

# Thermal expansion of oxide systems on the basis of $ZrO_2$

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## Abstract

The structure and phase composition of the ceramic-based system  $ZrO_2$ -MgO is studied. The dependence between the structural-phase state and the coefficient of thermal expansion of ceramic materials based on solid solutions  $ZrO_2$ -MgO is demonstrated. The coefficient of thermal expansion of the system increases proportionally to the increase of the MgO content. The thermal expansion of the  $ZrO_2$ -MgO ceramic materials can be described in the framework of the mixture rule taking into account the phase composition of  $ZrO_2$  and the amount of magnesia grains in the matrix.

Keywords:  $ZrO_2$ -MgO solid solutions, coefficient of thermal expansion, mixture rule

## 1. Introduction

Today's industrial progress leads to the need for materials that retain their functional properties when operating under high temperature conditions [1-6]. Good candidates in this respect are the oxide ceramic materials, particularly the ones on the basis of  $ZrO_2$ -MgO solid solutions. Materials of the  $ZrO_2$ -MgO system are known to have high melting temperature, chemical resistance, crack resistance and strength, which make possible their operation under high temperature conditions in aggressive media. Of particular importance in such conditions is the thermal expansion of the material. The literature provides the values of the coefficient of thermal expansion for stabilized  $ZrO_2$  [7-10], but neither the qualitative nor the quantitative composition of the materials is considered. It is therefore pertinent to study the thermal expansion of the  $ZrO_2$ -MgO systems of variable composition.

The aim of this paper is to study the structure and phase composition and their relation to the coefficient of thermal expansion of the  $ZrO_2$ -MgO ceramic materials.

## 2. Experimental procedure

$ZrO_2$ -MgO ceramics of the following compositions have been studied:  $ZrO_2$  + 8.6 mole% MgO (hypo-eutectoid);  $ZrO_2$ +13.9 mole% MgO (eutectoid);  $ZrO_2$ +25.4 mole% MgO,  $ZrO_2$ +35 mole% MgO,  $ZrO_2$ +43.3 mole% MgO (hyper-eutectoid).

Specimens were compacted from powders produced by thermal decomposition of salt solutions in low-temperature plasma. Powder compaction was carried out under a pressure of 70 MPa. The compacts were sintered at 1650°C and then subjected to one hour of isothermal exposure in air.

The structure of the obtained ceramics was analyzed by scanning electron microscopy on a microscope Philips SEM 515. The accelerating voltage was 30 kV. Specimens for SEM examination were mirror polished with diamond pastes of different sizes.

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### Prof. László A. Gömze

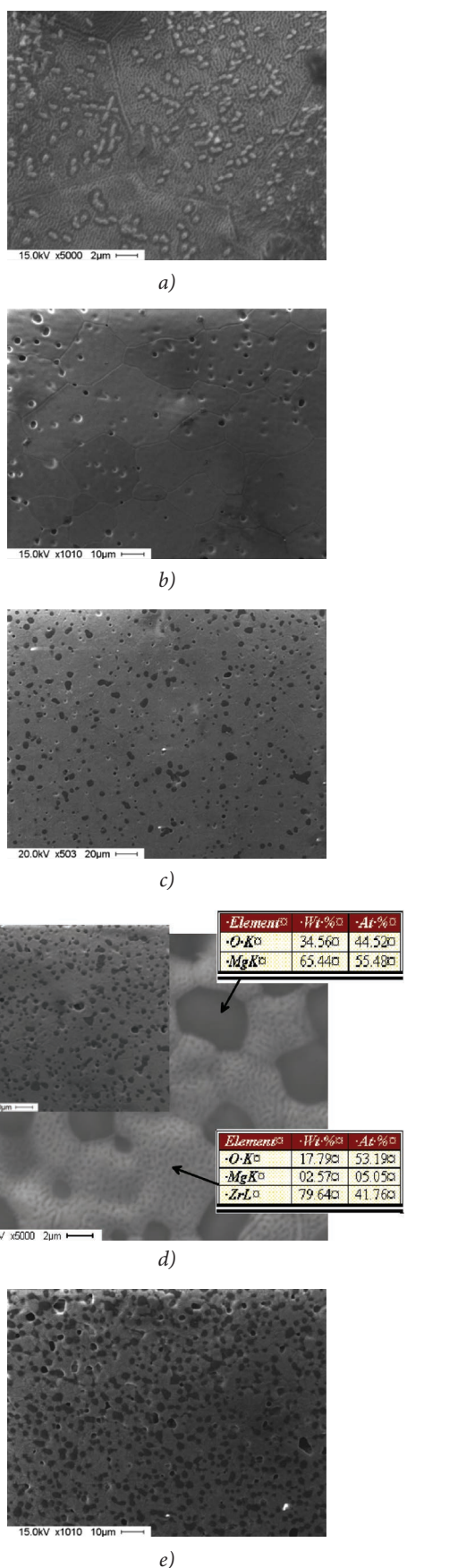
Establisher (in July 1st, 1999) and head of Department of Ceramics and Silicate Engineering in the University of Miskolc, Hungary. Since then 7 students from the department have successfully completed their PhD theses and 4 of them were managed by Prof. Gömze. He is author or co-author of 2 patents, 5 books and more than 250 scientific papers. Recently, he is the chair of the International Organization Board of **ic-cmtp3** the 3<sup>rd</sup> International Conference on Competitive Materials and Technological Processes (2014) and **ic-rmm2** the 2<sup>nd</sup> International Conference on Rheology and Modeling of Materials (2015).

The phase composition and crystal structure parameters were studied by X-ray diffraction patterns obtained using filtered  $CuK_{\alpha}$  radiation. The zirconia phase content was estimated by the ratio of the integral intensities of the tetragonal and cubic diffraction lines I(111), and the monoclinic diffraction lines I(111), I(-111).

Thermal expansion was measured using a mechanical dilatometer in air. The specimen temperature was increased at a rate of 10 °C/min. The specimens were heated up to 1100 °C, which, according to the phase diagram of the  $ZrO_2$ -MgO system, corresponds to the temperature of transition from the low-temperature monoclinic  $ZrO_2$  phase to the high-temperature tetragonal modification of  $ZrO_2$ .

## 3. Results and discussion

The SEM images of the  $ZrO_2$ -MgO ceramics structure with different magnesia content are given in Fig. 1. The structure



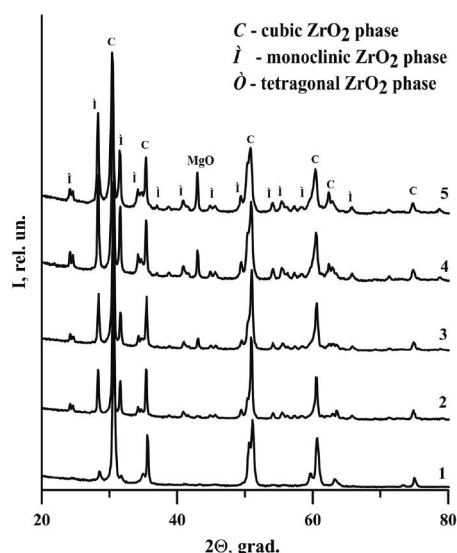
a – ZrO<sub>2</sub> (8.6 mole% MgO), b – ZrO<sub>2</sub> (13.9 mole% MgO); c – ZrO<sub>2</sub> (25.4 mole% MgO), d – ZrO<sub>2</sub> (35 mole% MgO); e – ZrO<sub>2</sub> (43.3 mole% MgO)

Fig. 1. SEM images of the ceramics structure:

1. ábra A vizsgált cirkon-kerámiák anyagszerkezetének SEM felvételei

of the specimens of the hypoeutectoid composition shows lenticular grains of the tetragonal ZrO<sub>2</sub> phase, along with grains of the cubic ZrO<sub>2</sub> solid solution (Fig. 1a). The structure of the ZrO<sub>2</sub> (13.9 mole% MgO) ceramics is represented in Fig. 1b. This composition is characterized by grains of the cubic modification of ZrO<sub>2</sub> [11, 12]. The specimens of the hypereutectoid compositions have magnesia inclusions in the ZrO<sub>2</sub> matrix. In this case, the content of MgO inclusions increased from 9 to 22% with the magnesia content growth in the ZrO<sub>2</sub>-MgO system from 25.4 to 43.3 mole%, respectively.

According to X-ray phase analysis data, the X-ray diffraction patterns of the hypoeutectoid ceramics have reflections from three zirconia phases, namely, cubic (C-ZrO<sub>2</sub>), tetragonal (T-ZrO<sub>2</sub>) and monoclinic (M-ZrO<sub>2</sub>) (Fig. 2), with the monoclinic phase content increasing with the growing magnesia content in the initial mixture.



1 – ZrO<sub>2</sub> (8.6 mole% MgO); 2 – ZrO<sub>2</sub> (13.9 mole% MgO); 3 – ZrO<sub>2</sub> (25.4 mole% MgO); 4 – ZrO<sub>2</sub> (35 mole% MgO); 5 – ZrO<sub>2</sub> (43.3 mole% MgO).

Fig. 2. X-ray diffractograms of the ceramics of the ZrO<sub>2</sub>-MgO system: 2. ábra A ZrO<sub>2</sub>-MgO kerámiák röntgen-diffraktogramjai

The phase composition of the eutectoid ceramics is represented by the high-temperature cubic modification of ZrO<sub>2</sub>. The X-ray diffraction patterns of the hypereutectoid ceramics have, along with the ZrO<sub>2</sub> reflections, diffraction maxima corresponding to MgO.

Measurements of the coefficient of thermal expansion of the studied materials (Fig. 3) showed that the coefficient of thermal expansion measured in the temperature range 400-1250 K depends linearly on the magnesia content in the initial mixture. The measured thermal expansion coefficients agree well with the values calculated by the mixture rule taking into account the phase composition of the studied materials: the content of the monoclinic ZrO<sub>2</sub> modification for the composition with 8.6 mole% MgO is 15%, which determines low values of the coefficient of thermal expansion equal to 6.7 · 10<sup>-6</sup> K<sup>-1</sup>, since, according to the literature data, the coefficient of thermal expansion of the monoclinic ZrO<sub>2</sub> phase is 6 · 10<sup>-6</sup> K<sup>-1</sup> and that of the cubic ZrO<sub>2</sub> phase is 8 · 10<sup>-6</sup> K<sup>-1</sup>. The coefficient of thermal expansion of the eutectoid specimens is defined by thermal

expansion of the cubic  $ZrO_2$  phase, while the main factor that contributes to the thermal expansion of the hypereutectoid specimens is an increase in the amount of magnesia grains in the zirconia matrix.

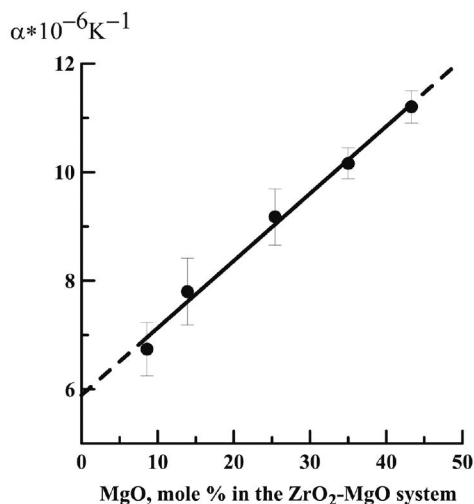


Fig. 3. Coefficient of thermal expansion vs. magnesia content in the  $ZrO_2$ -MgO system

3. ábra A  $ZrO_2$ -MgO kerámiák hőtágulási együtthatója a MgO tartalom függvényében

In extrapolating the obtained dependence to the zero MgO content, the coefficient of thermal expansion corresponds to the thermal expansion of the monoclinic  $ZrO_2$  modification. In extrapolating the obtained dependence to the 100% magnesia content, the coefficient of thermal expansion is  $14.9 \cdot 10^{-6} K$ , which is close to the thermal expansion of magnesia equal to  $14.4 \cdot 10^{-6} K$ . So, the coefficient of thermal expansion of the  $ZrO_2$ -MgO system is defined by the mixture rule taking into account the phase composition and amount of magnesia inclusions in the  $ZrO_2$  matrix.

#### 4. Conclusions

It is found that the coefficient of thermal expansion is governed by the phase composition of the sintered ceramics, with a ratio of the fractions of the high- and low-temperature  $ZrO_2$  modifications and the amount of magnesia grains in the  $ZrO_2$  matrix. The coefficient of thermal expansion of the system increases proportionally to the increase of the MgO content. The thermal expansion of the  $ZrO_2$ -MgO ceramic materials can be described in the framework of the mixture rule taking into account the phase composition of  $ZrO_2$  and the amount of magnesia grains in the matrix.

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#### ZrO<sub>2</sub> alapú kerámia rendszerek hőtágulása

Jelen munkában a szerzők a  $ZrO_2$ -MgO alapú kerámia rendszerek anyagszerkezete, fázis összetétele és a hőtágulási együttható kapcsolatát vizsgálják. Az elvégzett vizsgálatok azt igazolják, hogy az eltérő kémiai összetételű  $ZrO_2$ -MgO szilárd oldatok hőtágulási együtthatója jelentős mértékben függ az anyagszerkezeti szerkezeti fázisoktól. Ugyanakkor az adott vizsgálati hőmérsékleten a MgO tartalom növelésével arányosan növekszik a hőtágulási együttható. A kutatás eredményeként a  $ZrO_2$ -MgO kerámia rendszerhez tartozó anyagok hőtágulási együtthatója a keverék szabály figyelembevételével leírható az adott  $ZrO_2$  fázis jelenléte és a MgO szemcsék anyag-matrixon belüli mennyiségének függvényében. Kulcsszavak:  $ZrO_2$ -MgO szilárd oldatok, hőtágulási együttható, keverék szabály