Abstract

The purpose of this study was to develop a synthesis conditions and produce samples of nanocrystalline zirconia powder in a high-temperature phase state. To increase the stability of this state at room temperature, Y$_2$O$_3$ was used as a dop in the two-stages chemical method including coprecipitation mixture of the corresponding hydroxides and air drying. To reduce agglomeration of nanoparticles during heat treatment of precursors the microwave oven instead of a muffle was used. Different characterisation methods have been used to determine that the obtained powders are nano-scale corresponds to a high-temperature tetragonal phase of ZrO$_2$. It is shown that such nanocrystalline powders may be used to produce highly-dense nanoceramics.

Keywords: nanopowders; tetragonal zirconia, two-step chemical method, nanoceramics.

1. Introduction

Zirconia (ZrO$_2$) is one of the most developed materials by Ferrari et al. (2015) for use as a structural and functional ceramics, as a high temperature solid electrodes, optical and other materials. It has a high melting temperature (2800 K) and the unique properties by Bouvier et al. (2000) in high-temperature phase state (above 1343 K tetragonal and above 2640 K cubic): chemical, corrosion and heat resistance, biocompatibility and, most importantly, high mechanical strength, comparable to the strength special steel. Nonequilibrium at room temperature, but the most interesting tetragonal and cubic phase generally stabilized by small additions (<15 mol%) of other oxides, such as CaO, MgO and Y$_2$O$_3$. But the properties of stabilized ZrO$_2$ by additives may differ from those of pure ZrO$_2$. There is an alternative way to get high-temperature phase of ZrO$_2$ using nanostructured state by Petrunin (2014). In this paper, both the methods are used to obtain nanocrystalline powders of ZrO$_2$ doped Y$_2$O$_3$.

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which, in turn, were compacted to produce nanostructured ceramic.

2. Materials and methods

Used in this work method is doping of ZrO₂ by cations capable to form a solid solution with the formation of the required crystal structure (tetragonal or cubic) by Popov et al (2010). The conditions of formation of solid solution of cubic ZrO₂ with various oxides as follows: a cation ionic radius of additives should be close to the ionic radius of zirconium; additive should preferably have a cubic crystal lattice.

The basis of used in this study two-stage chemical co-precipitation method involves a precipitation of a mixture hydroxide and a stabilizer on the principle of simultaneous deposition of a mixture of components by main precipitant. Thus there should be no complex compound soluble components in the deposition process. Precipitant is selected depending on the composition of a solid solution. Zirconium and yttrium hydroxides precipitated together from the nitrates and/or chlorides solution with aqueous ammonia at pH 8-9 by the reaction:

\[ \text{ZrOCl}_2 + Y(\text{NO}_3)_3 + \text{5NH}_4\text{OH} \rightarrow \text{ZrO(OH)}_2 + Y(\text{or Dy})(\text{OH})_3 + 2\text{NH}_4\text{Cl} + 3\text{NH}_4\text{NO}_3 \]

Used as the starting material high purity zirconium oxychloride ZrOCl₂ • 9H₂O (99.3 wt.%) and an aqueous yttrium nitrate Y(NO₃)₂ • 6H₂O (98.5 wt.%). Simultaneous precipitation of components after heat treatment, providing the completeness of solid solutions formation was achieved by introducing of zirconium and stabilizing additives solution mixture by small doses in a precipitant solution with vigorous stirring of the entire mass in the reactor. The process for obtaining zirconium dioxide by chemical coprecipitation from salt solutions comprising the steps of: preparing stock solutions of zirconium, yttrium salts and the alkaline agent; the synthesis of the mixed hydroxide / oxyhydroxide of zirconium and yttrium; flushing of sediment mixed hydroxide / oxyhydroxide of zirconium and yttrium; heat treatment mixed hydroxide / oxyhydroxide of zirconium and yttrium sludge.

The synthesized powders and compacts in the form of tablets after compression were analyzed by complex of the following instruments: 160 I-ionometer (Russia) for determining the pH (Eh) solutions and suspensions; photon correlation spectrometer PhotoCor Compex 1 (Russia) to determine the size of particles in the sols and suspensions; simultaneous thermal analyzer STA 409 Luxx PC (Netzsch, Germany) to determine the effects of heat and mass changes of the samples during heating; gas sorption analyzer Nova 1000 e (Quantachrome, USA) to determine the specific surface area of powders, of particle size and porosity of the samples; X-ray diffractometer DRON-1UM (Russia) to determine the phase composition and parameters of the crystalline lattice and crystallite size as cogerent diffraction domain (CDD)

3. Results and Discussion

Synthesis of a mixed hydroxide / oxyhydroxide zirconium, and yttrium (precursor) solution by coprecipitation of salts ZrOCl₂ and Y(NO₃)₃ aqueous NH₄OH was performed in a laboratory. Heat treatment of mixed / zirconium and yttrium hydroxide / oxyhydroxide precipitate carried out both in a muffle furnace Nabertherm HT 08/18, and microwave Hamilab 61500. In the case of microwave heating, the drying process was combined with the crystallization of the sample.

As a result of the potentiometric titration of the solution of zirconium oxychloride aqueous ammonia (NH₄OH) found that the formation of zirconium hydroxide precipitate begins at first portions already adding an alkali agent. Deposition ends at a molar ratio OH / Zr of about 2 (pH ~ 9). Measurements of samples PhotoCor Complex during titration have showed that in the initial moment of neutralization scattering centers are formed with a radius of particles of 250 - 300 nm. In the course of the neutralization process, this value remains substantially constant up to a pH of 2.5 - 3.0. Forming centers are kinetically stable for a long period of time (several days). A further increase in the pH ≥ 3 - 4 leads to a sharp increase in the size of 1 - 1.5 m (Figure 3) and the viscosity of the system to form a gel-like precipitate. At the end of the neutralization at a pH of 9 - 9.5 radius again decreases to the original value.

XRD analysis of the precursor powder have showed that during the co-precipitation of solutions of salts ZrOCl₂ and Y(NO₃)₃ solution with aqueous NH₄OH at pH 9 - 10 are formed crystallographically amorphous particles of mixed zirconium and yttrium hydroxide. To study the thermal behavior of the synthesized precursors the method of simultaneous thermal analysis (STA) comprising the simultaneous use of differential scanning calorimetry (DSC) and thermogravimetry (TG) was used. It was found (Figure 1) that originally when heated in the DSC curve
precursors exhibit an endothermic process with a minimum temperature region 130 -140°C. Simultaneously, the TG curve is recorded a significant reduction in weight of the sample by removing water vapor, i.e. samples dehydration occurs.

A further increase in temperature up to ~ 450 °C leads to the appearance on the DSC curve sharp extremum corresponding to the exothermic process in ever decreasing sample weight. It should be noted that all tested samples crystallization firmly hold moisture in the crystalline lattice, as evidenced by a decrease in sample mass observed above the temperature up to 800 °C, temperature limit 1400 °C.

Using X-ray revealed that the introduction of Y^{3+} ions in an amount of 1.5 - 7 wt. % can effectively stabilize a high temperature tetragonal ZrO_{2} phase at temperatures of 1000 - 1200 °C (Figures 1, 2), while remaining nanoscale region (Table 1). Thermoannealing of the precursor by microwave heating also leads to the formation of nanocrystalline powders of zirconia stabilized with yttrium ions. The use of microwave heating can significantly reduce (by several times as compared to using a muffle furnace) while nanocrystalline powders ZrO_{2}, but leads to an increase in the content of monoclinic phase.

As a method of producing ceramics in the form of tablets an uniaxial pressing of mechanicactivated nanocrystalline zirconia powder was used with subsequent annealing of compacts. In this isothermal annealing was performed using as a muffle furnace, as well as a microwave oven. For mechanical activation of the starting powders planetary mill brand «Pulverisette 7 premium line» was used. Terms mechanoactivation: material glasses and grinding media - zirconia stabilized magnesium oxide; powder ratio: grinding media = 1: 3 (wt.); operation time 30 min; rotation speed of glasses-revolutions 900 min. It was found at both types of powders mechanical activation the size of crystallites (amorphization) reduces, microstressing values growth (accumulation of structural defects) and partial phase transition t-ZrO_{2} \rightarrow m-ZrO_{2}.

| Mol. % Y_{2}O_{3} | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|-----------------|-----|-----|-----|-----|-----|-----|
| 1000°C T, % (CDD), nm | 19.9 (30) | 76.0 (45) | 97.5 (49) | 98.9 (47) | 99.1 (42) | 99.5 (50) |
| M, % (CDD), nm | 80.0 (21) | 24.0 (34) | 2.5 (-) | 1.1 (-) | 0.9 (-) | 0.5 (-) |
| 1200°C T, % (CDD), nm | 2.9 (-) | 4.5 (19) | 74.4 (60) | 99.4 (75) | 99.3 (73) | 99.3 (73) |
| M, % (CDD), nm | 97.1 (34) | 95.5 (33) | 25.6 (42) | 0.6 (-) | 0.7 (-) | 0.7 (-) |
Pressing mechanically activated powders were carried out on hydraulic presses brand «CrushIR» at the pressure of 180 MPa and a pressing 3 minutes. Compressed unfired compacts were calcined in a muffle furnace «HT 08/18» with induction heating (heating rate of 10°C/minute at 1500 °C annealing temperature, the duration 3 hours), and the microwave oven «HAMIab-C1500» (Synotherm, China) with a microwave annealing (heating rate 10 °C/min at 1437°C annealing temperature, duration 3 hours) in air. It has been found that the isothermal annealing of compacts zirconia stabilized yttrium dops in the muffle and a microwave oven produces a dense ceramic tablets. Annealed zirconia tablets have a density of from 5.63 to 5.79 g/cm³ (relative density of from 92.6 to 95%). XRD analysis showed that in both isothermal annealing muffle and a microwave oven results in well crystallized samples. It can be seen from Table 2 almost all ceramic samples have nanoscale range of CDD.

Table 2 - Influence of the annealing conditions on the phase composition of the tablets, the parameters of the atomic-crystalline structure and a density of tablets ZrO₂, stabilized with yttrium additives.

| Type/Annealing conditions tablets | Phase, % | CDD, nm | Microdistortions, % | Lattice parameters, Å | ρ, g/cm³ before/after annealing |
|----------------------------------|----------|---------|---------------------|-----------------------|-----------------------------|
|                                 |          |         |                     |                       |                             |
| ZrO₂(7.1 weight. % Y) muffle 1500°C/3 h | t-ZrO₂ 91 | 34      | 0,1764              | a=3,6207 c=5,1876      | 3,21/5,63                   |
|                                 | m-ZrO₂ 9 | 12      | 0,3977              | a=5,2270 b=5,1138 c=5,4338 β=99,3035° |                             |
| ZrO₂(7.1 weight. % Y) MW 1437°C/3 h | t-ZrO₂ 94 | 55      | 0,1186              | a=3,6207 c=5,1876      | 3,20/5,79                   |
|                                 | m-ZrO₂ 6 | 7       | 0,7399              | a=5,2270 b=5,1138 c=5,4338 β=99,3035° |                             |

4. Conclusion

As a result of this work investigated a modes of two-stage chemical synthesis using microwave annealing of precursor to receive a single-phase nanocrystalline powders of zirconia stabilized with yttrium oxide additives was investigated. An experimental samples of zirconia nanopowders in a high state of phase (tetragonal lattice), with a crystallite size (CDD) is less than 75 nm, which can be used for structural and functional ceramics for various purposes were prepared. Pressing optimal modes of nanocrystalline powders of yttria-stabilized zirconia, to obtain a high-density (92,5-95% of theoretical density) ceramics, keep the size of the crystallites (CDD) in the nanoscale by Springer Handbook were determined.

5. Thanks

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