The effect of transition metal oxides on the sintering and properties of ceramics in the ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system

T O Obolkina<sup>1</sup>, M A Goldberg<sup>1</sup>, V V Smirnov<sup>1</sup>, S V Smirnov<sup>1</sup>, O S Antonova<sup>1</sup>, D D Titov<sup>1</sup> and S M Barinov<sup>1</sup>

<sup>1</sup>A.A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninsky prospect, 49, Moscow, Russia

Abstract. The paper presents the results of the investigation of the transition metals oxides – cobalt and iron additives influence on the sintering and properties of the ceramic material based on ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system with 10 wt.% Al<sub>2</sub>O<sub>3</sub>. It is shown that the addition of the oxides resulted in the significant increase of the sintered ceramic materials ZrO<sub>2</sub>-10%Al<sub>2</sub>O<sub>3</sub> strength and decrease of sintering temperature. The maximum bending strength was more than 800 MPa (sintered at 1450 °C) and porosity was less than 1%.

E-mail: tobolkina@imet.ac.ru

1. Introduction
The main requirements for the materials for the manufacture of the hip joint prosthesis (acetabular insert and head of the hip) are biocompatibility, corrosion resistance, wear resistance, high strength and crack resistance. Ceramic materials of the zirconia-alumina system (ZrO<sub>2</sub>-10%Al<sub>2</sub>O<sub>3</sub>) are the most promising in this direction. However, the cost of these materials remains the main drawback to full implementation in the field of medicine due to the high sintering temperature (1600-1750 °C). To achieve the high temperatures, expensive and less productive equipment are used (hot pressing, isostatic pressing). The decrease in the sintering temperature will allow the use of traditional methods for producing ceramic materials.

The introduction of additives is one of the effective ways to reduce the sintering temperature and obtain a nanoscale structure of ceramics. The main studies for ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> materials are carried out using oxide additives of divalent metals — Ca, Mg, Ba, and also some rare-earth metal oxides — these are mainly Y, Yb, and Ce [1], which contribute to the production and stabilization of high-strength ZrO<sub>2</sub> in a tetragonal modification.

Some studies deal with the complex introduction of additives - together with stabilizing additives, oxide additives were introduced to decrease the sintering temperature and prevent the recrystallization [1-3]. The action of additives that decrease the sintering temperature is based on the incorporation into the lattice of cations of greater valency or cations with a larger or smaller radius compared to the Zr<sup>4+</sup> cation [3, 4]. As a result of the additive introduction, the numerous lattice defects which intensify the sintering are formed.

In this paper, we show the effect of transition metal oxides additives on the phase composition, sintering and mechanical properties of ceramics based on ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> containing 10 wt.% Al<sub>2</sub>O<sub>3</sub>. 
2. Materials and method

ZrO₂ nano dispersed powder containing 3 mol% of yttrium oxide was used to obtain low-temperature ceramic materials. 10 wt.% alumina was added to the material to inhibit the recrystallization process. The powder was obtained by chemical precipitation. An aqueous solution of zirconium oxychloride (ZrOCl₂·8H₂O), aluminum chloride (AlCl₃·6H₂O) and yttrium chloride (YCl₃·6H₂O) in 9% aqueous ammonia were added. After synthesis, the resulting precipitate was filtered on a Buchner funnel, then dried and calcined at a temperature of 650 °C. The mechanochemical activation of the powders was carried out in a planetary mill in the ethanol media. Then, the obtained after synthesis ceramic powder was introduced into the aqueous solutions contained transitions metals (NH₄)Fe(SO₄)·12H₂O and CoCl₂. The amount of additive was calculated from the content of Fe and Co metal cations in mol.% - 0 mol.%; 0.33 mol.%; 1 mol%; 3 mol.% with respect to the ZrO₂-10% Al₂O₃ composite.

The phase composition of the powders was determined by X-ray phase analysis (XRD, Diffray 401 diffractometer) using Cr Kα radiation using a JCPDS and PCPDFWIN file cabinet. The morphology of the obtained powders was studied by transmission electron microscopy (TEM, JEOL JEM 2100 microscope). The specific surface area (SSA) was determined by the BET method (Tristar micrometics).

The powders were pressed in the form of barrels with measuring of 30x4x4 mm in a metal mold at a pressure of 100 MPa by uniaxial pressing. Samples were sintered in a furnace with siliceous heaters in an air atmosphere. Dilatometric investigations were carried out at temperatures up to 1500°C with 10 °C /min rate in Ar atmosphere 70 ml/min flow (NETZSCH DIL 402 C dilatometer). The phase composition of the sintered samples was studied by XRD. Porosity was determined in accordance with GOST 2409-2014. The strength of the materials was determined by three-point bending on an Instron 3382 tensile testing machine.

3. Results and discussion

A TEM study of the morphology of the synthesized powder particles showed that the powders of ZrO₂-10% Al₂O₃ composite materials consisted of rounded particles of less than 10 nm in size (figure 1).

![Figure 1. Micrographs of ZrO2 - 10% Al2O3 powders obtained by TEM](image-url)
increase of materials sintering activity. For ZrO2-10%Al2O3 materials - the most pronounced effect was observed with the introduction of iron. The linear shrinkage increased from 13.8% for material without additives to 24.1% with the Fe additive. The introduction of Co also provided an intensification of the sintering and shrinkage increased up to 19.6%. The beginning of the fastest sintering stage for materials containing iron was observed at a temperature of 1010 °C.

An increase in the content of metal oxides in ZrO2-10%Al2O3 materials led to a more pronounced difference in the behavior of the materials during sintering. Thus, an increase in the Co content in materials to 3 mol.% led to a decrease in the linear shrinkage to 5.6%, while the temperature of the beginning of the shrinkage increased to 1145 °C. The introduction of 3 mol.% Co led to a decrease in the activity of materials for sintering. Materials containing Fe oxides in an amount of 3 mol.% of the cation showed trends similar to materials containing 0.33 mol.%, while the linear shrinkage increased to 26.2% in both cases. Materials containing Fe oxide began to sinter at a temperature of 930 °C, and also showed accelerated compaction at 1335 °C. Thus, for ZrO2-10%Al2O3 materials, the most pronounced positive effect on the sintering activity of materials is exerted by the introduction of iron oxide, which even at low concentrations contributes to a significant increase in shrinkage and a decrease in the temperature of compaction beginning.

According to XRD, pure ZrO2-10%Al2O3 materials, sintered at 1450 °C had zirconia of tetragonal modification (t-ZrO2), as well as a small amount of monoclinic modification of m-ZrO2 - up to 5 wt.%. The amount of m-ZrO2 increased with growth of sintering temperatures up to 1500 °C, also Al2O3 crystallized in the form of corundum (figure 3). The introduction of Co oxide in minimal amounts (0.33 mol.% Co) led to a decrease in the amount of m-ZrO2 at 1450 and 1500 °C compared to pure materials without additives. An increase in the Co content led to an increase in the amount of m-ZrO2.

Iron oxide introduced into the ZrO2-10%Al2O3 composite material in the amount of 0.33 and 1 mol.% promoted an increase in the amount of t-ZrO2 with the almost complete disappearance of m-ZrO2 (figure 3). An increase in the amount of additive to 3 mol.% led to the formation of up to 20 wt.% m-ZrO2. The intensity of Al2O3 peaks remains practically unchanged. The increase in sintering temperature up to 1500 °C led to growth of m-ZrO2 content up to 40% as the amount of additive increases to 3 mol.% Fe. In this case, the introduction of 3 mol.% Fe led to the disappearance of the peaks splitting at 2θ of 49.46 and 50.06 with the formation of a single peak at 50.22, which is typical for zirconia of the pseudo-cubic modification (c-ZrO2).

![Figure 2](image_url)

**Figure 2.** Diffraction patterns of powders ZrO2-10%Al2O3 containing Co after sintering at 1450 °C (a) and 1500 °C (b), where * - t-ZrO2 (JCPDS # 42-1164), o - m-ZrO2 (JCPDS # 37-1484), ▽ - Al2O3 (JCPDS # 10-0173), ◊ - c-ZrO2 (JCPDS # 49-1642)
Figure 3. Diffraction patterns of powders ZrO$_2$-10%Al$_2$O$_3$ containing Fe after sintering at 1450 °C (a) and 1500 °C (b), where * - t-ZrO$_2$ (JCPDS # 42-1164), o - m-ZrO$_2$ (JCPDS # 37-1484), ▽ - Al$_2$O$_3$ (JCPDS # 10-0173), ◊ - c- ZrO$_2$ (JCPDS # 49-1642)

The values of the sintered materials porosity measuring are presented in Table 1. It was shown that all ZrO$_2$-10%Al$_2$O$_3$ materials containing additives were characterized by a densely sintered state with porosity of less than 1% already at 1450 °C. Additive-free pure materials had a porosity of 7.7% at 1450 °C.

Table 1. The dependence of porosity on the composition of the material and sintering temperature.

| Material composition | Sintering temperature, °C | Porosity, % |
|----------------------|---------------------------|-------------|
| ZrO$_2$ - 10%Al$_2$O$_3$ | 7.77 |
| ZrO$_2$ - 10%Al$_2$O$_3$-0.33%Co | 0.26 |
| ZrO$_2$ - 10%Al$_2$O$_3$-1%Co | 0.91 |
| ZrO$_2$ - 10%Al$_2$O$_3$-3%Co | 0.45 |
| ZrO$_2$ - 10%Al$_2$O$_3$-0.33%Fe | 0.82 |
| ZrO$_2$ - 10%Al$_2$O$_3$-1%Fe | 0.75 |
| ZrO$_2$ - 10%Al$_2$O$_3$-3%Fe | 0.02 |
| ZrO$_2$ - 10%Al$_2$O$_3$ | 0.29 |
| ZrO$_2$ - 10%Al$_2$O$_3$-0.33%Co | 0.26 |
| ZrO$_2$ - 10%Al$_2$O$_3$-1%Co | 0.41 |
| ZrO$_2$ - 10%Al$_2$O$_3$-3%Co | 1500 | 0.76 |
| ZrO$_2$ - 10%Al$_2$O$_3$-0.33%Fe | 0.61 |
| ZrO$_2$ - 10%Al$_2$O$_3$-1%Fe | 0.54 |
| ZrO$_2$ - 10%Al$_2$O$_3$-3%Fe | 0.18 |

Materials heat-treated at 1500 °C were characterized by a densely sintered state for all ZrO$_2$-10%Al$_2$O$_3$ compositions (figure 4). The introduction of additives of Co and Fe oxides contributed to a substantial increase in the strength of sintered ZrO$_2$-10%Al$_2$O$_3$ ceramic materials. Materials without additives were characterized by an average strength at 1450 °C - 470 and at 1500 °C - 530 MPa, respectively. Due to the achievement of a densely sintered state at 1450 °C and stabilization of t-ZrO$_2$, for compositions containing Fe and Co, the strength was more than 750 and 800 MPa, respectively. The increase of sintering temperature up to 1500 °C resulted in growth of bending strength up to 860 MPa for materials with 0.33 mol.% Co.
Figure 4. The strength of ZrO$_2$-10% Al$_2$O$_3$ ceramics sintered at 1450 °C (a) and 1500 °C (b).

Thus, the introduction of Co and Fe additives significantly affects sintering and led to the increase in the bending strength of ZrO$_2$-10% Al$_2$O$_3$ ceramic materials.

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