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Investigation of the Properties of Zirconia Based Ceramics

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Zirconia based ceramics properties were investigated utilizing it as a reference material for thermal conductivity measurements. Zirconia based ceramics (YSZ) containing 7 wt % Y_2O_3 were fabricated using fine powders prepared by the hydrolysis technique. The mechanical properties of these ceramics – crushing strength and elongation were evaluated. These properties are discussed on the basis of their stability at the experimental conditions at 1000 °C temperature. Microstructure of polished cross-section of the samples was investigated by optical and scanning electron microscopy (SEM). Phase analysis was identified by X-ray diffractometry (XRD). Thermal conductivity of the ceramics was measured at various temperatures using hot-wire (cross-array and parallel) and inverse methods.
Keywords: YSZ ceramics, thermal treatment, microstructural investigations, XRD, thermal conductivity.

1. INTRODUCTION

High temperature oxide ceramics, based on zirconium oxide are widely used as engineering ceramics due to their superior properties, such as high heat resistance, high mechanical strength at high temperature, low and constant thermal conductivity in a large temperature region, etc. [1 – 3]. This is one of the several reasons for regarding zirconia ceramics as a promising reference material for thermal conductivity measurements at high temperatures [1].

Thermal characteristics of standard samples, used for the revise of high-temperature thermal conductivity estimation facilities' measurement accuracy, have to be stable, and almost independent upon the temperature. These characteristics must remain unchanged under the repeated heating-cooling conditions. The sample should not react with the environment, it should not change the form and should not decompose [4]. Besides, standard samples should not react with the experimental material and measuring gauges. One of such materials, which corresponds to the determined requirements is zirconium dioxide (ZrO_2) ceramics. This material is distinguished for insignificant conductivity (up to 2 $Wm^{-1}K^{-1}$), which almost is independent on the temperature and for large resistance to oxidizing, as well as reduced environment [5]. In principle, the reference material could be any substance that has properties which are accurately known over the temperature range of interest [6, 7].

Microstructural features have a great influence on the properties of polycrystalline zirconia ceramics [3, 5]. Porous material has better insulating properties due to the pores filled with air [4, 8].

Literature studies of thermal conductivity of yttria-stabilized zirconia containing various mol% of the stabilizer showed that thermal conductivity of the ceramics strongly depends on the content of Y_2O_3 [9, 10]. Thermal conductivity of zirconia decreases with the increase of yttria content up to 5.12 mol% (9 wt%). However, thermal conductivity is increased for the compositions containing higher content of yttria [9].

The purpose of this study was to evaluate the stability of the properties at the operating conditions for YSZ ceramics, containing 7 wt% yttria, as a reference material for thermal conductivity measurements. In this paper an examination of the microstructure and properties was performed at 1000 °C temperature. Treatment duration varied from 6 to 190 h.

Experiments were carried out to study dimensional stability, thermal degradation and structural changes of heat treated zirconia in comparison to the untreated one.

2. EXPERIMENTAL

Initial zirconia powders were synthesized by hydrothermal method. Inorganic salts solutions have been used as raw materials. Precursors of Zr (IV) and Y (III) – aqueous solutions of zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8\,H_2O$) and yttrium nitrate hexahydrate ($Y(NO_3) \cdot 6\,H_2O$) respectively, were mixed in the ratio 93 : 7. The materials used had a purity of 99 %. The reaction product was precipitated with the aqueous ammonia solution. After the reaction was completed, the liquid was poured off and the powder precipitates were washed carefully with distilled water to remove chlorine ions (test with a $AgNO_3$ solution for an absence of Cl^-).

The hydrolysis product, hydrous zirconia, was dried and calcined at 1000 °C. The powders were granulated (with the addition of polyvinyl alcohol as a binder), then dried and sintered in air at 1300 °C for 3 h. The obtained product was ball milled for 6 hours with zirconia balls in the grinding-mill covered with YSZ layer.

The particle size of obtained powder varied from 3 to 50 μm. The samples have been obtained by cold uniaxial two-directional pressing at 60 MPa. After drying at 90 °C for 8 h, the pressed pellets were sintered in the furnace with carborundum heat elements in air atmosphere at 1340 °C for 2 h. The pellets were used for the evaluation of the mechanical properties and for structural analysis. One group of samples was left untreated as controls, other were

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heat treated up to 190 h at 1000 °C temperature. In order to understand the stability of the properties at the operating conditions, the cylinder-shaped samples were annealed at 1000 °C for 6 h, 12 h, 24 h, 30 h, 36 h, 42 h, 56 h, 90 h, 140 h and 190 h.

Optical (Olympus) and SEM (JSM 5600) micrographs of the samples were taken before and after heat treatment under differential treatment duration. Polished cross-sections have been used for structural analysis. The phase composition of the powder was determined using X-ray diffraction method (DRON-UM1 with Cu-Kα radiation).

Ceramics density and porosity have been determined by water immersion method [11]. The crushing strength of the specimens was determined by the traditional technique [12]. Thermal conductivity was measured by two standard techniques [13, 14] and by inverse method [15, 16]. The experimental devise in detail was presented in [17].

3. RESULTS AND DISCUSSION

According to the results, the dimensional stability of samples treated at 1000 °C temperature for 140 h was decreased by 0.1 % over the untreated one. Variation of shrinkage of zirconia samples with the heat treatment duration at 1000 °C is presented in Fig. 1.

The measured values of density and porosity of the treated samples showed negligible change after 190 h exposure to thermal attack under 1000 °C environmental conditions (Fig. 2). Marginal decrease of porosity from 35 % to 32 % and, as a result some increase of density (0.3 %) after heat treatment was noticed.

The X-ray diffraction patterns of started samples and heat treated specimens as a function of annealing duration are presented in Fig. 3. The main diffraction peaks at 2θ between 20 and 70 degrees exhibit the phase composition of untreated sample as a mixture of monoclinic (M), tetragonal (T) and cubic (C) phases of zirconia. The crystal orientation is indicated in the Fig. 3.

By the XRD analysis data of heat treated samples, shown in the Fig. 3, the proportion of zirconia crystalline phases and intensity of main diffraction peaks remain the same as in the untreated sample. No changes in crystal orientation were noticed in the XRD patterns of thermally treated zirconia.

Figure 4 shows cross-sectional optical views of the polished surfaces of heat-treated ceramics. In comparison the samples treated by different regimes with untreated ceramics, the morphology of the samples does not differ, as shown in Fig. 4. The structure of the zirconia is characterized by porous nature (Fig. 4). The distribution of pores is quite homogeneous. Ball-shaped pores of different sizes are predominated in the structure. Less porosity is typical for the ceramics treated for higher treatment duration.

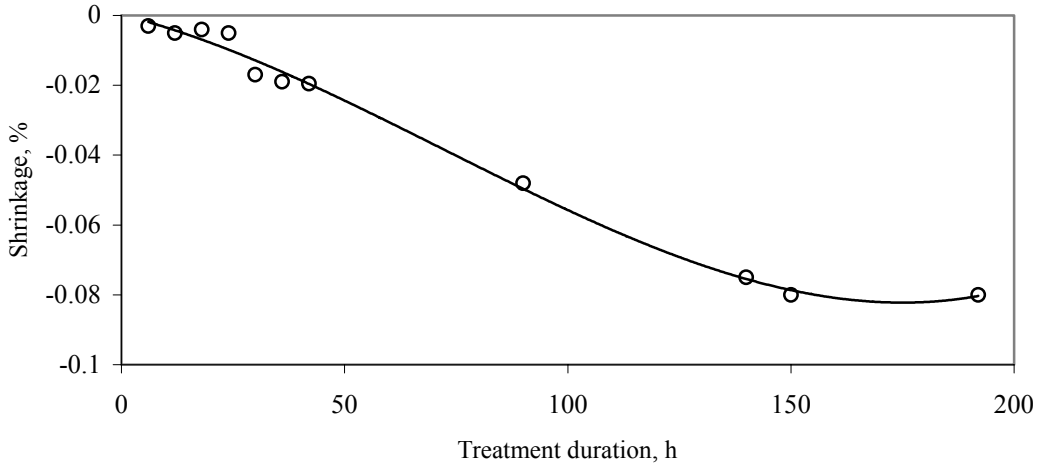


Fig. 1. Variation of shrinkage of zirconia samples with the heat treatment duration at 1000 °C

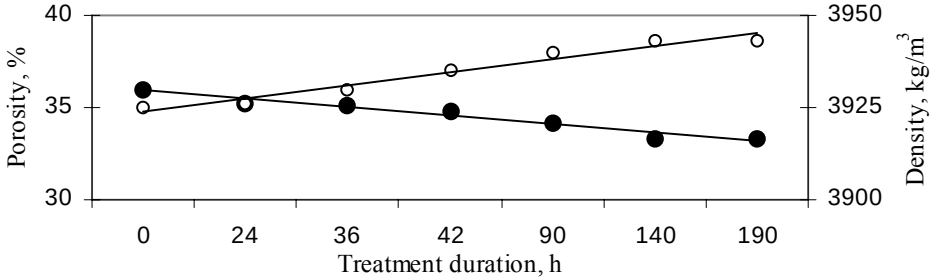


Fig. 2. The influence of heat treatment duration on the density and porosity of YSZ ceramics: white points – density, black points – porosity

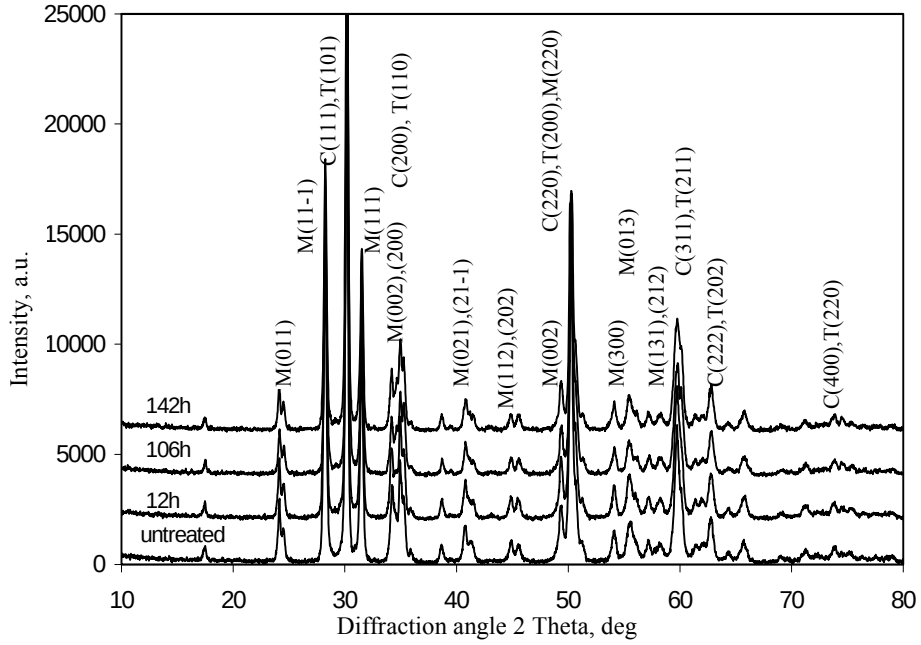
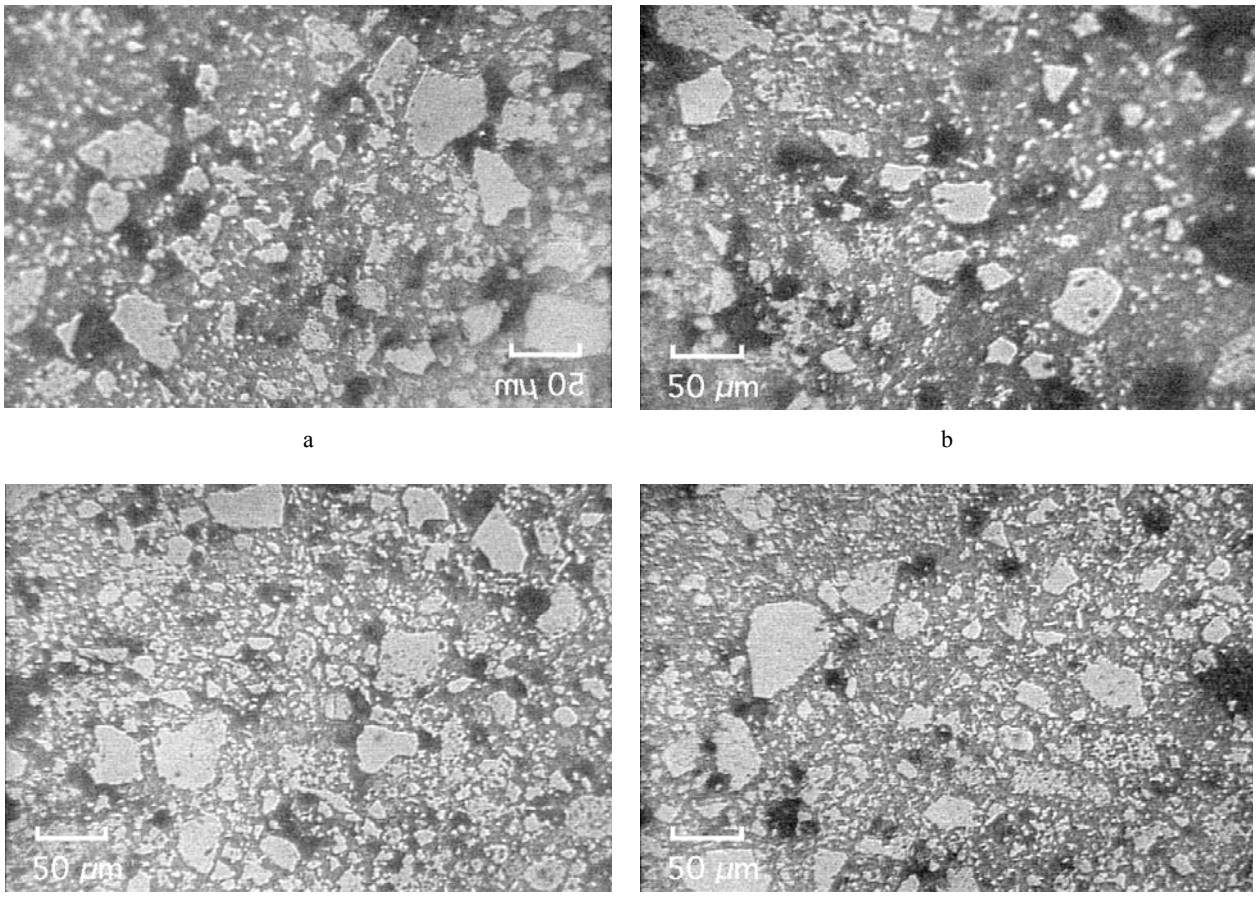


Fig. 3. The XRD patterns of zirconia samples: untreated and post-treated at 1000 °C for 12, 106 and 142 h. Crystal phases of zirconia is: C – cubic phase, T – tetragonal phase and M – monoclinic phase



a b

c d

Fig. 4. Optical micrographs of zirconia samples showing the cross section surface morphology: untreated (0 h) and heat-treated at 1000 °C. Treatment duration is: a – 0 h, b – 30 h, c – 90 h, d – 140 h

All structural elements are more evidently seen in the SEM micrographs (Fig. 5). From the SEM observations, heat treatment at 1000 °C does not greatly affect the microstructure of YSZ.

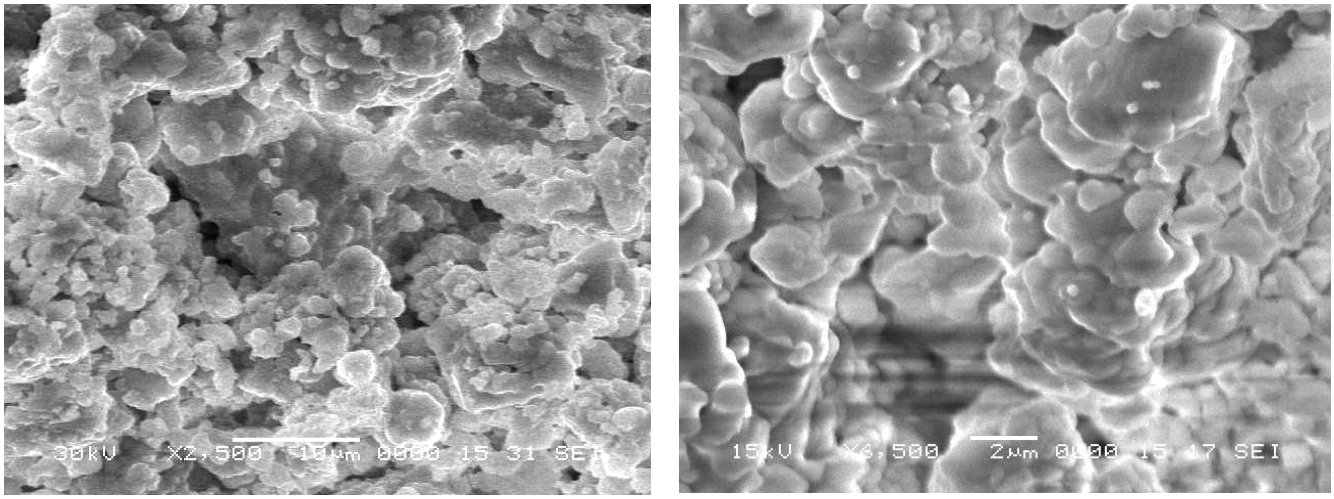
Grain shape is quite uniform in both structures. The microstructure of heat treated sample is characterized by larger grain size (Fig. 5, b). The average grain size of treated sample is about 1 μm.

According to the results of crushing strength measurements, the ageing resulted in an improvement of crushing strength by 8.5 % for the samples heat treated for 150 h.

Fig. 6 and Fig. 7 shows the thermal conductivity measurements data of the YSZ samples obtained by different measurement techniques. Test results of thermal conductivity measurements obtained by hot wire methods as a function of temperature are presented in Fig. 6. Dark points depict experimental data obtained by cross-array technique [13]. For comparison, the line represents the data measured by parallel wires technique [14]. The results obtained by both techniques are in good congruence (~2.4 %). This confirms the reliability of those hot wire techniques.

The thermal conductivity values at the temperature region < 600 °C show a steady decrease as a function of temperature (Fig. 6). However, the thermal conductivity values can be considered as constants for the temperature range from 600 °C to 1000 °C. From the data obtained, thermal conductivity of YSZ ceramic are quite stable in the temperature region up to 600 °C.

Thermal conductivity of the studied zirconia specimens was also determined by the method of the inverse task solution (AUS). The thermal conductivity values measured by inverse method are presented in Fig. 7.



a b

Fig. 5. SEM micrographs showing the microstructure of zirconia samples: untreated (a) and post treated at 1000 °C for 190 h (b)

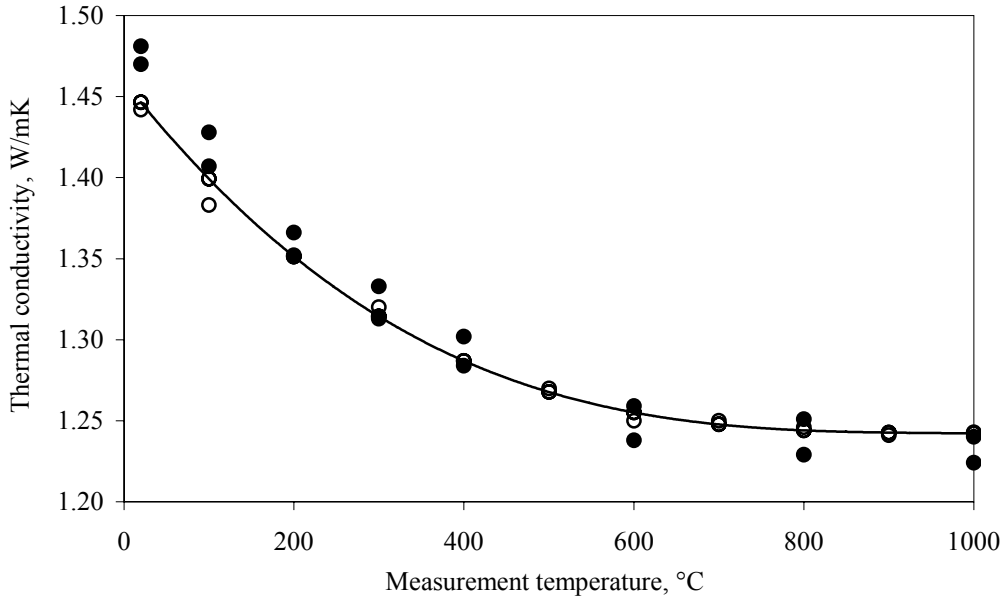


Fig. 6. Thermal conductivity data of zirconia ceramic measured by different techniques: black points – cross-array method (LST EN 993-14), curve with white points – parallel wires method (LST EN 993-1)

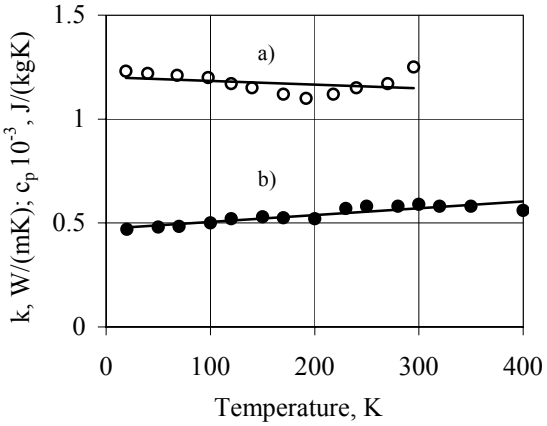


Fig. 7. Thermal conductivity (white points) and specific heat (black points) of the YSZ samples versus temperature obtained by inverse method

In the low temperature region (<400 °C) the results are differ from the data measured by hot wire method approximately ~14 %. At the elevated temperatures (> 600 °C) this difference is < 5 %. The values of specific heat (c_p) are presented in this Figure too. Variation of specific heat values for studied zirconia samples as a function of temperature is quite linear.

It was noticed that thermal conductivity values measured by hot wire method and by inverse task method disagree to a considerable degree in low temperature region (up to 400 °C). At higher temperature (> 600 °C) the thermal conductivity is practically independent of temperature and its values are coincident with the values determined by inverse task method.

4. CONCLUSIONS

It was determined the effect of thermal ageing at 1000 °C on the thermal degradation, performance and reliability of zirconia ceramics.

According to the results, the treated samples were found to be thermally quite stable at the conditions investigated. Annealing at the operating conditions for 140 h results in enhanced crushing strength of the samples. A marginal change in the percentage of elongation of the samples during annealing at 1000 °C was noticed.

Experimental results show that heat treatment at 1000 °C for 190 h does not cause any substantial changes in the microstructure and properties of the treated zirconia. Heat treatment for 140 h influences the stability of YSZ properties very slightly and it can be used as additional stabilization process for treated zirconia samples.

Heat treatment has no influence on the crystal orientation of zirconia. Marginal decrease of porosity up to 3 % and, as a result some increase of density (0.3 %) was noticed after heat treatment.

The suggested YSZ ceramics can be used for the production of standard samples intended for the verification thermal conductivity facilities' measuring accuracy.

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