ISSN 1027-4510, Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques, 2009, Vol. 3, No. 3, pp. 464–467. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © N.A. Zaporina, O.A. Doynikova, A.P. Krumina, D.A. Bocharov, J.P. Grabis, 2009, published in Poverkhnost'. Rentgenovskie, Sinkhrotronnye i Neitronnye Issledovaniya, No. 6, pp. 60–63.

Methods of Electron Microdiffraction and X-Ray Analysis in Structure Study of Nanodisperse Partially Stabilized ZrO_2 Powders[1]

N. A. Zaporina[a], O. A. Doynikova[b], A. P. Krumina[a], D. A. Bocharov[c], and J. P. Grabis[a]

[a]*Institute of Inorganic Chemistry, Riga Technical University, 34 Miera str., Salaspils, 2169 Latvia*

[b]*Institute of Ore Deposits Geology, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 109017 Russia*

[c]*Institute of Solid State Physics, University of Latvia, Kengaraga str. 8, Riga, 1063 Latvia*

Received January 20, 2008

Abstract—Analytical electron microscopy (AEM) has been used to study both structure and morphology of partially yttria-stabilized zirconia dioxide nanopowders (YSZ) obtained by wet-chemical methods (glycine and azeotropic distillation) and ceramics produced from them. Both morphological and structural inhomogeneity of nanopowders obtained by glycine (glc) method has been estimated. Besides the tetragonal ZrO_2 phase (results of X-ray analyses) the cubic phase of ZrO_2 with different degree of crystallinity has been estimated by Electron Microdiffraction (EMD) methods. In powders obtained by azeotropic distillation (dest) method besides the amorphous phase (identified in X-ray investigations) the high disperse cubic zirconia phase has been identified using high local EMD method. It has been detected the yttrium influence on the degree of crystallinity in nanopowders obtained by azeotropic distillation method without yttria (dest-0YSZ) and with 5 wt % Y_2O_3 (dest-5YSZ). It has been determined the difference in ceramic morphology produced from these powders. Ceramics mode of nanopowders containing yttria (glc-5YSZ and dest-5YSZ) have a homogeneous surface which consists of different size globules (0.1–0.6 μm) and contains some little pores (~370 nm). Ceramics mode of nanopowders without yttria have inhomogeneous surface with numerous cracks. Separate parts of the latter ceramics consist of globules, their sizes are of 0.2–0.5 μm.

DOI: 10.1134/S1027451009030227

INTRODUCTION

The production of sintered materials is being developed in Latvia [1–3], and these materials find a growing application. The structure, phase and chemical composition, size and shape have influence both on physicochemical properties of nanopowders and on properties of composite materials. Thus, their study is of prior importance. Partially yttria-stabilized zirconia (YSZ) possesses enhanced corrosion and wears resistance, high fracture toughness and ionic conductivity and, therefore, it is widely applied as a structural and electrolyte material, as a thermal barrier and protective coating [4]. However, characteristics of zirconia-based and other similar materials [5, 6] strongly depend on morphology and structure of precursor powders, as well as on a preparation method used [7]. This paper includes investigation of structure, morphology, physicochemical properties of YSZ bath nanoparticles obtained by wet-chemical routes and ceramics by means of analytical electron microscopy (AEM) to reveal the dependence of properties on synthesis conditions.

[1]The article is published in the original.

EXPERIMENTAL

Procedures of powders synthesis and ceramics production have been described in detail elsewhere [8].

Powders. The nanosized ZrO_2–Y_2O_3 powders (with 5 wt % Y_2O_3 and without Y_2O_3, 5YSZ and 0YSZ, respectively) are prepared by co-precipitation synthesis with the following azeotropic distillation (dest-5YSZ and dest-0YSZ) and glycine (glc-5YSZ) methods. In co-precipitation synthesis, $ZrO(NO_3)_2 \cdot 2\,H_2O$ and $Y(NO_3)_3$ as precursor material and *n*-butyl alcohol for distillation are used. Glycine method is based on the pyrolysis of nitrate solutions with the glycine addition.

Ceramics. Synthesized glc-YSZ and dest-YSZ powders were annealed, mixed with the solution of oleic acid in white spirit and pressed at 170 MPa. Obtained tablets (12 × 5 mm) are sintered in vacuum at 1500°C, 3 h.

Analytical electron microscopy (AEM) is used in this study. A high-resolution local method of selected area electron diffraction (SAED)—microdiffraction (MD) is probably the only reliable way of studying fine-disperse poorly crystallized (X-ray amorphous) powders. Similarly to the Debye–Sherrer diagrams

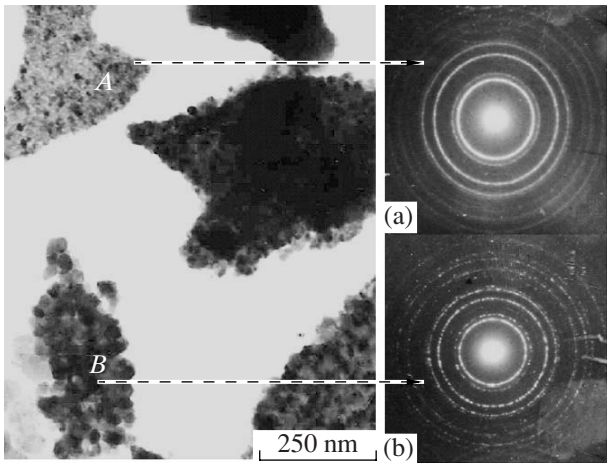

Fig. 1. TEM images illustrating morphological and structural non-homogeneity of nanopowders obtained by glycine method, and microdiffraction patterns (a, b) corresponding to *A* and *B* areas.

obtained in X-ray diffraction, the electron diffraction from a large number of randomly oriented crystallites yields diffraction patterns of nested rings. However, the scattering intensities for electrons are about 10^6 times higher than for X-rays [9]. This clearly favors electrons over X-rays when studying both extremely small sample volumes and X-ray amorphous object.

Powders are examined in the Transmission Electron Microscope (TEM) JEM-100 C operated at 100 kV. For TEM studies, the synthesized nanopowders have been dispersed in ethylalcohol. Typical time of dispergation is ~40 s. The powders are applied in the form of suspension to a copper grid covered by thin formvar film. Preliminary, about 10 nm thick gold layer was attached to a part of the copper grid by means of the sputtering deposition technique in a VUP-2K equipment. The gold film serves for in situ determination of constant λL of the instrument, accurate knowledge of which is important for analysis of diffraction patterns [10].

Morphological studies and analysis of elemental composition of ceramic surface have been performed using Scanning Electron Microscope (SEM) Karl Zeiss, model EVO 50 XVR, equipped with INCA 350 Energy Dispersive X-ray spectrometer (EDX).

Specimen mounted onto stubs with a glue and covered with a thin layer (~75 nm) of Au–Pd using plasma coating method, which prevents specimen charging while minimally affects the X-ray microanalysis. Electron probe microanalyses can be performed on a selected area at a point; the measurements were taken at 2000 magnification, at acceleration voltage of 25 kV, at 100 s live time, 1000 CPS and at working distance of 34 mm.

RESULTS AND DISCUSSION

Information about structure and morphology of YSZ nanopowders synthesized by wet-chemical routes is obtained in TEM. It was established that glc-5YSZ nanopowders are high disperse and inhomogeneous (Fig. 1). These powders consist of particles of different shape and size, larger crystallites have 3–5- and 6-form faceting. Circular MD patterns (Fig. 1a) from aggregate of area A (Fig. 1) indicate their high dispersity. From aggregate of area B (Fig. 1) we have MD pattern with sharp enough circular reflexes (Fig. 1b), that indicate crystalline structure. According to microscopic observations, the average crystallite size is in the range of 50–100 nm that confirms the results obtained by BET method [8]. Interplanar distances (d_{hkl}) calculated from cirucular MD patterns from aggregates of crystallites d_{hkl} = 2.93, 2.51, 1.79 and 1.51 Å, which are in a good agreement with JCPDS (27-997) data for cubic zirconia. According to the X-ray powder diffraction of glc-5YSZ, samples consist of tetragonal zirconia [8]. Thus, there results of [11–14] which found simultaneous coexistence of cubic and tetragonal ZrO_2 have been confirmed.

Nanopowders of dest-5YSZ (similar to dest-0YSZ) have a tendency for agglomeration and conglomeration of small spherical particles (Figs. 2a, 2b). Their sizes are considerably smaller (~5 nm), than those in powders obtained using glycine method, what can be seen from the TEM image (cf. Figs. 1, 2) and from a ring broadening on the MD picture (see Fig. 2a, insert).

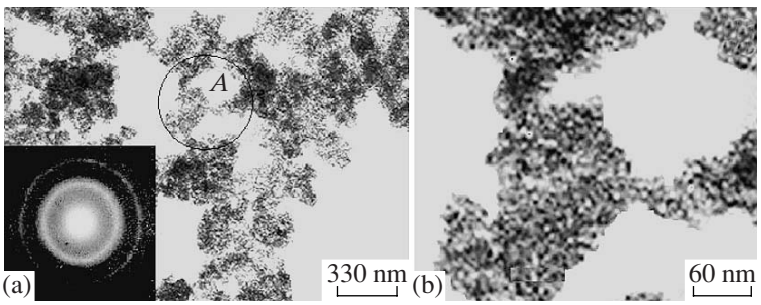

Fig. 2. TEM images of dest-5YSZ nanopowders: (a) combined with an inserted MD, (b) magnified image of area *A* (in circle).

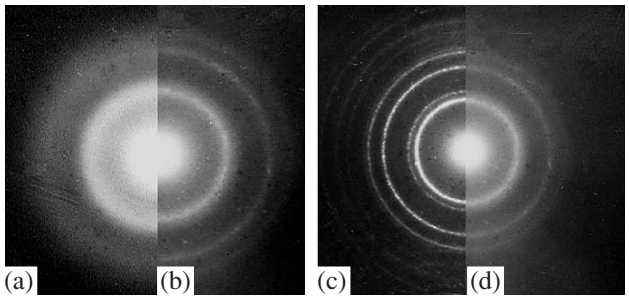

Fig. 3. Microdiffraction patterns form dest-0YSZ (a), dest-5YSZ (b), glc-5YSZ (c), and dest-5YSZ (d) nanopowders.

From MD calculations and analysis we can conclude about cubic structure of dest-5YSZ nanopowders (X-ray amorphous), however, their crystallinity is lower than that in glycine (cf. MD patterns shown in Figs. 3c, 3d). The latter can be explained by different temperatures of the producing powders (dest-YSZ at ~150°C, glc-YSZ—≤ 800°C). Dest-0YSZ has a tendency for full structure loosing (cf. MD patterns on Figs. 3a, 3b). Comparing results of AEM investigations of dest-0YSZ and dest-5YSZ nanopowders reveals yttrium influence on crystallinity of the powders.

Our preliminary studies show relationship between structure and morphology of initial powders and ceramics obtained from them, for example, difference in their topography. The ceramics from nanopowders with yttrium (glc-5YSZ and dest-5YSZ) have a homogeneous surface (Figs. 4b and 5a) consisting of globules of different size (0.2–0.8 μm), and containing a little pores (~370 nm). The ceramics from nanopowders without yttrium has inhomogeneous surface with numerous cracks (Fig. 4a). Separate part of the latter consists of globules; their size is 0.2–0.5 μm.

It is well known [12] that a stable modification of zirconia is of monoclinic structure at $T < 1150$°C, tetragonal at $1150°C < T < 2300°C$ and cubic at $T > 2300$°C. But latter can be exist at usual temperature with stabilizing addition [15]. Temperature interval for stability of structural modification can be changed depending on amount of Y dopant, size of crystallites, etc. [13]. For example, heating of thermally unstable salts of Zr resulted in existence of cubic and tetragonal phases at lower temperatures [12]. The transition from amorphous to crystalline modification firstly goes from cubic modification through tetragonal one towards monoclinic phase. The former transition is a short-term process, whereas the latter one takes more time. In [12] energetic calculation is presented, which explains the possibility of low temperature cubic zirconia existence. The TEM and electron diffraction methods used for the study of plasmochemical powders showed a partial coexistence of cubic and tetragonal zirconia [11], depending on size of crystallites and the amount of impurities. It was found to be a main reason why different researchers detected different a critical size of crystallites and different intervals of temperature stability for cubic and tetragonal zirconia. When studying the influence of Y on phase composition of YSZ powders [13], it was found that samples with a reduced Y content consisted of mainly cubic and tetragonal phases. The latter transformed in the cubic phase when yttrium contents increased.

Thus, our results confirm the conclusions of earlier studies on the possible existence of low-temperature cubic phase in studied samples. Our results indicate sensitivity of AEM method for investigation of morphology and structure of nanosized powders. As mentioned above, the possibilities of X-ray and electron diffraction drastically differ (cf. critical size resolutions resulted in appearance of halo, i.e., smaller than 10^4 and 10^2 Å, respectively).

CONCLUSIONS

AEM methods allow us to find a difference in structure and morphology between powders obtained by azeotropic distillation (dest-YSZ) and by glycine methods (glc-YSZ). Glc-5YSZ powders have a good crystallinity, whereas dest-5YSZ samples have a smaller size and worse crystallinity as compared to glc-5YSZ. The investigation of powders obtained by azeotropic distillation method containing yttria (dest-5YSZ) and without it (dest-0YSZ) allows us to estimate the yttria influence on powders structure: dest-0YSZ particles are characterized by smaller sizes as compared to dest-5YSZ, and they are

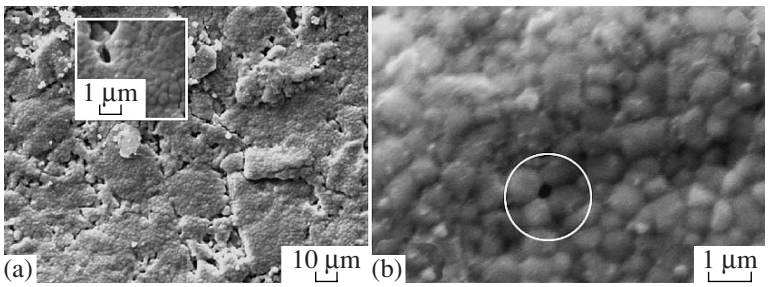

Fig. 4. Surface topography of ceramics produced from dest-0XYZ nanopowders in square-magnified part (a); from dest-5YSZ (b).

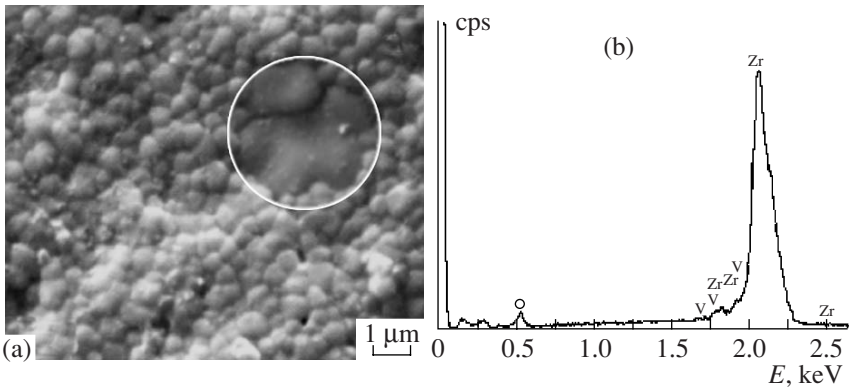

Fig. 5. Ceramic surface of glc-5YSZ powders after compacting and sintering at 1500°C in vacuum (a); the energy dispersive spectrum from the area inside circle (b).

amorphous in accordance with electron diffraction data. The ceramics obtained from these powders also have differences both in structure and in physicochemical properties.

ACKNOWLEDGMENTS

The authors thank colleagues from the Institute of Ore Deposits Geology, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences (A. Mohov, A. Sivtsov) and from the Institute of Solid State Physics, University of Latvia (Yu.F. Zhukovskii and R. Krutohvostov) for fruitful discussion and technical assistance.

D.B. gratefully acknowledges funding from the European Social Fund (ESF). This study was also partly supported by the Latvian Research programmes no. 05.0026.1.1 and no. 05.1554.

REFERENCES

1. I. Zalite, G. Boden, Ch. Schubert, et al., Latv. Kim. Z., No. 2, 153 (1992).
2. J. Grabis, Dz. Jankovica, M. Berzins, et al., J. Eur. Ceram. Soc., No. 24, 179 (2004).
3. D. Sciti, J. Vicens, N. Herlin, et al., J. Ceram. Proc. Res., No. 5, 40 (2004).
4. H. Zender and H. Leistner, Interceram., No. 39, 33 (1990).
5. A. Orlov, J. Grabis, N. Zaporina, and A. Krumina, in *Proc. of the Intern. Conf. on Advances in Nanostructured Mater, Process.-Microstruct.-Propert.* (Nanoved., Iesniegts J. Acta Metallurgica Slovaca, 2006).
6. N. Zaporina, V. N. Timofeev, D. Bocharov, et al., in *Proc. of the 2nd Latvian Conf. on Functional Materials and Nanotechnologies* (Riga, 2006), p. 81.
7. V. Ind. Hlavacek, Eng. Chem. Res, No. 35, 349 (1996).
8. L. Kuznetsova, J. Grabis, and G. Heidemane, in *Proc. of the X Intern. Baltic Conf. on Materials Engineering and Balttrib.* (2001), p. 27.
9. *Electron Microscopy of Thin Crystals*, Ed. by P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan (Plenum Press, New York, 1965; Mir, Moscow, 1968), p. 98.
10. K. Andrews, D. Dyson, and S. Keown, in *Interpretation of Electron Diffraction Patterns* (Adam Hilger, London, 1971; Mir, Moscow, 1971).
11. V. Ya. Shevchenko, O. D. Khasanov, G. S. Yur'ev, and Yu. F. Ivanov, Neorgan. Mater. **37** (8) (2001).
12. Yu. M. Polezhaev, Zh. Fiz. Khim. **41** (11), 2958 (1967).
13. Yu. V. Nikol'skii, S. K. Filatov, T. A. Zhuravina, and V. F. Frank-Kamenetskii, Neorgan. Mater. **8**, 1500 (1972).
14. M. A. Aboimov, M. A. Borik, G. A. Gogotsi, et al., Neorgan. Mater. **33**, 344 (1997).
15. *Chemical Encyclopedic Dictionary* (Sov. Entsiklopediya, Moscow, 1983), p. 686 [in Russian].