

Modeling of the Mechanism of Phase Transitions in ZrO_2 with Small Additions of In_2O_3 at High Temperatures in a Vacuum

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In the work were considered the models and analytical study crystallographic sequence of the phase transition in zirconium dioxide at heated. It has been shown, that mechanism of the transformation of monoclinic phase in tetragonal modification takes place at a move of two atoms of oxygen from of three in positions of the structure. At that a move is form a nodal anion vacancies, which are elements of the structure. The accumulation of such vacancies and the appearance of new anion vacancies, which form at evaporation of the oxygen from the lattice zirconium dioxide lead to the appearance zirconium cations of different valence. The transformations of phase of zirconium dioxide upon heating had : tetragonal – cubic, type C - cubic, type F, occur by shifting of the certain concentrations of anion vacancies in the non-structural position. The sequence of phase confirmed experimentally by heating in the temperature range 25 -1600°C in vacuum, samples of zirconium dioxide with addition 5 mol.% In_2O_3 , prepared with hot pressure. The existence in nature is of compounds Zr_2O_3 , with a cubic modification type C – pyrochlore, theoretically and experimentally confirmed.

Keywords: Zirconium dioxide, Oxide indium, Phase transformation, Structure, X-ray diffraction, Analytical study, Crystallographic sequence.

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1. INTRODUCTION

The materials on based zirconium dioxide have a high melting point, low thermal conductivity, resistance against aggressive media and a small cross-section of capture of the neutrons, are used in various areas of new technology, as sources of energy, solid fuel and medicine for tool making [1-5]

The zirconium dioxide in its pure form use not possible from out the presence of reversible polymorphic transition M – monoclinic phase to tetragonal –T- modification, occurs at a temperature of about 1100°C and transition the tetragonal –T-phase at cubic fluorite type F at 2300°C, accompanied by a significant jump in the volume of the unit cell [6].

The transition $M \leftrightarrow T$ in ZrO_2 is the transition of the first kind. This transition is reversible and can not be prevented even by quenching in liquid nitrogen. This fact indicates on existence displacement of mechanism a type of the martensit [7;8].

The study of these phase transformation in different conditions and at different of the temperatures was carried out in the middle of century is conducted to the present time.

Numerous works in this study indicate the complex mechanisms of the transformation from one modification to another.

The high metallographic study transformation $M \leftrightarrow T$ was observed the formation of lamellar and needle structure, characteristic of martensitic transformation [9].

The authors of works noted a very rapid attainment of a definite relation between the amount of monoclinic and tetragonal modifications during of the transition at temperature 1100°C. The transformation

$M \leftrightarrow T$ in zirconium dioxide depends on the number of defects in lattice, which are formed by the thermal processing and method for preparing the samples [10-12]. The authors of [13] found in zirconium dioxide of cluster ordering with the advent of various cubic structures, after of the laser irradiation. According to [14] in the zirconium dioxide with small additions of yttrium oxide discovered a new tetragonal modification T_1 with of the parameters unit cell near to cubic phase.

The literature data indicate a complex mechanism of phase transformations and no right models to explain the sequence of appearance of phases at phase transformations in of by analogy structural MeO_2 .

This work is dedicated to the construction of the mathematical and crystallographic models, that will explain the mechanisms of phase transformations and phase sequence in zirconium dioxide.

2. EXPERIMENTAL

The samples were prepared for investigation of ZrO_2 powder with addition of 5 mol. % In_2O_3 (os.ch. brands) with stirring, and subsequently molded at 400°C under a pressure of 0.5 GPa in air. The structural transformations in zirconium dioxide studied was carried out at high temperatures 25 – 1600°C in vacuum, with using the high-x - ray by the UVD - 2000 to the x-ray machine in a $Cu K_\alpha$ radiation (the vacuum of $(10^{-3} - 10^{-4} Pa)$).

The sample was heated with a speed of 10°C / min with a shutter speed of at each fixed temperature up to an equilibrium state. For this purpose used dense samples of ZrO_2 with the addition of 5 mol.% In_2O_3 . Measurement error with the elementary cell is ± 0.0001 nm. at the same time.

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3. RESULTS AND DISCUSSION

3.1 Models of Crystallographic and Analytical Basis Sequence Phase Transformations in the Zirconium Dioxide at Heating.

In nature are a class of compounds (ZrO_2 ; HfO_2 ; UO_2 ; PrO_2 ; CeO_2 ; ThO_2), which are structural analogs at the type structure of the fluorite. A distinguishing feature have zirconium and hafnium dioxides, these compounds are at room temperature, have a monoclinic structure, which upon heating goes to the tetragonal and then the cubic fluorite-type. These transformations are reversible at cooling.

Availability literary controversy in the sequence of new phases in the process of heating and cooling of samples indicate the complex mechanisms of phase transformations in ZrO_2 . The this problem can be solve, if we consider the sequence of crystal structures and analyze the possibility of the appearance of the correct sequence of structures.

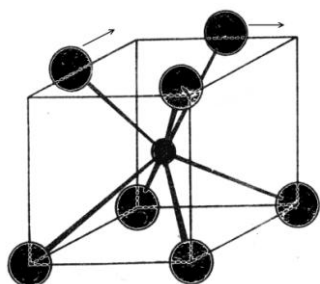


Fig. 1 – the structure of the monoclinic ZrO_2
 ● - cation of the zirconium; ● - ions oxygen

Figure 1 shows the structure of the monoclinic ZrO_2 phase baddeleyite type in which zirconium cation is in the center of the cube, the coordination of ions oxygen have seven positions, with half of the coordination number of oxygen ions is equal to four, and the others - three. The confirm [15], that in a series of tetravalent oxides have the baddeleyite occupies an intermediate position between the ruthenium-type structure (coordination number 6 and 3) and the fluorite (coordination number 8 and 4).

The tetragonal modification of the zirconium dioxide transform at to the primitive tetragonal cell. However, the choice may be used in axles of the tetragonal structure and a fluorite type cell parameters

$$\hat{a}^1 = \hat{a}\sqrt{2}; c^1 = c, \quad (3.1)$$

where $\hat{a}^1 = \hat{n}^1$ - are the lattice parameter for the cubic fluorite type, \hat{a} ; \hat{n} - are the parameter of lattice for the tetragonal modification.

The samples of zirconium dioxides at heated of the oxygen atoms possible shift (Fig. 1) in the angular positions (Fig. 1). The shift leads to the formation of tetragonal filled planes and free from oxygen angular positions, which indicates the martensitic mechanism phase transformation.

The empty positions can be grouped together to form defects. Such a structure with weakened bonds atoms of oxygen can be resistant to high temperatures,

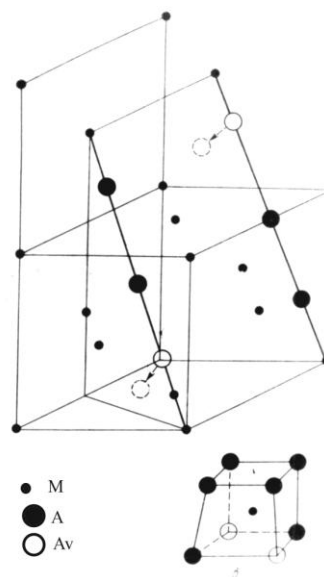


Fig. 2 – The structure of the ZrO_{2-x} is a cubic pyrochlore-type C. M – cation of the zirconium; A – anion oxygen; Av – anion vacancy.

but at certain temperatures this relationship breaks and oxygen out of the lattice.

The anion vacancies can accumulate in the lattice and at certain concentrations of such defects is possible phase transition in another modification.

A tetragonal modification and monoclinic phase are type space - centered. The reaching the 0,25% anion vacancies in the lattice of the zirconium dioxide is a transition to a cubic pyrochlore-type C (Fig. 2). A cell of oxygen consists from of two anion vacancies and six oxygen atoms and in the center is of the zirconium cation. Such a cell is distorted prism. A distortion of such a cell can be explained by the different size of the radius of the anion and anion vacancy. The unit cell parameter of this structure is determined by the formula

$$a = D_c(r_k + 0,75r_A + 0,25r_{Av}), \quad (3.2)$$

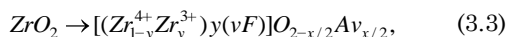
where \hat{a} - the parameter of lattice for C – modification; D_c - the coefficient of cubic structures such R_2O_3 ,

R – rare earth metal; r_k - the radius of the metal cation; r_k - the radius of the metal cation; r_A - the radius of the anion; r_{Av} - the radius of the anion vacancy.

The further increase of the temperature of heating can lead to a disordering of anion vacancies that may lead to the emergence of a new C¹-of-order. This process may take place in a temperature range and point diffusion mechanism.

The increasing the heating temperature in the structure of C-type are shift occurs anion vacancies in non-structural position, such a shift occur lead at appearance of the planes free from of the anion vacancies (Fig. 3). Such ordered the planes composed cations of zirconium cations and anions of oxygen. At higher temperature, the anion vacancies shifted in tetrahedral positions, forming between ourselves the connection and the cubic structure of type fluorite - F appear with facets which centered zirconium cations of different valence and with anions oxygen in the corner of the

lattice. This transformation formed by the following mechanism



The change of valence of zirconium leads to discoloration of the samples, this change is related to the probability of the process



where x - concentration Zr^{3+} cations and anions vacancies; y – concentration a center of color vF.

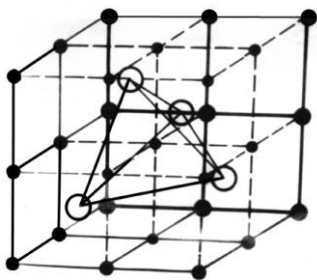


Fig. 3 – the structure of the zirconium dioxides with a type of fluorite - F.

The increase of structural defects in ZrO_{2-x} can lead to violation of the order and appearance of F^1 . Consequently, the sequence of phases occurs on heating: M-T-S-C¹-F-F¹. The appearance of one of the phases essentially depends on the method and conditions for producing the samples, the amount of additives soluble in zirconium, the impact of the irradiation energy.

The absence in the literature describing the sequence of phase transformations in zirconium dioxides and its analogues indicate the complexity of the experiments the observation and study of mechanisms patterns appearance modifications during heating of samples in different environments

3.2 Experimental Study of Phase Transformations in the Samples of Zirconium Dioxides by Heating in Vacuum Heating in the Temperature 25 – 1600 °C

The experimental results (Fig. 4) heating the samples zirconium dioxides with 5 mol.% In_2O_3 in the temperature range 25 - 1600°C in vacuum show that in the range of 25 - 1000°C, there is only monoclinic modification; appears at 1100°C the tetragonal phase with the monoclinic mixture; at 1200°C, a mixture of tetragonal, cubic C-type traces and monoclinic phases; in the temperature range 1300 – 1600°C there is a mixture of cubic type C and F. The X-ray line appears on the super lattice planes (211), (400), strong lines characteristic of the phases C and dual F (Fig. 5). After cooling to room temperature, the mixture of phases C and F are stored in a mixture appear of a small amount of monoclinic modification. The monoclinic phase is in the mixture appearance due to the disintegration of one of the cubic phase. The parameters of cell calculated from the data (Fig. 5) for phase C are 1,0469 nm; for phase F - 0,5059 nm. The experimental results do not differ much

from the theoretical to the cubic type C and F zirconium dioxides, which are given in [16]. These differences to be appear associated with the formation of the solid solutions on the basis of these phases.

The formation of solid solutions based on zirconium dioxide with additives indium oxide by the reaction proceeds $(1-2x) \cdot ZrO_2 + 2x \cdot In_2O_3 = [(Zr^{4+} Zr^{3+}) \cdot 2x(In^{3+})]O_{2-x} \cdot (x Av)$, where x - concentration Av - anion vacancy that occurs when dissolved x - indium oxide, supplements. One vacancy occurs in zirconium by substituting two cations indium.

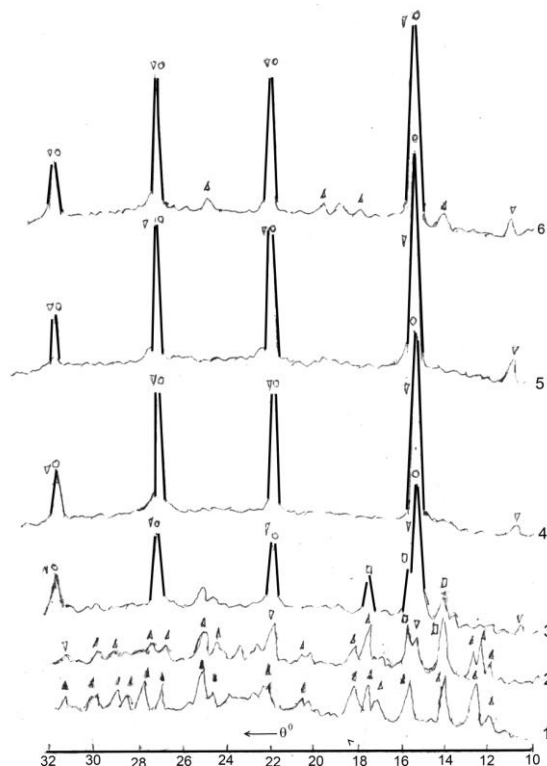


Fig. 4 – X –ray diffraction pattern zirconium dioxides with 5 mol.% In_2O_3 in the temperature range 25 - 1600°C in vacuum: 1- at 1000° C; 2- at 1100°C; 3- at 1200°C; 4- at 1300°C; 5- at 1600°C; 6- at 25°C, after heating
▲ - monoclinic phase; □ - tetragonal modification; ▼ - cubic type pyrochlore C; ○ - cubic type fluorite – F

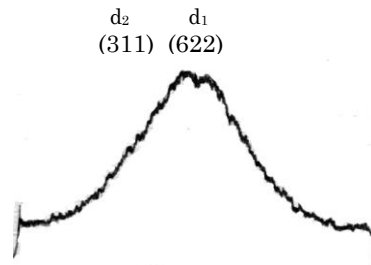


Fig. 5 - X –ray diffraction: (622) - cubic type pyrochlore C; (311) - cubic type fluorite – F- at 25°C, after heating

The proof of the existence of cubic modification of type C - pyrochlore can serve and the results of [14] - (Fig.6) 5 nm.

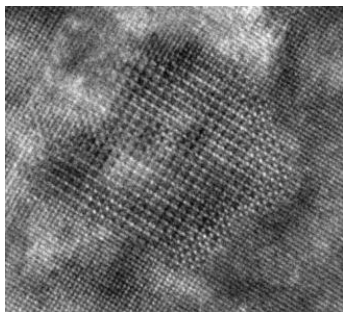


Fig. 6 - High-resolution image of inclusion monoclinic phase in the $ZrO_2+2,8 \text{ mol.}\% Y_2O_3$ sample after growth [14]

The appearance of the domains of size 5 nm zirconium dioxide with additives of 2,8 mol.% Y_2O_3 after heat treatment at 1600°C indicates cubic C-type (ZrO_{2-x}) and no new tetragonal modification ratio T^1 , $c/a = 1,004 - 1,005$.

On the date (Fig. 5) if we take the ratio enter plane distance $d_1/d_2 = 1,002$ and (Fig. 2), size of differences anion and of anion vacancies, calculated in the works [16] to zirconium dioxide show that if we take the ratio $r_A / r_{Av} = 1.004$ - the distortion which compare cubic C-type and T^1 [14]. Therefore it can be argued that in nature there cubic structure type C for connection of Zr_2O_3 .

The appearance of phase C^1 , F^1 in zirconium dioxide in this experiment could not be found, but if there

Zr_2O_3 , having a structure of type C - pyrochlore, all rare earth oxides, In_2O_3 , Y_2O_3 , Sc_2O_3 have such a structure by converting C - C^1 . Structural transformation of the F - F^1 observed on structural analog of CeO_{2-x} [17].

4. CONCLUSION

The sequence of phase transformations taking into account the type of point defects of substitution atoms and vacancies. It is shown that the structure of zirconium dioxide mechanisms exist shift of oxygen anions in the monoclinic modification, resulting in M - T-transformation and structural formation of anionic vacancies. The appearance of zirconium cations of different valences in the lattice and the accumulation of anion vacancies at 1300°C leads to the appearance of cubic modifications: C - pyrochlore type and F- type fluorite. This phase mixture is stable in the temperature range 1300 - 1600°C. Cubic phases are stored under cooling to room temperature with a small amount of monoclinic modification. The presence of the monoclinic phase is indicated by the partial decomposition of the solid solutions with the addition of indium oxide. Phase transformations occur shift anion vacancies in non-structural position. The unit cell parameters were measured for C and F phases. The presence of C-type phase zirconium dioxide indicates the existence of a direct connection to the nature of zirconium dioxide of in composite of is Zr_2O_3 .

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