INVESTIGATION OF THE STRUCTURAL-PHASE STATE OF ULTRAFINE PLASMOCHEMICAL ZrO_2 (Y) POWDERS

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Annotation. The methods of X-ray phase analysis, thermogravimetry and differential scanning calorimetry were used to study the structural and phase state of ultrafine powders (UFP) of ZrO_2(Y) obtained by plasmochemical synthesis. It is shown that these UFPs are in a highly nonequilibrium state due to the presence of adsorbates and bound water, and the distribution of the stabilizing impurity in the volume of the particles is nonuniform.

Keywords: zirconia, structural-phase state, X-ray diffraction, differential scanning calorimetry, ultrafine powders, plasmochemical synthesis.

1. Introduction

Advancement of science and technology is impossible without materials which possess a unique combination of physical and mechanical properties and improved performance characteristics. Over the last few years, great emphasis has been put into the problem of producing ceramics for structural and instrumental purposes with high mechanical strength and fracture strength.

There are two basic approaches to tackle the problem. One of them is to produce nanostructered ceramic materials. Currently, this problem can be solved due to a substantial progress in the technology of UFP production. Since the surface energy of UFP is high if compared to coarse powders, the powders can be sintered at lower temperatures, and this reduces the rate of grain growth due to intense recrystallization processes. The second approach is based on the effect of polymorphic transformation under external mechanical loads.

Both of the approaches can be realized in ceramic structures made on the base of the nano-size particles of stabilized zirconia [1–5].

In practice, to develop high-strength nanoceramics a wide range of additional factors that contribute to its physical and mechanical properties is to be considered. These factors include characteristics of the nanodispersed powder medium used (grain-size composition, morphology, degree of agglomeration, presence of stabilizing additives), which essentially depend on the technology of UFP production. There are currently more than 15 fundamentally different methods of oxide UFP synthesis. The efficiency of compacting and sintering of UFP depend on the method of their manufacturing. Therefore, ceramic materials may acquire a particular set of properties depending on the nature of the initial green powder.

An efficient plasmochemical technology to manufacture a wide range of oxide nanopowders, including UFP of stabilized zirconia, has been developed at the Siberian Chemical Combine, Tomsk, [6]. High-performance of this technology makes it attractive to be used in mass production.

To choose the technological regime of powder compaction and sintering it is necessary to obtain sufficiently full data on the structural-phase state of ultrafine zirconia plasmochemical powders, which can significantly impact the effectiveness of compression, the shrinkage kinetics and properties of the sintered ceramics. In [7], features of the structural-phase state of composite ultrafine plasmochemical powders of the (ZrO_2-Y)-Al_2O_3 system and phase transformations during thermal heating are investigated.

The present research addresses the study of thermally-stimulated structural-phase transformation in ultrafine plasmochemical powders of stabilized zirconia.

2. Experimental techniques

UFPs of the ZrO_2 – 3 mol. % Y_2O_3 solid solution were synthesized at the Siberian Chemical Combine by decomposition of aqueous solutions of zirconium nitrate salts and yttrium in HF discharge plasma. The change in mass and thermal effects which occurred during heating of the test nanopowders were recorded simultaneously using the analyzer STA 449 C Jupiter (Netzsch, Germany), the sensitivity of weights being 0.1 μg. For correct measurement of the baselines a reference crucible was loaded with the inert Al_2O_3 powder, its mass being equal to the mass of the test material. Heating was carried out in air. The X-ray phase analysis of the powders was carried with the ARL X 'tra powder diffractometer using monochromatic Cu K□.

3. Experimental Results

Figure 1 shows the TG and DSC curves for UFP of the partially stabilized zirconia ZrO_2 – 3mol. % Y_2O_3.

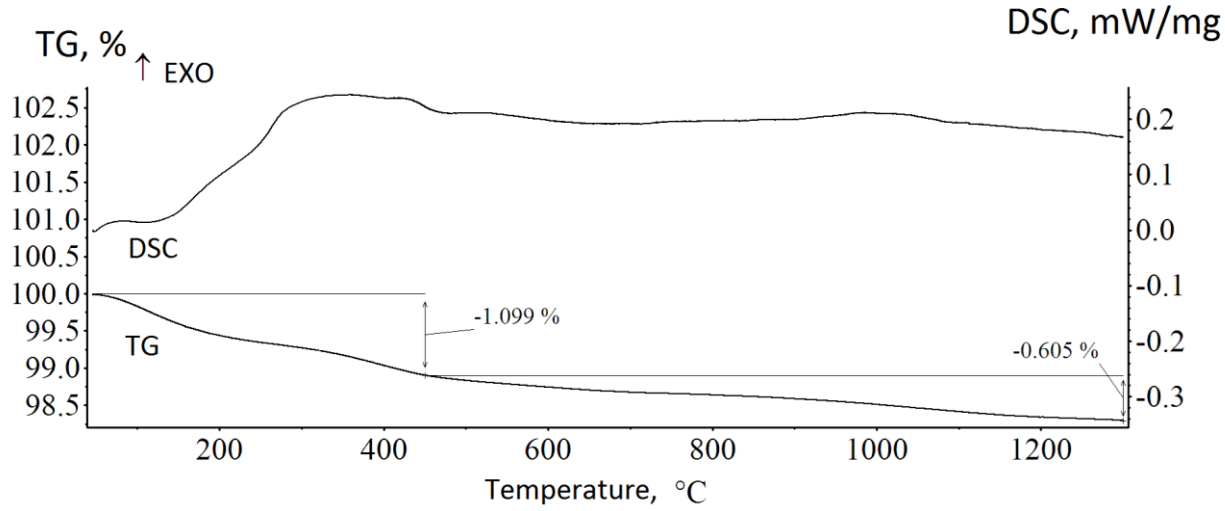

Fig.1. TG and DSC curves for zirconia powder

Noteworthy is the fact that during heating the mass of the powder reduces. When heated to T = 1300°C, the total mass loss is about 1.8 %.

The process of the powder mass reduction occurs in several stages. The first stage, which falls within the temperature range T = (100–200)°C, is due to the removal of the adsorbed moisture, and this is confirmed by the presence of the low-temperature endothermic peak in DSC at T = 110°C. The second stage, during which the powder mass reduces, covers the temperature range T = (300–500)°C, and within this stage an exothermic effect occurs. The exothermic peak is nonelementary.

The mass-spectrometric studies [8] showed that in this temperature interval, the bound water evolves from zirconia nanoparticles synthesized by plasmochemical method. This process is irreversible. The

exothermic heat effect is due to the structural changes in the particles caused by changes in their chemical composition as a result of water removal. The subsequent stages of the process most probably are due to the removal of crystallization and constitution water.

The X-ray phase analysis showed that the test zirconia UFP consisted of a mechanical mixture of monoclinic and tetragonal phases in the amount of 36 and 64 mass%, respectively. At T□1000°C the monoclinic phase is known to be unstable, and it is to transform to a tetragonal modification. This transformation should be accompanied by an endothermic peak in the DSC curve. Our results indicate the absence of this peak in the DSC curve.

Figure 2 shows the diffraction patterns of ZrO_2-Y_2O_3 powder annealed at T = 300, 500, 700 and 1000°C for 30 minutes.

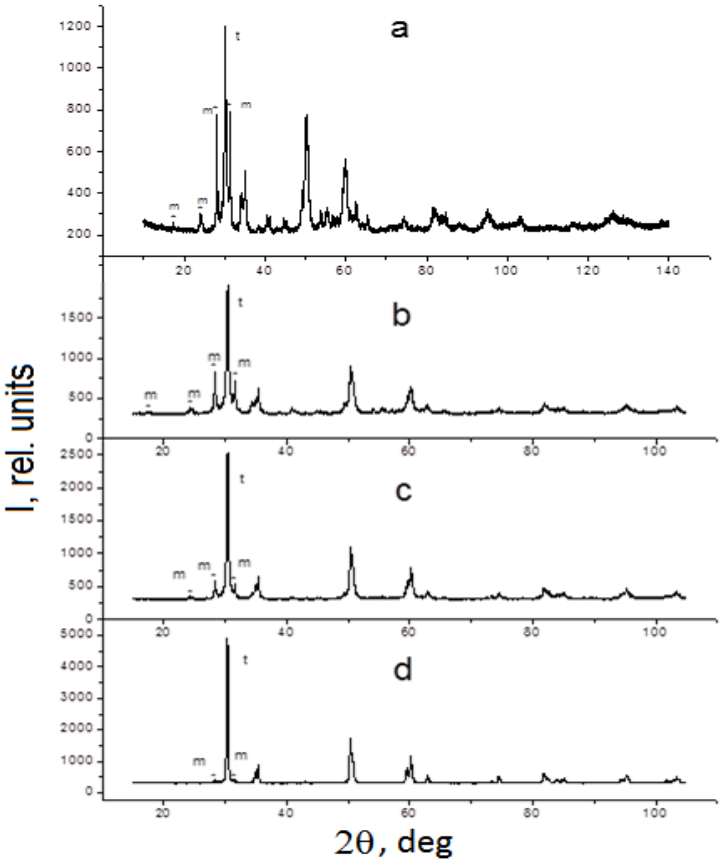

Fig. 2. Diffraction patterns for zirconia powder after annealing at different temperatures: *a is* unannealed and after annealing at T = 300 and 500 °C; *b*, *c*, and *d* are after annealing at T =700, 900 and 1000°C, respectively.

In our opinion, this fact can be consistently interpreted if we take into account the existence of the volume chemical heterogeneity of the synthesized plasmochemical powder of ZrO_2-Y_2O_3 [6]. It is well known that impurities in solid solutions tend to segregate in different interface regions including those on the surface of the particles and grains [9].

This means that there are a smaller number of yttrium ions in the particle volume than that on the particle surface. This heterogeneous chemical composition of the powder contributes to the increased content of the monoclinic phase. During sintering of the compact the diffusion of the impurity into the grain volume is stimulated, and this causes increase in the content of the tetragonal phase in ceramics. Since t-phase formation is limited by the impurity diffusion, the heat effects are observed as if prolonged over the time and within a wide temperature range.

This is what can account for a considerably wide minimum in the DSC curve which covers the temperature range T = (500–1000)°C, within which the monoclinic phase transforms into a tetragonal one. This assumption is confirmed by the results obtained in the study of the effect of stepped annealing in the temperature range T = (300–1000)°C on the structural-phase state of the test powders.

The summarized results of the analysis of the diffraction patterns are presented in Table 1. According to the data in Table 1, thermal annealing stimulates the transition of the monoclinic modification of zirconia in a tetragonal one.

Table 1. The phase composition and structural characteristics of $ZrO_2 – Y_2O_3$ powder

Annealing temperature T, °C	m-phase content mass%	t-phase content mass%	Lattice parameters of t-ZrO_2, Å	Lattice parameters of m-ZrO_2, Å	L,nm t-ZrO_2	L,nm m-ZrO_2	□d/d □ 10^{-3} t-ZrO_2	□d/d□ 10^{-3} m-ZrO_2
Unannealed	38	62	a=в=3.609; c=5.172	a=5.174; в=5.216; c=5.329	31	25	0.4	1.4
300	39	61	a=в=3.609; c=5.172	a=5.174; в=5.224; c=5.327	23	-	1.2	-
500	34	66	a=в=3.608; c=5.170	a=5.178; в=5.212; c=5.331	27	37	0.9	1.2
700	20.8	79.2	a=в=3.610; c=5.173	a=5.174; в=5.214; c=5.337	35	27	0.9	0.8
1000	4.0	96.0	a=в=3.608; c=5.174	-	53	-	-	-
1200	-	100	a=в=3.607; c=5.173	-	96		0.2	-
1400	-	100	a=в=3.607; c=5.174	-	73		0.2	-
1500	-	100	a=в=3.606; c=5.174	-	101		0.3	-
1600	traces	90	a=в=3.605; c=5.175	-	120		0.3	-

Note: L is the size of coherent-scattering region of X-rays; □d/d is the value of microstrains.

4. Conclusion

The studies conducted have revealed that UFP of the stabilized zirconia obtained by plasmochemical method are in a strongly nonequilibrium state. They contain a significant amount of adsorbates and bound water. It is shown that the test zirconia UFP consists of a mechanical mixture of the monoclinic and tetragonal phases in the amount of 38 and 62 mass%, respectively. This can be attributed to a nonuniform distribution of the stabilizing yttrium impurities in the volume of the powder particles. Under heating, the phase composition of the powders changes as a result of diffusion of the stabilizing additive from the particle surface into the particle volume, where it is incorporated into ZrO_2 lattice.

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5. References

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