DOI 10.1007/s11182-015-0423-y

Russian Physics Journal, Vol. 57, No. 11, March, 2015 (Russian Original No. 11, November, 2014)

AN INVESTIGATION OF PHASE STABILITY OF A COMPOSITE ATZ CERAMIC MATERIAL

A. P. Surzhikov, T. S. Frangylyan, S.A. Ghyngazov, and I.P. Vasiliev UDC 666.3

An investigation of phase transformations, taking place in a composite $ZrO_2(Y)–Al_2O_3$ *ceramic material sintered from ultrafine powders manufactured by a plasmochemical process, is performed during its storage and subsequent thermal heating. The composite low-porosity ceramics based on zirconium dioxide is found to be stable in interactions with the environment during long-term storage under standard conditions and thermal heating. A high efficiency of a spontaneous t→m phase transformation is observed in the composite ceramics with an open porosity of more than 6%. The composite ceramics, in which low porosity is combined with a reduced content of the stabilizing yttrium impurity in the crystal lattice of zirconium dioxide, is characterized by the lowest phase stability.*

Keywords: zirconia, phase stability, composite ceramics, dilatometry, calorimetry.

INTRODUCTION

Zirconia ceramics belongs to high-demand materials due to a perfect combination of a large number of physical-mechanical properties [1–3]. The state-of-the-art engineering makes extensive use of yttria-stabilized zirconia. An introduction of yttrium cations, having a different valence, into the crystal lattice of zirconium dioxide increases the number of oxygen vacancies, thus ensuring stabilization of the high-temperature tetragonal modification of zirconium dioxide at room temperature [4]. The grains of the tetragonal modification in the zirconia ceramics under mechanical stresses can undergo a martensitic *t→m*-transition, which is accompanied by a pronounced dilatometric effect. It is this particular effect, which underlies the mechanism of transformation hardening of ceramics, consisting in absorption of the transformation energy due to phase transitions. When a crack initiates and propagates under critical stresses, the grains of a metastable tetragonal phase transfer into a monoclinic modification, which is accompanied by an increase in their volume. As a result of this structural transition, the crack losses its energy and stops, thus increasing the material strength [5, 6].

In order to provide a high level of physical-mechanical properties of a ceramic material based on yttrium-stabilized zirconia, it is necessary to sustain the metastable tetragonal phase for a sufficiently long period. On the other hand, zirconia ceramics is known to be subjected to such an undesirable phenomenon as so-called low-temperature aging. In the course of time, due to interaction with the environment it undergoes a spontaneous transformation from the metastable *t*-phase to a monoclinic phase. Since this process is accompanied by an increase in the volume, cracking of the specimens is likely to occur up to their complete fragmentation into pieces. Thus, the issue of phase stability of zirconia ceramics is especially critical.

While low-temperature aging is discussed in a large number of works [7–11], there is no complete understanding of the physics of this phenomenon. On the other hand, all investigators unanimously agree that the most important role in the low-temperature *t→m*-phase transition of $ZrO_2(Y)$ belongs to interaction between the yttrium-

---

National Research Tomsk Polytechnic University, Tomsk, Russia, e-mail: ghyngazov@tpu.ru. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 11, pp. 124–129, November, 2014. Original article submitted June 10, 2014.

stabilized crystal lattice of zirconia and the water molecules. According to a viewpoint reported in [11], destabilization of the *t*-phase of ZrO_2 occurs as a result of a decrease in the stabilizer concentration in the ZrO_2 lattice due to the penetration of water molecules into the ceramics and the formation of yttrium hydrates or oxyhydrates. A different viewpoint [9] states that the reason for the *t*-phase destabilization consists in a decreased concentration of oxygen vacancies stabilizing the tetragonal lattice, which are filled by the hydroxyl $(OH)^-$ ions forming a proton defect, whose fast diffusion controls the process of aging in zirconia ceramics.

It is impossible to predict the efficiency of aging of ceramics, since it could be affected by a large number of technological factors determining the structure-phase state of the end product. From this perspective, it is always necessary to examine phase stability of the materials made from zirconium dioxide.

The present work is a continuation of the earlier studies [12–14] of the structure-phase state and properties of zirconia ceramics sintered from ultrafine plasmochemical powders. It deals with investigation of phase transitions taking place in the specimens of composite $ZrO_2(Y)–Al_2O_3$ ceramics during their storage and subsequent high-temperature heating. A special focus is made on the relationship between phase transitions and chemical composition of this ceramic material, as well as between its structural characteristics such as pore volume and grain size.

EXPERIMENTAL PROCEDURE

The investigations were performed using composite specimens made from alumina-toughened zirconia ceramics (ATZ), $ZrO_2(Y)–Al_2O_3$. The ceramic material was sintered from ultrafine powders manufactured by the plasmochenical process at the Siberian Chemical Combine. The phase composition of the powders was as follows mass%: $80ZrO_2(Y) – 20Al_2O_3$ and $85ZrO_2(Y) – 15Al_2O_3$. The state of ZrO_2 was stabilized by introducing 2.5 or 3 mol.% of Y_2O_3 impurity.

The specimens for sintering were compacted by a static uniaxial pressing to form tablets measuring 9 mm in diameter and 3–4 mm in thickness at the pressure P = 150 MPa. The resulting compact density was 2.65 g/cm^3. Sintering was performed in a resistance furnace in air under different temperature-duration regimes; the heating and cooling rate was 10°C /min.

The apparent density and open porosity of ceramic specimens were measured by the method of hydrostatic weighing in distilled water using a Shimadzu analytical balance equipped for this purpose with a special attachment.

It is well known [3–5] that martensitic $m\to t$- and $t\to m$-phase transformations in zirconium dioxide are accompanied by thermal effects and changes in the linear dimensions of the specimen. To study the dynamics of these processes, we used the methods of differential scanning calorimetry (DSC) and dilatometry. Prior to the measurements, the specimens were subjected to normalization annealing which consisted in heating of the specimens up to T = 1300°C and tempering at this temperature for 20 min.

During DSC examinations of phase transformations in the sintered specimens use was made of an STA 449 C Jupiter analyzer (Netzsch, Germany). The crucible used in the experiments was made from Al_2O_3 and shaped as a cup. To ensure a correct measurement of the baselines, the crucible was filled with an inert substance – Al_2O_3 powder, whose mass was equal to that of the material under study. The heating and cooling rate was 30 K/min.

Variations in the linear dimensions (ΔL) of the sintered ceramic specimens during heating were detected by a DIL 402 high-temperature dilatometer (Netzsch, Germany). The resulting dependences ($\Delta L/L_0$, where L_0 – initial specimen length) were calibrated, taking into account the effect of heating on the state of the measurement system. The baselines were measured under identical experimental conditions using corundum reference samples. Heating of the specimens was carried out in air at the rate 10 deg/min. The temperature interval under study was T = 25–1300°C.

The X-ray diffraction analysis of the sintered ceramic specimens was performed in an ARL X'tra diffractometer using monochromated CuK_α-radiation. The resulting diffraction patterns were subjected to a full-profile analysis using a Powder Cell 2.4 powder pattern calculation program.

The ceramic microstructure was examined by the method of scanning electron microscopy (SEM). The SEM analysis of the fracture surfaces of ceramic specimens was performed at the TPU Nano-Center (Tomsk) in a SEM JSM-7500F electron microscope.

TABLE 1. Characteristics of Specimens from Composite ATZ Ceramics

Specimen designation	Content of Y_2O_3, mol%	Phase composition, mass%	Porosity,%	Open porosity,%	Grain size, μm
ATZ -1	3	80 (t-ZrO_2) + 20(α-Al_2O_3)	4–5	<1	1.5
ATZ -2	3	85 (t-ZrO_2) + 15(α-Al_2O_3)	6–7	1	0.9
ATZ -3	3	85 (t-ZrO_2) + 15(α-Al_2O_3)	14	7	0.55
ATZ -4	2.5	80 (t-ZrO_2) + 20(α-Al_2O_3)	15	11	0.7

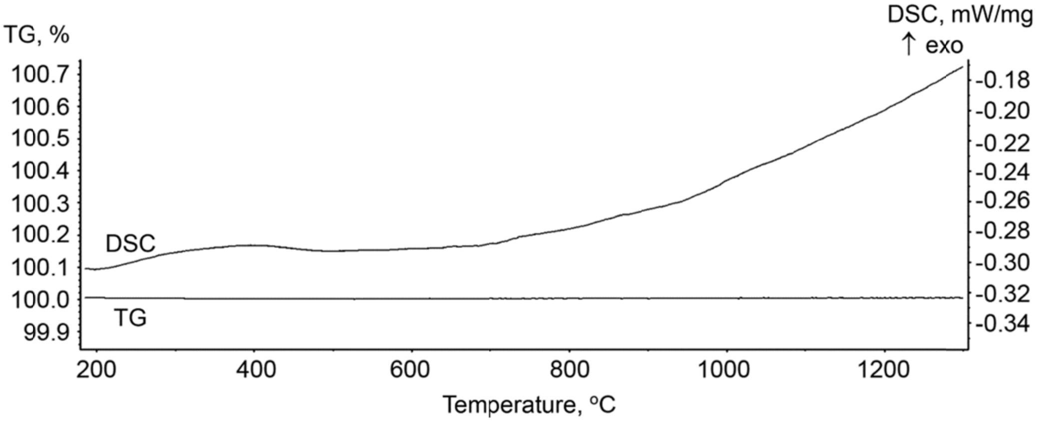

Fig. 1. DSC and TG curves from composite ATZ-2 ceramics specimens (exo – direction of exothermal effect).

EXPERIMENTAL RESULTS AND DISCUSSION

Characteristics of the ceramics types under study, which differed in their chemical and phase compositions, porosity (Θ) and grain size (R_3), are listed in Table 1.

In the first stage of investigations, we performed thermal analysis of the ceramic specimens immediately after their sintering. The investigations demonstrated that after sintering none of the specimens, irrespective of their chemical composition, porosity or grain size, exhibited any tendency to thermally-stimulated phase transitions. This is supported by the calorimetric and dilatometric measurement data.

Shown in Fig. 1 are sample DSC and TG curves from the specimens of composite ATZ ceramic specimens, obtained immediately after sintering. It is evident that within the entire heating temperature interval under study, there are no extrema in the DSC curves related to polymorphic transitions. Qualitatively, the curves obtained via measuring the other ceramic types had a similar shape.

The temperature dependence of relative variation in the linear size of a ATZ-2 specimen under heating is given in Fig. 2 (curve *1*). A similar shape of the curves was observed for the other ceramics types.

This dependence is strictly linear, which is indicative of a classical process of linear dilatation of the material with increasing temperature. The fact that in the temperature interval under study there are no stepwise changes in the linear dimensions of the specimen associated with phase transitions is in a satisfactory agreement with the calorimetric data presented above.

In the second stage, we performed phase and thermal analyses of the specimens of all ceramics types under study after a long-term storage in air at room temperature.

We have found out that storage of ceramic specimens of the ATZ -1 and ATZ -2 types did not result in any changes in their phase compositions. Moreover, the behavior of the measured calorimetric and dilatometric curves was

TABLE 2. Phase Compositions of ATZ-3 and ATZ-4 Ceramics Specimens after Their Long-Term Storage

Storage time, months	Phase composition of ATZ-3, mass%	Phase composition of ATZ-4, mass%
0	85 (t-ZrO_2) + 15(α-Al_2O_3)	80 (t-ZrO_2) + 20(α-Al_2O_3)
6	-	($30m + 50\ t$) ZrO_2 + 20(α-Al_2O_3)
12	($14m + 71\ t$) ZrO_2 + 15(α-Al_2O_3)	($42m + 38\ t$) ZrO_2 + 20(α-Al_2O_3)

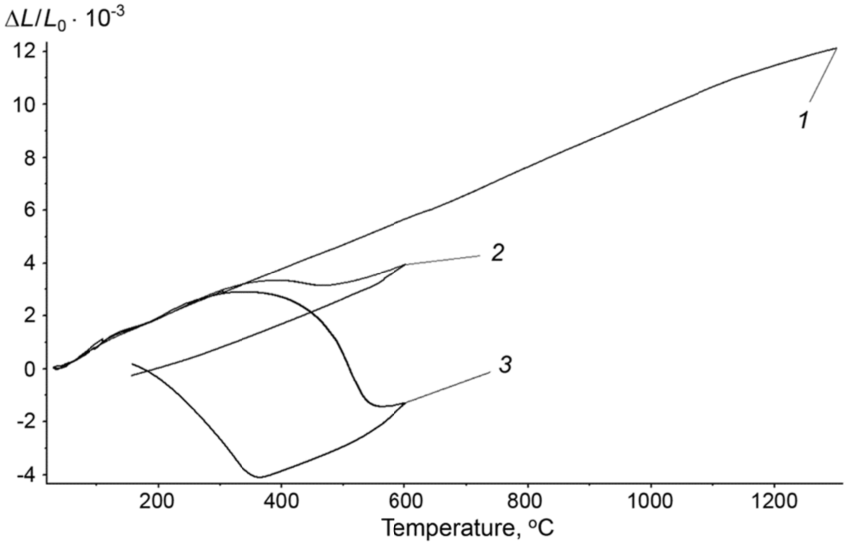

Fig. 2. Dilatometric curves obtained from the measurements performed immediately after sintering of the ATZ-2 ceramics specimens (curve *1*) and after storage of the ATZ-3 and ATZ-4 specimens for one year at room temperature (curves *2* and *3*, respectively).

similar to those presented in Figs. 1 and 2 (curve *1*), respectively. All these data indicate a relatively high phase stability of these types of ceramic materials.

Unlike the case of the ATZ-1 and ATZ-2 specimens, a long-term storage of the ATZ-3 and ATZ-4 specimens was accompanied by considerable changes of their phase compositions, which is clearly demonstrated in Table 2.

The experimental data listed in Table 2 suggest that storage of ceramic specimens under normal atmospheric conditions is followed by the appearance of a monoclinic phase, whose content increases in time. The spontaneous $t \to m$-transformation is most effective in ATZ-4 ceramics characterized by an increased fraction of open porosity and a lower content of stabilizing impurity. These types of ceramic structures are most vulnerable to low-temperature aging and exhibit exceptionally low phase stability. Moreover, the thermal analysis data indicate that after long-term storage ATZ-3 and ATZ-4 ceramics become prone to thermal-stimulated phase transitions.

Typical DSC and TG curves presented in Fig. 3, which were obtained from the ATZ-4 specimens, are characterized by wide exothermic and endothermic peaks, whose maxima fall within $T = 360$ and 550°C, respectively.

According to the TG analysis (see Fig. 3), there is a loss of specimen's mass in the temperature region of the exothermic effect. It is evident from Fig. 4 that after re-heating the exothermic peak disappears. This suggests that the exothermic peak is likely to be due to the removal of the adsorbed water molecules from the specimen.

Of principal interest is the observed endothermic effect. Our investigations have demonstrated that structural transformations responsible for this effect are reversible. It is evident from Fig. 4 that after re-heating of the specimens to $T = 700$°C the endothermic peak does not disappear. We believe the endothermic effect within the temperature region $T = 500$–580°C to be due to a low-temperature $m \to t$-transformation. This viewpoint is supported by the dilatometric data (Fig. 2, curve *3*) clearly demonstrating that within the temperature interval $T = 400$–600°C the classical

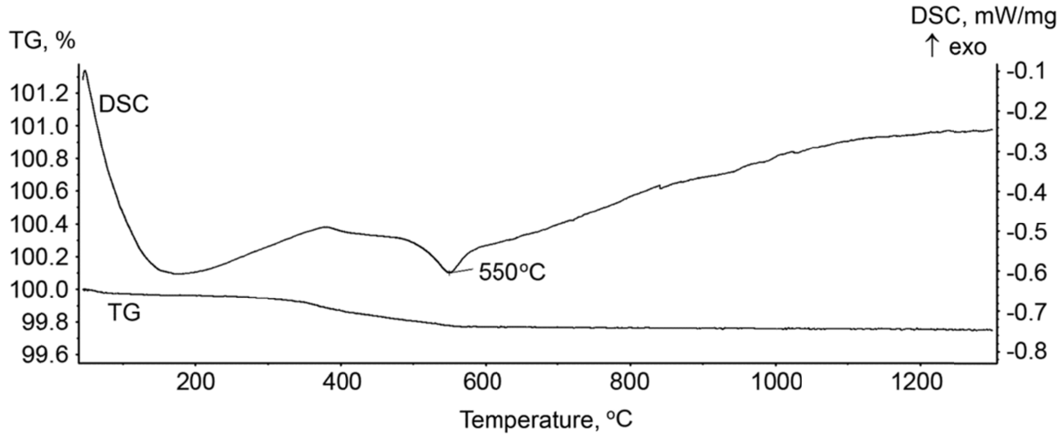

Fig. 3. DSC and TG curves from composite ATZ-4 ceramics specimens after one-year storage.

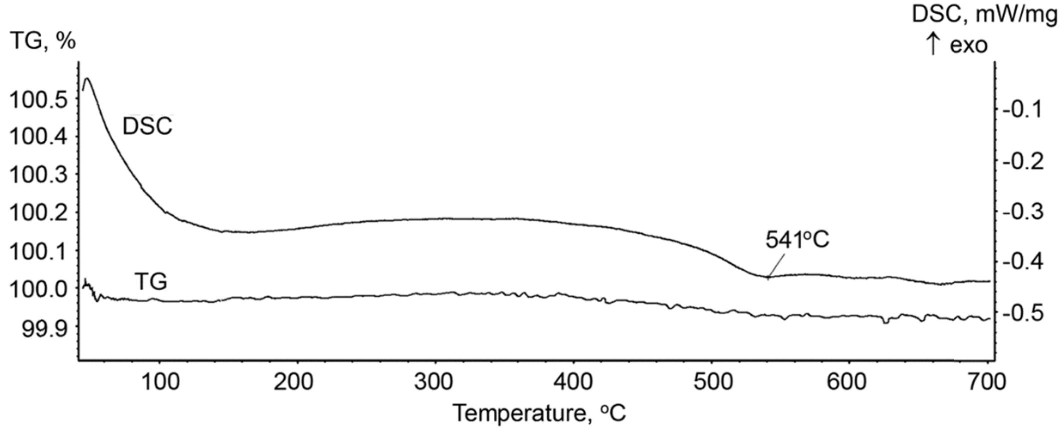

Fig. 4. DSC and TG curves from composite ATZ-4 ceramics specimens after one-year storage followed by re-heating to *T* = 700°C.

temperature trend of dilatation of the ATZ-3 and ATZ-4 specimens is distorted, which results in a stepwise decrease in their linear dimensions. There is a satisfactory direct correlation relationship between the value of a stepwise decrease in the linear specimen dimensions and the content of the *m*-phase formed in the course of low-temperature aging. This effect is most pronounced in the ATZ-4 specimens, wherein the content of the monoclinic-phase formed during aging is maximal. Under cooling, the linear dimensions of these ceramic specimens begin to increase.

The results presented in this work provide an unambiguous evidence of thermal-stimulated structural-phase transformations taking place in the composites under study. A comparison of the data of dilatometric and calorimetric investigations allows us to argue that a change in the linear dimensions of the ceramic specimens within the xperimental temperature region is associated with a low-temperature $m \rightarrow t$-transformation during heating and a reverse low-temperature $t \rightarrow m$ transformation during cooling.

The lowest phase stability among all ceramic types investigated is demonstrated by the ATZ-4 ceramics. From our viewpoint, this is due to two factors, in particular: a high level of open porosity and a lower content of the stabilizing yttrium impurity in the crystal lattice of ZrO_2. In the representative SEM images obtained from the fracture surfaces of this ceramics (Fig. 5) one can clearly see the presence of considerable inter-granular porosity, which would favor diffusion-induced penetration of water molecules into the ceramic specimen.

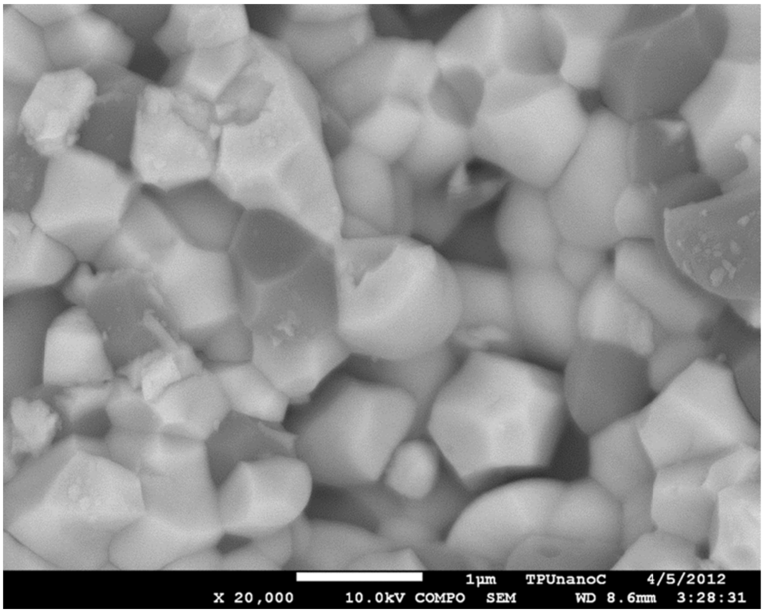

Fig. 5. Micrograph of the fracture surface of a ATZ-4 ceramic specimen in the initial state.

CONCLUSIONS

1. Composite ATZ ceramics sintered from ultrafine plasmochemical powders, characterized by a low level of open porosity, has been shown to demonstrate phase stability in interactions with the surrounding medium during standard long-term storage and under thermal heating.

2. A high efficiency of the process of a spontaneous $t\rightarrow m$-phase transformation has been revealed in composite ceramics with an open porosity of up to 6% under standard conditions.

3. The lowest phase stability has been observed in the composite ceramics, wherein a high level of open porosity is combined with a low content stabilizing yttrium impurity in the crystal lattice of zirconia.

The authors express sincere gratitude to A. G. Melnikov, a colleague at the Tomsk Polytechnic University for his assistance in manufacturing the specimens for investigations.

This work has been performed using funding of the RF Ministry of education and science within the governmental terms of reference “Science”.

REFERENCES

1. Physical-Chemical Properties of Oxides (Ed. G. V. Samsonov) [in Russian], Moscow, Metallurgiya (1978).
2. V. Ya. Shevchenko and S. M. Barinov, Engineering Ceramics [in Russian], Moscow, Nauka (1993).
3. New Ceramic Materials (Ed. P. P. Budnikov) [in Russian], Moscow, Stroyizdat (1969).
4. R. C. Garvie, J. Phys. Chem., **82**, No. 2, 218–224 (1978).
5. S. Yu. Pliner and A. A. Dabizha, Refr. Tech. Ceram. J., No. 3, 58–62 (1986).
6. F. F. Lange, Mater. Sci., **17**, No. 1, 240–246 (1982).
7. K. Castkova, H. Hadraba, and J. Cihlar, Ceramic-Silikaty, **3**, 85–92 (2004).
8. Th. Oberbach, S. Begand, and J. Schneider, Eur. Cells Mater., **19**, No. 2, 18 (2010).

9. G. Xin, Chem. Mater., **16**, 3988 (2004).
10. V. I. Alekseenko and G. K. Volkova, Zh. Tekh. Fiz., **70**, No. 9, 57–62 (2000).
11. F. F. Lange, G. P. Dunlop, and B. I. Davis, J. Am. Ceram. Soc., **69**, 237–240 (1986).
12. A. P. Surzhikov, T. S. Frangulyan, and S. A. Ghyngazov, J. Therm. Anal. Calorim., **115**, No. 2, 1439–1445 (2014).
13. A. P. Surzhikov, T. S. Frangulyan, S. A. Ghyngazov, and N. N. Koval, Nucl. Instrum. Methods Phys. Res., **B267**, 1072–1076 (2009).
14. A. P. Surzhikov, T. S. Frangulyan, and S. A. Ghyngazov, Russ. Phys. J., **55**, No. 3, 345–352 (2012).