Ceramics based on zirconium dioxide stabilized with indium oxide and praseodymium oxide

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Abstract. The solid solutions based on Zirconia doped with indium oxide and praseodymium oxide with different concentration was obtained by the method of inverse heterophase co-deposition.The physico-chemical properties of obtained samples were examined. The highest properties have been achieved in samples of the composition Zr1-xRxO2-δ (R=23 mol .% In). This composition has a density of 5.38 g/cm3; open porosity is 0 %, the bending strength is 203 MPa.

1. Introduction

Modern technology requires the development of new materials which possess ideal structures with high-performance characteristics. Currently, research works are aimed at the improvement of materials structures in order to enhance properties such as physical-mechanical and thermo-mechanics [1]. On the other hand, there is a need to decrease the sintering temperature. Additionally, the improved properties can promote the expansion of the application area.

One of the leading materials for the development of new structures is ceramics. It is the third most prevalent industrial material after metals and plastics.

The combination of unique properties determines an increase in the area of application of ceramic-based materials in the industry. It can be explained by the limit of some characteristics of present metals and alloys which does not allow their use for engineering of new constructions and new products. These characteristics include heat durability, heat resistance, corrosion resistance, etc.

The main ceramic disadvantages are fragility, sensitivity to thermal shocks (especially overcooling), and the complexity of mechanical restoration. These features set a task for the further development of technology and a properties improvement.

Recent achievements have shown a possibility of formation of new ceramic materials based on oxides and their derivatives which have high mechanical strength, resistance to abrasion, to simultaneous exposure to high temperatures and to stresses.

The current ceramic-based materials progress can be explained by the success in powder technology, the new methods development for products formation of highly disperse powders, the use of more advanced principles of the additives selection, the sintering theory development. All these factors promote the existing technologies modernisation and the properties improvement, as a result, it expands the application area.

The present study purpose was the preparation of solid solutions based on zirconia doped with indium oxide and praseodymium oxide and subsequent investigation of their physicochemical properties.

In order to achieve this goal, the main areas of research include:

- A zirconium dioxide cubic solid solution with additions of indium oxides and praseodymium synthesis;
- Study of the physicochemical properties of solid solutions of zirconia with different concentrations of the doping component;
- Study of the influence of the firing temperature and the concentration of the doping component on the ceramic properties of the samples.

2. Materials and Method

The monoclinic phase (m) ZrO_2 is thermodynamically stable below 1170 °C. It is tetragonal (t) in the range 1170 – 2370 °C and cubic (c) above 2370 °C. The transition t-ZrO_2 ↔ c-ZrO_2 has a diffusion nature and plays a very important role in the production of so-called partially stabilised zirconia. The m-ZrO_2 ↔ t-ZrO_2 transformation proceeds according to the martensitic mechanism and accompanies by volumetric changes of 5-9 %. Such a significant expansion of the material upon cooling, accompanied by cracking, does not allow the production of compact products of unalloyed ZrO_2. For this reason, only solid solutions of various ZrO_2-based oxides are of practical value, or composites with a rigid matrix capable of stabilizing the high-temperature phases of ZrO_2 at low temperature.

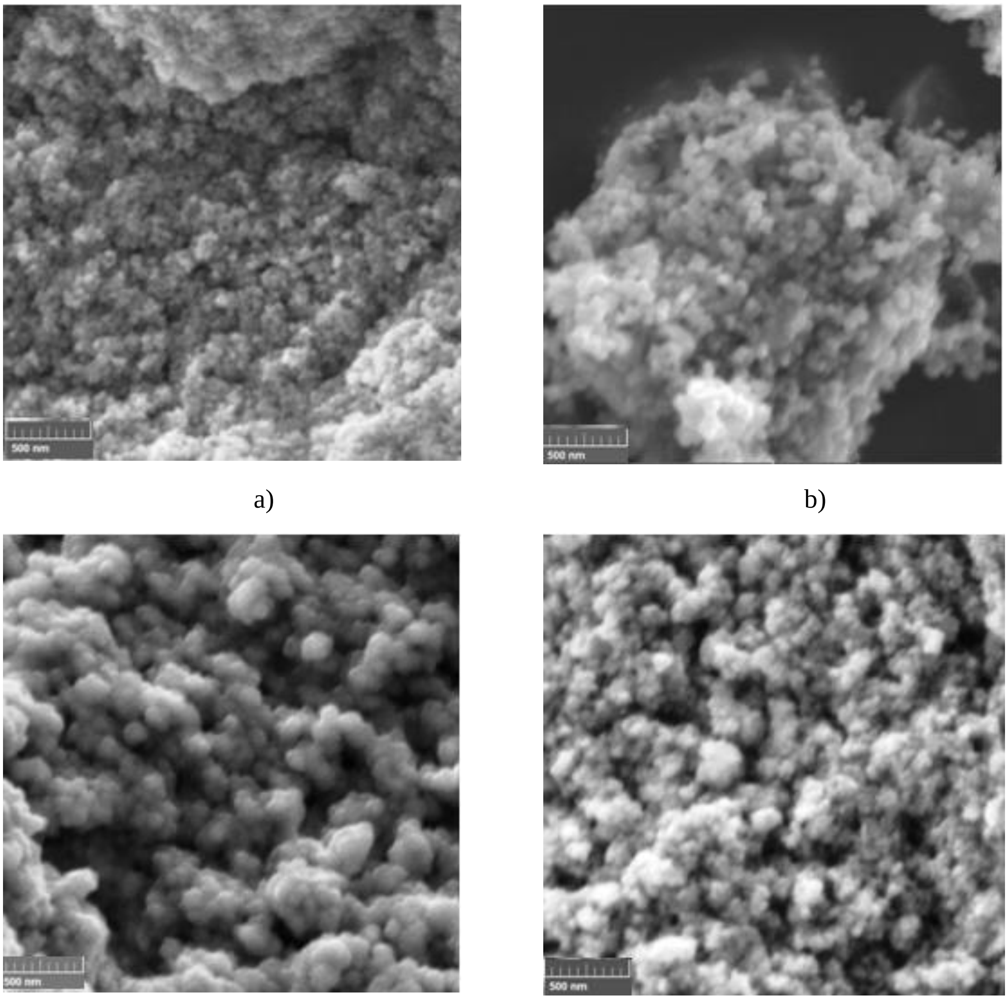
The majority of researchers explain the stabilization of solid solutions upon doping of zirconium dioxide with metal oxides in the tetragonal and cubic phases due to the presence of oxygen vacancies that ensure electroneutrality for the heterovalent character of the Zr^{4+} substitution in the trivalent or divalent cation in the alloying oxide, rather than the actual M^{3+}, M^{2+} cations [2]. With the formation of only oxygen vacancies in the crystal lattice of ZrO_2, the formation of t-ZrO_2, rather than m-ZrO_2, becomes energetically favorable. However, this mechanism alone is not enough to describe the stabilization of the tetragonal and cubic phases of zirconium dioxide when the oxides of elements are doped with oxidation states of 2+ and 3+. This is indicated by the discrepancy between the phase diagrams of the ZrO_2-stabilizer, constructed in the coordinates of the concentration of oxygen vacancies [3]. It is obvious that for all the attractiveness of the mechanism of stabilization by oxygen vacancies, some influence on phase stability is exerted by the alloying cations themselves, differing in valence and ionic radius.

The systematic research of the role of various ions in the stability of the tetragonal and cubic phases was carried out using X-ray absorption spectroscopy, in which the influence of trivalent and quadrivalent cations was investigated, as well as the effect of stabilizers with the ionic radius larger (Y^{3+}, Gd^{3+}, Ce^{4+}) and smaller (Fe^{3+}, Ga^{3+}, Ge^{4+}) of the ionic radius Zr^{4+}. In the case of doping with trivalent metal oxides, the oxygen vacancies arise in order to compensate the charge. In the case of the ions with the large radii, the oxygen vacancies appear to be associated with Zr^{4+}, whereas, in the case of the ions with the small radii the vacancies are bound to two ions of the addition. Both configurations are advantageous for the sevenfold coordination of the Zr^{4+} cations (CN = 7) by oxygen anions, which leads to the stabilization of the tetragonal and cubic phases of zirconia dioxide.

Apart from the achievement of a stable fluorite structure, these additives are also resistant to evaporation and it leads to a significant expansion of the homogeneity region of the solid solution of ZrO_2.

A zirconium oxychloride stabilized with different compounds was used as initial components for the preparation of ultradispersed powders of solid solutions based on zirconia dioxide. The first option is praseodymium oxide, whereas, the second option is indium oxide. The choice of stabilizer oxides was based on the proximity of the ionic radius (according to Belov and Bockiy), which corresponds with substituting elements (Zr^{4+} = 0.82 Å, In^{3+} = 0.92 Å, Y^{3+} = 0.97 Å, Pr^{3+} = 1.00 Å) [4].

The salt of zirconium oxychloride with oxides of indium and praseodymium was dissolved in distilled water at 105 °C. The resulting solution was evaporated to 90% concentration of the limiting solubility at the given temperature. The solution concentration was controlled by density. The salt solution at 100±5 ºC was sprayed with compressed nitrogen under pressure (1÷2) 10^4 Pa through a glass capillary with a diameter of 1.0÷1.5 mm into a saturated cooled ammonia solution. The resulting suspension was transferred to the Buchner funnel and washed with distilled water to pH 6.0 in the filtrate. The drying of the precipitate was carried out in natural conditions (Figure 1).



a) b)

c) d)

Figure 1. SEM micrographs ZrO_2 powder with: a) 10 mol.% Pr_2O_3;b) 15 mol.% Pr_2O_3; c) 23 mol.% In_2O_3; d) 25 mol.% In_2O_3

The 5 % polyvinyl alcohol aqueous solution (PVA, TU 10779-99) was used as the temporary technological binder for semi-dry pressing, it was introduced in an amount of 15 % by weight of the powder. The pressed powder was twice wiped by a No. 01 sieve in order to homogenize the polyvinyl alcohol aqueous solution. The samples with the size of 40×6×6 mm were formed by a method of double-sided uniaxial semi-dry pressing at the pressure of 100 MPa. The samples were fired in the air at 1550 °C, with the holding time at the final temperature of 3 hours.

3. Results and discussion

In determining the main parameters of the ceramic samples which were sintered at different temperatures with the different content of the additive, it has been established that sintering of the ceramic improves with a rise in the sintering temperature, as well as, with an increase in the content of the doping additive. Such observations as the density increase, the significant linear shrinkage and the decrease in porosity were made. The samples obtained were examined for physical and mechanical properties (Table 1). According to the data, samples of the composition $Zr_{1-x}R_xO_{2-\delta}$ (R = 23 mol% In) have demonstrated the most enhanced characteristics. These samples have the density of 5.38 g/cm^3, the open porosity of 0 % and the flexural strength of 203 MPa.

Table 1. Properties of the ceramics based on ZrO_2 doped with praseodymium oxide and indium oxide

Doping additive	The amount of additive added mol %	The average density of the compact, g/cm^3	The average density of the burned product, g/cm^3	The linear shrinkage, %	The open porosity, %	The flexural strength, MPa
Pr_2O_3	10	2.82	5.21	20	0	155±5
	15	3.08	5.33	21	0	176±5
	20	2.92	5.15	21	0	192±5
In_2O_3	23	3.01	5.38	22	0	203±5
	25	3.23	5.67	25	0	230±5

4. Conclusion

Traditionally, the ceramics based on zirconium oxide has been used in the metallurgical industry for the manufacture of crucibles for metals smelting. Nowadays, this type of ceramics is one of the most promising ceramic materials for structural and instrumental use and it has been utilized in the production of gas turbine’s parts, diesel engines, friction units, sealing rings of pumps, elements of stop valves, nozzles of spray chambers, wire drawing dies and cutting tools. Moreover, the ceramics based on zirconium oxide is used in the medical application for the manufacture of bone tissue implants.

During this research, the solid zirconium dioxide-based solutions doped with indium oxide and praseodymium were obtained by the method of inverse heterophase co-deposition. The most enhanced properties were achieved in the samples of the composition $Zr_{1-x}R_xO_{2-\delta}$ (R = 23 mol% In). The resulting ceramic samples have the density of 5.38 g/cm^3, the open porosity of 0 % and the flexural strength which equals 203 MPa.

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