NANOSTRUCTURED MATERIALS

HYDROTHERMAL SYNTHESIS OF NANOCRYSTALLINE POWDERS IN THE ZrO_2 – Y_2O_3 – CeO_2 SYSTEM


UDC 621.762:546-31

The paper examines the properties of the nanocrystalline powder 95 mole% ZrO_2 – 2 mole% CeO_2 – 3 mole% Y_2O_3, synthesized using a combination of two methods: coprecipitation and hydrothermal decomposition. It is established that coprecipitation produces an x-ray amorphous gel consisting of hard agglomerates from 5 to 10 \( \mu \text{m} \) and having a specific surface area of 120 m\(^2\)/g and a bottle density of 2.94 g/cm\(^3\). Hydrothermal synthesis results in a low-temperature metastable cubic solid solution based on ZrO_2 (F-ZrO_2). Its specific surface area is 101.6 m\(^2\)/g and bottle density is 4.65 g/cm\(^3\). Soft agglomerates (0.5-10 \( \mu \text{m} \)) consist of primary particles with sizes to 10 nm. The change in hydrothermal suspension processing steps results in soft agglomerates with branched internal porosity. This method allows synthesizing powders of needed compositions in the ZrO_2 – CeO_2 – Y_2O_3 system.

Keywords: zirconia, nanocrystalline powder, hydrothermal synthesis, metastable solid solution.

The bioinertia, high strength, and high fracture toughness of ceramics based on stabilized zirconia stimulated studies intended to create various bioimplants. Researchers focus on the ZrO_2 – Y_2O_3 system as the basis for obtaining fine-grain and high-strength materials, i.e. Y-TZP (tetragonal zirconia polycrystal). These materials are currently used to produce prostheses of femoral heads [1, 2].

The adequate lifetime of Y-TZP-based ceramic bioimplants results from their resistance to slow crack growth and in vivo ageing effect. The ageing is caused by the phase transition of zirconia from tetragonal to monoclinic modification (T-ZrO_2 \( \rightarrow \) M-ZrO_2) found, as a rule, on the ceramic surface. The transition may occur during sterilization of bioimplants. This phenomenon is accompanied by the expansion of the material and microcracking of its surface; which, in turn, impair mechanical properties and, ultimately, cause the degradation of bioimplants [3-5]. It is established that CeO_2 additives contribute to the Y-TZP resistance to low-temperature ageing in a humid environment. The partial replacement of cerium oxide with yttrium oxide in Ce-TZP reduces the grain size and enhances the thermodynamic stability of T-ZrO_2 [6-10]. In addition, material whose critical coefficient of fracture toughness exceeded 25 MPa \( \cdot \) m\(^{0.5}\) was obtained in the ZrO_2 – CeO_2 system [11]. Therefore, complex alloying of ZrO_2 with yttrium and cerium oxides can increase its fracture toughness, yet reduce the adverse effect of the humid environment on the strength characteristics. Thus, it is natural that researchers are so interested in developing ZrO_2 – Y_2O_3 – CeO_2-based materials.

The metastable tetragonal phase in Y-TZP is known to exist for a long time needed for proper functioning of the main joint if the following requirements are met when the powder is synthesized, formed, and thermally treated. First, when the initial powders are synthesized they should be optimally alloyed with the needed amount of additives uniformly distributed over ZrO_2. Second, billets (not necessarily high-density) with a regular unstrained microstructure and uniformly distributed pores, whose sizes are commensurable with those of the initial powder, should be obtained.
Fig 1. Production of nanocrystalline powder of ZrO₂ (Y₂O₃, CeO₂) solid solution by combining coprecipitation and hydrothermal decomposition

by compaction. Third, the thermal treatment conditions should ensure that the billets are sintered within a limited temperature range (as a rule, no higher than 1200 to 1300°C); abnormal grain growth and diffusion of alloy additives and admixtures on their boundaries being limited, and pure grain boundaries with a low concentration of potential defects (silicate films, entrapped gas, cracks, etc.) being formed. The above conditions lead to materials with the lowest possible residual stress, which causes in-service defects.

The foregoing suggests the conclusion that the microstructure and properties of ZrO₂-based ceramics significantly depend on the characteristics of initial powders, which, in turn, rely on the production method [12, 13]. Much attention has currently been focused on the hydrothermal synthesis of nanocrystalline oxide powders. This is because nanocrystalline powders with required characteristics are obtained under hydrothermal conditions and controlled changes in process parameters. Powder properties (size of primary particles, phase composition, size distribution of particles, agglomeration) are determined by synthesis conditions, such as pH of solutions, salt concentration, and reaction temperature and duration [14-17]. Hydrothermal treatment of preliminary precipitated gels is an efficient method for obtaining soft-agglomerated nanocrystalline powders with narrow particle size distribution [18, 19].

This research is intended to examine the properties of the nanocrystalline powder 95 mole% ZrO₂ – 2 mole% CeO₂ – 3 mole% Y₂O₃, synthesized by combining coprecipitation and hydrothermal decomposition. This method permits synthesizing powders of the needed composition in the ZrO₂ – Y₂O₃ – CeO₂ system. Powders of the above composition fall within the area of a tetragonal solid solution in the ternary system ZrO₂ – CeO₂ – Y₂O₃. The composition was chosen assuming that the ZrO₂-based tetragonal solid solution with 3 mole% Y₂O₃ would become more resistant to the ageing effect in humid environment at 200 to 400°C if some amount of CeO₂ is introduced (1 to 4 mole%).