



Characteristics of Nanocrystalline Zirconia Powder in the ZrO_2 - Y_2O_3 - CeO_2 - Al_2O_3 system with 0.1wt.% CoO

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Matrix (mol%) $95ZrO_2$ - $3Y_2O_3$ - $2CeO_2$ was produced by hydrothermal synthesis from a mixture of previously precipitated hydroxides. α - Al_2O_3 and $Co(NO_3)_3$ were added by mechanical mixing. The properties of nanocrystalline powders with a complex chemical composition (wt.%) $[90(ZrO_2-CeO_2-Y_2O_3)-10Al_2O_3]$ - $(0,1Al_2O_3-0,1CoO)$ after heat treatment in the temperature range from 400 to 1300 °C were investigated by XRD phase analysis and BET measurements. During heat treatment powders retained in nanocrystallite state (primary particle size of the zirconia solid solution varies from 14 to 83 nm), and its specific surface area decreases from 99,7 m²/g to 1.51 m²/g.

Keywords: Hydrothermal Synthesis, Nanocrystalline Powders, Zirconia.

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1. INTRODUCTION

Zirconia is one of the most promising bioinert materials owing to the best mechanical properties among oxide ceramics. Ceramics based on ternary systems may possess higher strength (ZrO_2 - Y_2O_3 - Al_2O_3) or higher strength and fracture toughness (ZrO_2 - Y_2O_3 - CeO_2). Cobalt oxide can enhance the contrast of the implants on the background of the surgical field. At the formation stage of solid solutions of cobalt oxide with different metals oxides can be produced products, colored in blue, green, pink and other colors. Cobalt-aluminate spinel or Thenard's blue ($CoAl_2O_4$) widely used as a ceramic blue pigment Coloration is created by dispersion of colouring pigment particles in the mass for producing the composite.

Design of new ceramic materials from the nanocrystalline powders with complex chemical composition associated with the use of non-equilibrium processes at the stage of powder preparation in open thermodynamic systems. Characteristic features of these systems are an incomplete course of heterophase transformations and the formation of intermediate products.

Few information can be found in science literature about the influence of cobalt oxide addition on zirconia based ceramics. Therefore investigation in the ZrO_2 - Y_2O_3 - CeO_2 - Al_2O_3 - CoO system are actual. The investigation of the processes occurring during heat treatment of nanocrystalline powders of complex composition is necessary to optimize the designing of ceramics.

The purpose of this work was to investigate the nanocrystalline powder properties in the ZrO_2 - Y_2O_3 - CeO_2 - Al_2O_3 system with 0.1 wt.% CoO.

2. EXPERIMENTAL

Two different zirconia-based powders with following compositions (wt%) 90 (ZrO_2 - Y_2O_3 - CeO_2)- $10Al_2O_3$ (sample with notation A) and $[90(ZrO_2-CeO_2-Y_2O_3)-10Al_2O_3]$ - $(0,1Al_2O_3-0,1CoO)$ (sample with notation 0.1C) were synthesised from reagent-grade

chemicals: zirconium oxychloride ($ZrOCl_2 \times 8H_2O$), yttrium nitrate ($Y(NO_3)_3 \times 6H_2O$), cerium nitrate ($Ce(NO_3)_3 \times 6H_2O$), α - Al_2O_3 and cobalt nitrate ($Co(NO_3)_3 \times 2H_2O$). Zr, Ce and Y hydroxides were obtained through homogeneous coprecipitation from an appropriate mixture of aqueous solutions of the starting salts, using aqueous NH_4OH as the precipitant. The obtained hydroxide mixture was reached to the gel-like substances for the hydrothermal treatment. The treatment was performed in a laboratory autoclave at 210 °C for 3 h. α - Al_2O_3 and Cobalt Nitrate were added to the nanocrystalline powder in the $95ZrO_2$ - $3Y_2O_3$ - $2CeO_2$ system by mixing at the planetary mill. Characterisation of the heat treated nanocrystalline powder were determined by X-ray diffraction (XRD) and low-temperature nitrogen adsorption (BET). XRD characterisation was performed with a DRON-1.5 powder diffractometer (CuK α radiation, Ni filter). The scan rate varied from 1 to 4 °/min. The average crystallite size was determined using the Scherrer formula [1]. The specific surface area of the nanocrystalline powders after different processing steps was determined by low-temperature adsorption of nitrogen in the flow of nitrogen/helium mixture on MPP 2 unit (Sumperk, Slovakia). The characteristics of the nanocrystalline powders were investigated after heat treatment in the temperature range from 500 to 1200 °C.

3. RESULTS

Hydrothermal treatment of the hydroxides, which synthesized through homogeneous coprecipitation from an appropriate mixture of aqueous solutions allowed to obtain metastable low-temperature cubic solid solution based on ZrO_2 (F- ZrO_2). The formation of the metastable F- ZrO_2 during hydrothermal treatment can be accounted for a number of factors. The polymeric zirconium hydroxycomplex, forming during hydrothermal treatment, $[Zr(OH)_2 \cdot 4H_2O]_{s^{+4}}$, is close to the cubic ZrO_2 structure [2]. Consequently, the formation of the metastable F- ZrO_2 is consistent with the Dankov principle [3].

According to XRD result, low-temperature metastable cubic solid solution of zirconia was formed in the nanocrystalline powders of both compositions after hydrothermal treatment. XRD patterns of powder with and without cobalt oxide have the same pictures at the equal temperatures. This can be explained by very small content of cobalt oxide which could not be identified. A peaks of Al_2O_3 with a small intensity is observed at all patterns of powders. The average size of particles was 13-14 nm. (Fig.1)

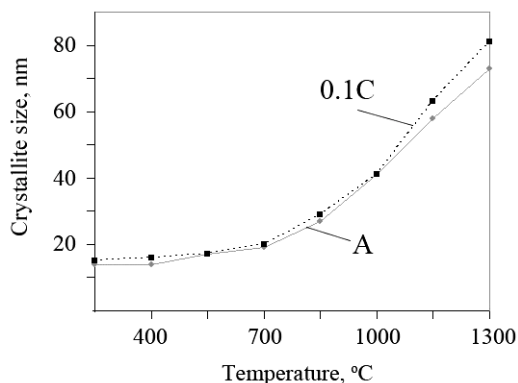


Fig. 1 – Effect of heat treatment on the crystallite size of nanocrystalline powder in the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-CeO}_2\text{-Al}_2\text{O}_3$ system with 0.1 wt.% CoO

Phase transformation from F- ZrO_2 to tetragonal ZrO_2 (T- ZrO_2) begin after heat treatment at temperature 400 °C and finished about 1300 °C for both powders. After heat treatment at 1300 °C the formation of M- ZrO_2 was not identified.

REFERENCES

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Size of the primary particles have close values and a similar character of dependence with increase in temperature. The primary particle size begins to dramatically increase after 850 °C that indicated about increment of crystallinity.

Specific surface area varied from 99,7 to 1,5 m^2/g in powder and from 72,3 to 1,5 m^2/g in powder 0.1C (Fig. 2).

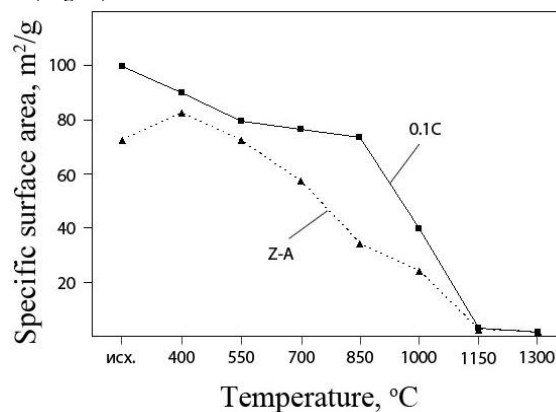


Fig. 3 - Effect of heat treatment on the specific surface area of the nanocrystalline powder in the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-CeO}_2\text{-Al}_2\text{O}_3$ system with 0.1 wt.% CoO

4. CONCLUSION

Properties of nanocrystalline powder in the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-CeO}_2\text{-Al}_2\text{O}_3$ system practically did not varied with addition of 0.1wt.% CoO. It was found slight increasing of the average primary particle size as well as the specific surface area in the powder with cobalt oxide.