization, which is determined by the amount of the c and t modifications,[1] we mean by the ‘degree of stability’ (S) the reciprocal of variation in the amount of the m phase of ZrO_2 with $S = 1/(C_{m_2} - C_{m_1})$, where $C_{m_2} - C_{m_1}$ is the concentration difference of the monoclinic modification of ZrO_2 after storage and in an as-calcined sample, respectively.

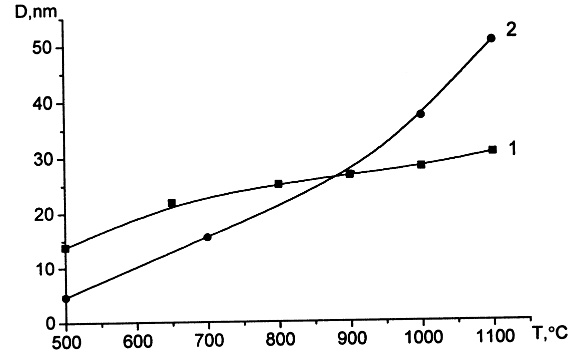

Fig. 1. Average microparticle diameter of samples of the composition $0{\cdot}97ZrO_2{\cdot}0{\cdot}03Y_2O_3$ as a function of hydroxide precipitation method and calcination temperature: (1) SPH,(2) MPH.

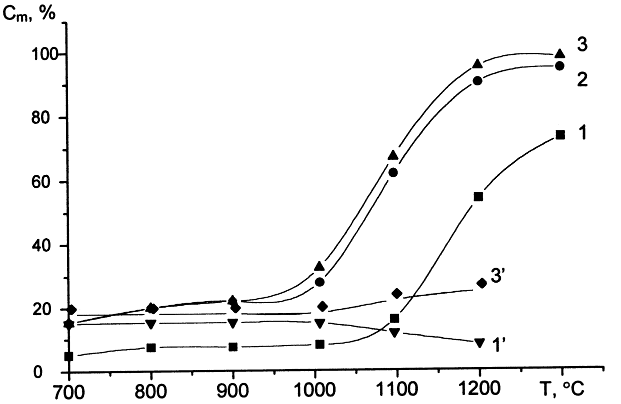

Fig. 2. Amount of the monoclinic modification of zirconium dioxide of the composition $0{\cdot}97ZrO_2{\cdot}0{\cdot}03Y_2O_3$ as a function of precipitation conditions (SPH and MPH), precipitate calcination temperature and heat treatment product storage time: (1,2,3) SPH: as-calcined and after 1·5 and 3 years; (1′ and 3′) MPH: as-calcined and after 3 years.

As the amount of yttrium oxide increases, the degree of ZrO_2 stabilization increases and the rate Of ZrO_2 degradation decreases (Figs 2–4).

Figure 5 shows the dependence of the degree of stability (S) of zirconium dioxide in time (3 years) on the amount of Y_2O_3 and calcination temperature. As follows from Fig. 5, the degree of stability

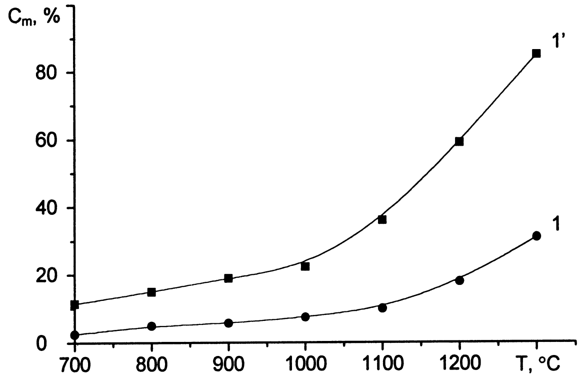

Fig. 3. Amount of the monoclinic modification of zirconium dioxide of the composition $0{\cdot}96ZrO_2{\cdot}0{\cdot}04Y_2O_3$ as a function of precipitate calcination temperature and storage time (SPH): (1) as-calcined, (1′) 3-years storage.

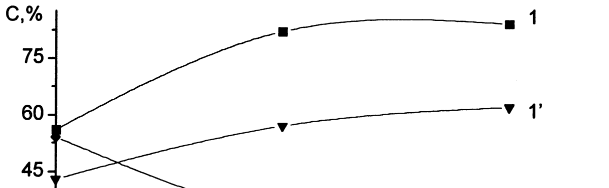

Fig. 4. Polymorphic composition for $(1\text{-}x)ZrO_2{\cdot}Y_2O_3$ samples after storage (3 years): (1,2,3) $x = 0{\cdot}03$ (C_m,C_t,C_c, respectively); (1′,2′,3′) $x = 0{\cdot}04$ (C_m,C_t,C_c, respectively).

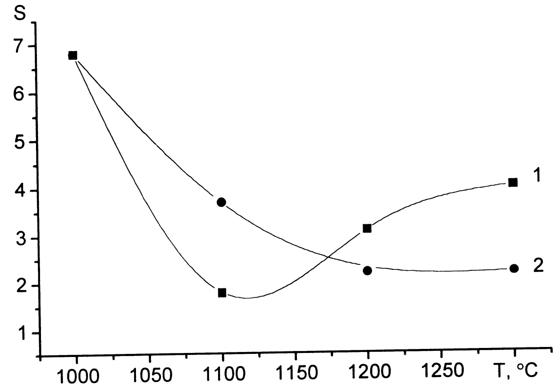

Fig. 5. Degree of stability of $(1\text{-}x)ZrO_2{\cdot}xY_2O_3$ samples in time (3 years) as a function of the amount of Y_2O_3 and calcination temperature: (1,2) $x = 0{\cdot}03$ and $x = 0{\cdot}04$, respectively.

increases unambiguously with the amount of Y_2O_3 for samples calcined at 750–1000°C. Whereas there is a general tendency towards a decrease in the degree of stability as well as in the degree of ZrO_2 Stabilization with increasing calcination temperature, which is due to recrystallization and grain coarsening processes, an increase in S is observed on calcination at over 1155°C (Fig. 5, curve 1) for the composition $0{\cdot}97ZrO_2{\cdot}0{\cdot}03Y_2O_3$. Analyzing the results shown in Figs 4 and 5 (curves 1 and 2), we came to the conclusion that the degree of structure stability for partially stabilized $(1\text{-}x)$ $ZrO_2{\cdot}xY_2O_3$ ($x = 0{\cdot}03$ and $0{\cdot}04$) is determined by the ratio of the c and t modifications of ZrO_2. Increasing C_c contributes to higher S. According to Ref. 5, the said above is accounted for by the fact that cubic crystals in a multiphase mixture limit tetragonal-grain growth and hence the transition t→m-ZrO_2.

4 Conclusion

Polymorphous transformations of ZrO_2 in the products of heat treatment of sequentially and mutually precipitated zirconium and yttrium hydroxides have been studied. During calcination, the transition t→m-ZrO_2 takes place in sequentially precipitated hydroxides and the transition m→t-ZrO_2 takes place in coprecipitated hydroxides.

It was noted that when sequentially precipitated hydroxides are heat-treated, soft readily destroyable aggregates are formed. This makes it possible to produce fine ZrO_2 powders ($d = 50$–100 nm), avoiding disaggregation and (or) milling.

It has been shown that the particle growth rate of coprecipitated hydroxides increases, as against sequentially precipitated hydroxides, with raising the temperature above 730°C. Particle growth inhibition at high temperature facilitates obtaining a fine-grain microstructure, which is very important to the production of high-strength and high–density ZrO_2 ceramic.

It has been found that the zirconium dioxide degradation process, which is caused by the t→m-ZrO_2 transformation, is suppressed by increasing the amount of Y_2O_3 and the cubic modification of ZrO_2 in heat treatment products and when using coprecipitation of hydroxides.

References

1. Yanagida, K. *Commercial Fine Ceramics*. Metallurgiya, Moscow, 1986 (in Russian).
2. Chusovitina, T. V., Toropov, Y. S. and Tretnikova, M. G., Properties of ceramic based on zirconium dioxide partially stabilized with yttrium concentrate. *Ogneupory*, 1991, **6**, 14–16.
3. Lange, F. F., Dunlop, G. L. and Davis, B. I., Degradation during aging of transformation-toughened ZrO_2-Y_2O_3 materials at 250°C. *J. Amer. Ceram. Soc.*, 1986, **69**(3), 237–240.
4. Garvie, R. C. Stabilization of the tetragonal structure in zirconia microcrystals. *J. Phys. Chem.*, **82**(2), 218–223.
5. Lange, F. F., Transformation-toughened ZrO_2: correlations between grain size control and composition in the system ZrO_2–Y_2O_3. *J. Amer. Ceram. Soc.*, 1986, **69**(3), 240–242.