PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 3, 03CNN11(3pp) (2012)

Structure and Properties of Ceramics Based on ZrO_2, Synthesis by Solvotermal Method

V.V. Sirota*, V.V. Ivanisenko

Belgorod State University, Joint Research Centre
"Diagnostic of structure and properties of nanomaterials", 85, Pobedy Str., 308015 Belgorod, Russia

(Received 18 June 2012; published online 22 August 2012)

Nanosized powders ZrO_2-NiO with a particle size of 10 – 20 nm were obtained by the method of solvotermal synthesis. It is shown that the processes of formation of nanoparticles of c(t)-ZrO_2 and m-ZrO_2 at the given parameters of solvotermal synthesis take place at different speeds. Ceramic material based on nanosized powders of ZrO_2 was obtained by the cold isostatic pressing and further sintering. The microstructure, phase composition and strength properties of ceramics were determined by the scanning electron microscopy (SEM), transmission electron microscopy (TEM) with diffraction, X-ray phase analysis. Mechanical properties of ceramic were evaluated by the value of compressive strength. Compressive strength of the experimental samples was at 700 MPa.

Keywords: Solvotermal synthesis, Ceramic, Nanocrystalline, Zirconium dioxide.

PACS numbers: 62.23.Pq, 81.07.Bc, 68.37.Hk, 68.37.Lp

1. INTRODUCTION

The interest into nanocrystalline ceramic materials is increasing, due to their unique physical and chemical properties. It is established that microstructure and properties can vary considerably depending on the dispersion composition of initial powders, method and mode of sintering ceramic materials [1-3].

Ceramics based on zirconium dioxide today is widely used as structural and functional materials [4,5]. The use of nano-sized powders with desired morphology, phase composition, the properties of the bulk phase and the surface to produce a new generation of ceramic materials based on zirconium dioxide leads to an increase in the strength and functional properties of the final material [6].

For obtaining a nanocrystalline materials are currently being used the following methods: sol-gel, coprecipitation, hydrolysis of alkoxides, organometallic synthesis, pyrolysis, gas-phase methods and detonation synthesis. Most of these methods are fairly labor-intensive and multi-step, which complicates the widespread introduction a well-studied nanocrystalline materials in a variety of high-end technology cycles and processes. In this regard, the development of new methods for high-performance of the nano-sized ceramic powders is an important task.

One of the most perspective methods for manufacturing of the oxide nanocrystalline materials is the solvotermal synthesis under which mean the heterogeneous reactions in aqueous solutions at temperatures and pressures above 373 °C and 0.1 MPa, or the use of the organic solvents and supercritical CO_2.

The experimental conditions of obtaining oxides can vary considerably. It can be as soft solvotermal synthesis at relatively low temperatures and pressures [7] as synthesis in supercritical water [8]. Solvotermal method allows obtaining nanocrystalline powders of oxides with the given particle size and phase composition, specific surface area that is often impossible when using traditional methods.

The aim of this work was attestation of the structure and properties of ceramics based on ZrO_2, obtained by the method of solvotermal synthesis.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The initial powders of ZrO_2 were obtained by using of water solutions oxynitrat zirconia ($ZrO(NO_3)_2 \cdot 4H_2O$) and nitrates of yttrium ($Y(NO_3)_3 \cdot 6H_2O$). Salt oxynitrat of zirconium and yttrium was dissolved in a given ratio in warm water. In a water solution of the nitrate of zirconium and yttrium was added ammonium until pH = 8. Obtained ammonium-salt solution was loaded into the reactor R-401 (South Korea) and heated during 1.5 hours to a temperature of 330 °C and pressure of 250 bar with a further exposure to the maximum temperature and pressure during 45 min.

Obtained powder was dried at 70° C and annealed at 900 °C during 1 hour. Powder of ZrO_2 was forming by method of cold isostatic pressing (CIP) at a pressure of 300 MPa using isostatic press EPSI CIP 400 200 *1000Y.

Sintering of compacted materials was carried out at a temperature of 1350 °C in air during 2 hours.

Study of morphology of particles of the synthesized nano-sized powder was carried out by transmission electron microscope JEOL JEM-2100. Measurement of specific surface area of the synthesized nano-sized powder was carried out using the analyzer specific surface TriStar 3020. Investigation of structure and phase composition of the experimental samples were performed by X-ray powder diffractometer ARL X'TRA IV (Cu kα, Ni-filter) in the angular range $15 \le 2\theta \le 100$ deg., step 0.02°, the speed counter 2 deg./min. Analysis of the microstructure of the ceramic samples was obtained by electron microscope Quanta 600. Determination of tensile strength was carried out by testing machine Instron 300LX accordance with GOST 473.6-81.

* Sirota@bsu.edu.ru

3. EXPERIMENTAL RESULTS AND DISCUSSION

In the reactor by a chemical reaction was obtained suspension a brown color, high dispersion. The study of the microstructure of the obtained suspension by transmission electron microscopy (TEM) was found that the resulting nanosized powder consists of spherical particles with average size of 10 – 20 nm (see. Fig. 1).

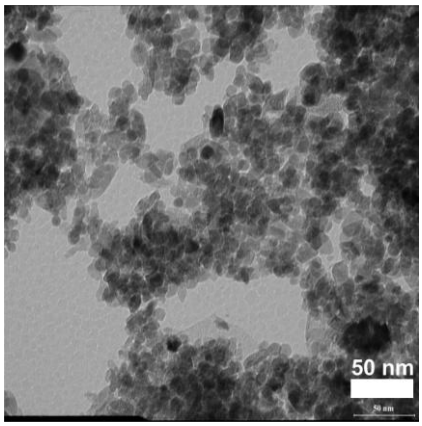

Fig. 1 – TEM image of nanosized powder of ZrO_2 obtained in supercritical conditions at a temperature of 330 °C and a pressure of 250 bar

The regions of coherent scattering with the size of 20 and 40 nm were identified for the powders after synthesis and annealing at 900 °C by of X-ray analysis, which confirmed by results of TEM (see. Fig. 1).

The greatest difficulty which arises when working with sub-and supercritical water is the problem of corrosion of parts installation. Even the deionized water in a supercritical state is quite an aggressive environment, which causes the destruction of many alloys used in the manufacture of reactors. In hydrothermal conditions often use water solutions of oxidants salts, acids and alkalis, which even in the normal conditions lead to corrosion of equipment [9].

Investigation of the elemental composition of powders after synthesis and annealing at 900 °C by X-ray microanalysis showed the presence of nickel oxide, which is a technological impurity, which appeared due to corrosion of the reactor walls.

Specific surface area of powder after annealing at 900 °C, obtained by the method of BET was 12 m^2/g. Sintering was carried out on the basis of results of dilatomtric analysis the obtained compact. Found that the sintering process begins at 900 °C and the maximum actively materials are sintered at 1350 °C. The analysis of the phase composition of powders compacted and sintered materials are shown in Table 1.

A result of research of the surface of cleaved of samples of the ceramics which obtained from nano-sized powder of ZrO_2-NiO using scanning electron microscopy (SEM) was found that the samples have the formed-grained structure, which feature is two fractional composition (see. Fig. 2). The crystallites with grain sizes from 2 to 5 microns quite uniformly distributed in the volume of the submicron and nanoscale fraction with grain size of 375 nm.

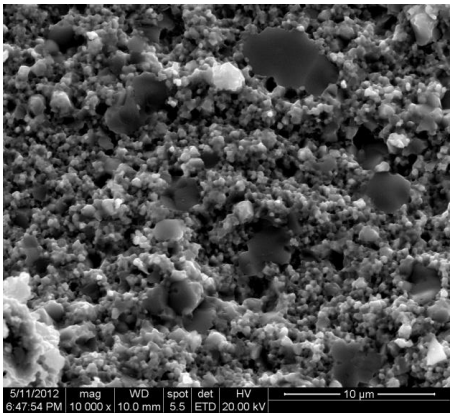

Fig. 2 – SEM image of the surface of the cleaved samples of ceramics based on ZrO_2 after sintering at 1350° C during 2 h

Since the studies have not identified significant differences in the chemical composition both of fractions the cause of the formation of such structure is the agglomeration of the initial powder.

More dense packing of the initial nano-sized powder in the agglomerates has allowed to intensify the process of sintering of the powder, by increasing the contact area of the powders and the gradient of diffusion coefficient, which greatly accelerates the mass transfer, thus takes place packing material in the agglomerate to a dense crystallite.

Table 1 – Analysis of the phase composition of powders.

Sample	ZrO_2		NiO, %	$Zr_xY_{1-x}O_y$, %
	Phase composition	Amount, %		
Nanosized powder produced by synthesis	ZrO_2 cubic/a = 5.1184 Å	8.3	< 1	-
	ZrO_2 monoclinic/a = 5.1322 Å, b = 5.1896 Å, c = 5.3081 Å, β = 99.05	91.7		
Nanosized powders after annealing at 900 °C	ZrO_2 cubic/a = 5.1313 Å	44.7	8.0	-
	ZrO_2 monoclinic/a = 5.1374 Å, b = 5.1898 Å, c = 5.3135 Å, β = 98.00	47.3		
Material based on ZrO_2 after compaction and sintered at 1350 °C	ZrO_2 tetragonal / a = 3.60670 Å, c = 5.12900 Å	7.9	8.1 NiO rhombohedral a = 2.9552 Å, c = 7.2275 Å	84 $Zr_{0.86}Y_{0.14}O_{1.93}$ a=3.63090 Å, c = 5.15320 Å

Mechanical properties of ceramic samples basis on ZrO_2 were evaluated by the value of compressive strength. Studies of mechanical properties of ceramics sintered at 1350 ºC were carried out on samples in the form parallelepipeds (15 × 10 × 10 mm). Tests were carried out with constant velocity of loading, fixed axial compressive load and deformation of the samples Compressive strength of the experimental samples was at 700 MPa.

4. CONCLUSION

The nanosized powders of ZrO_2-NiO with a particle size of 10 – 20 nm were obtained by the method of solvotermal synthesis. It is shown that the processes of formation of nanoparticles of c (t)-ZrO_2 and m-ZrO_2 at the given parameters of solvotermal synthesis take place at different speeds. Ceramics with a limit of compressive strength – 700 MPa was obtained from nanosized ZrO_2-NiO powders by isostatic pressing. The absence of monoclinic modification of zirconium dioxide in the obtained ceramics after compaction and sintering was found.

AKNOWLEDGEMENTS

Work is carried out by Joint Research Center of Belgorod State University in the framework of the federal target program under Grant application № P-713.

REFERENCES

1. M.I. Alimov, S.V. Semichev, *Physics and Chemistry of Materials Treatment* No**5**, 56 (1999).
2. K.K. Strelow, I.D. Kashcheev, *The theoretical foundations of the technology of refractory materials* (Moscow, Metallurgy: 1996).
3. V.V. Skorokhod, S.M. Solonin, *Physical and metallurgical fundamentals of sintering powders* (Moscow, Metallurgy: 1984).
4. V.B. Glushkov, V.P. Popov, P.A. Tikhonov, L.I. Podzorova, A.A. Il'ichev, *Glass Phys. Chem*. **32** No. 5, 803 (2006).
5. D.S. Rutman, Y.S. Toropov, S.Y. Pliner, A.D. Neuimin, J.M. Polezhaev, *Highly refractory materials of zirconia* (Moscow, Metallurgy: 1985).
6. O.V. Almyasheva, E.N. Korytkova, I.A. Drozdov, V.V. Gusarov, *J. Gen. Chem*. **69** No8, 1265 (1999).
7. M.S. Whittingham, *Curr Opin Solid State Mater Sci*. **1**, 227 (1996).
8. T. Adschiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc*. **75**, 1019 (1992).
9. A.A. Galkin, V.V. Lunin, *Prog. Chem*. **74** No1, 24 (2005).