MODELING THE MECHANISM OF INTERACTION OF DEFECTS IS IN CeO$_{2\text{-}x}$ AT HIGH TEMPERATURES IN AIR

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The consequent of mathematical models with elements of theory probability and experimental results, calculations permitted to determinate the energy formation of: anion vacancies ($u_{в}$~0.9 eV), border and screw dislocations ($u_{\perp}$~ 1.67 eV; u_{s} ~ 2.08 eV), and the energy of movement point defects (u_{d}~ 1.8 eV) and of movement the borders grain ($u_{з}$ ~ 0.65 eV), strain which were connected with co-operation action point defects with admixture (0.25 eV – energy of formation center painting) in CeO$_{2-x}$ at high temperatures in air.

The evaporation and disintegration harden solution on the base CeO$_{2-x}$ were determinate on the base obtained facts the next structure cubic phases $F - F^1 - C$. The process oxidation at 1500 °C accompanied of disappear the border, spiral dislocations and point defects.

Keywords: mathematical models, theory probability, process oxidation, point defects, spiral dislocations, disintegration harden solution.

Последовательность математических моделей с елементами теории вероятностей и экспериментальные результаты расчеты позволили найти энергии образования: анионных вакансий ($u_{в}$ ~ 0.9 эВ), краевых и винтовых дислокаций ($u_{\perp}$ ~ 1.67 эВ; u_{s} 2.08 эВ) и энергию движения анионных вакансий (u_{d} ~ 1.8 эВ), энергию напряжения, которая связана с объединением точечных дефектов с примесями, энергию образования центров окраски в структуре CeO$_{2-x}$ при высоких температурах на воздухе. Восстановление и распад твердого раствора приводит к фазовому превращению и появлению фаз типа $F - F^1 - C$. Процесс окисления при 1500 °C сопровождается исчезновением краевых, винтовых дислокаций, точечных дефектов.

Ключевые слова: математические модели, теория вероятности, процесс окисления, точечные дефекты, винтовые дислокации, распад твердого раствора.

Послідовність математичних моделей з елементами теорії ймовірностей та експериментальні результати, розрахунки дозволили знайти енергію утворення: аніонних вакансій – точкових дефектів ($u_{в}$ ~ 0.9 еВ), крайових та гвинтових дислокацій ($u_{\perp}$ ~ 1.67 еВ; u_{s} ~ 2.08 еВ) та енергію руху аніонних вакансій (u_{d} ~ 1.8 еВ), енергію напруження яка пов'язана з єднання точкових дефектів з домішками, енергію утворення центрів окраски (0.25 еВ) у CeO$_{2-x}$ при високих температурах у середі повітря. Випарювання та розпад твердого розчина на базі CeO$_{2-x}$ утримали фазові перетворення у структурі та появи фаз $F - F^1 - C$. Процес окислення при 1500 °C супроводжу зникати крайових та гвинтових дислокацій, точкових дефектів.

Ключові слова: математичні моделі, теорія ймовірності, процес окислення, точкові дефекти, гвинтові дислокації, розпад твердого розчина.

INTRODUCTION

The grain boundaries in polycrystalline compounds are imperfections in the crystal structure, which promotes the release of a new phase in polymorphic transformations during decomposition of solid solutions [1].

The study of the processes of interaction of grain boundaries with vacancies, with impurity atoms and dislocations is an important task for creating materials with specific properties [2].

The lack of direct observations, which could explain the mechanism of interaction of defects with grain boundaries in polycrystalline materials, indicate the difficulty of the experiments are therefore used data obtained from indirect experiments of interaction boundariies with impurity atoms and defects in oxide compounds [3 – 5].

Difficulties in determining the strength of interaction of defects (vacancies, impurity atoms and dislocations) and grain boundaries consist of a complex process. In addition to the elastic interaction, it also depends on the thermodynamic potentials, that arise is due to the appea-

rance of the boundary of the concentration gradients, as well as, electronic and chemical interactions, that occur noticeably at a considerable distance from the grain boundary [6].

One of the most important properties of the grains is their ability to move (migration) due to the influence of the effort, the interaction of impurity atoms, temperature, environment, etc. The sequence of movements of individual boundaries is a source of information about the structure of crystals [7].

In [8] provides information about what certain deviation from regular order in structure control of phase transformations of cerium dioxide at high temperature annealing in air and vacuum.

In the present work use mathematical models with elements of theory probability for the definitions energy: the formation structural defects in of cerium dioxide at high temperatures in air; the interaction of grain boundaries with defects and movement the borders grain; strain, which were connected with co-operation action of the different defects.

EXPERIMENTAL REZULTS

THE MATHEMATICAL MODELS WITH ELEMENTS OF THEORY PROBABILITY USE FOR THE FORMATION STRUCTURAL DEFECTS IN CERIUM DIOXIDE AND INTERACTION BETWEEN THEM

The samples of cerium dioxide used for the studies were obtained by the technology [8, 9] at 1800 °C (3 hours), 1900 °C (3 hours), 2000 °C (1 h), hardened in water.

They had: mostly single-phase cubic structure of type F^1 with larger unit cell parameters, and small quantity of Ce_2O_3 in the samples tempered from 2000 °C. All samples contained various defects, and grain size (~100 – 138 microns), respectively.

The microstructure of these samples is shown in fig. 1a; b; c; d: a) – samples obtained at 1800 °C had: wide grain boundaries, the color samples was of dark brown, which indicates the formation of anion vacancies, which trap the free electrons and form the centers of paints; b) – the samples obtained at 1900 °C contained: wide more angle boundaries of the grains, edge dislocations with the density equal ~6·10^{13}·1/m^2, which form low angle boundaries with different orientations to the more angular borders, the color samples was black; c) – microstructure of the grains samples obtained at 2000 °C, included: the wide boundaries of grain, the screw dislocations with different orientations and, cracked, chipped grain, color patterns was black.

Black paint samples obtained at 1900; 2000 °C indicate on the formation of new centers of paints, and the presence of edge and screw dislocations show growing stress in the samples.

The mechanism of formation defects in cerium dioxide can be described of the next formula

$$CeO_2 \rightarrow Ce_{1-x}^{4+}Ce_x^{3+}O_{2-x/2}€_{x/2},$$
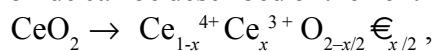
where, $€$ – anion vacancy, x – a deviation from regular order in structure .

Change the color of the samples at 1900 °C; 2000 °C due to the fact, that there is some probability of the process

$$Ce^{3+} + € \rightarrow Ce^{4+} + centers of paints.$$
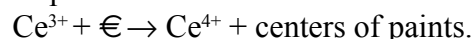
The more of these complexes are in structure of cerium dioxide it is the stronger change the color of the samples, the parameter of lattice increase considerable form consist of Ce^{3+}. The increase in the unit cell parameter of cerium dioxide in F^1-phase indicates the formation of a solid
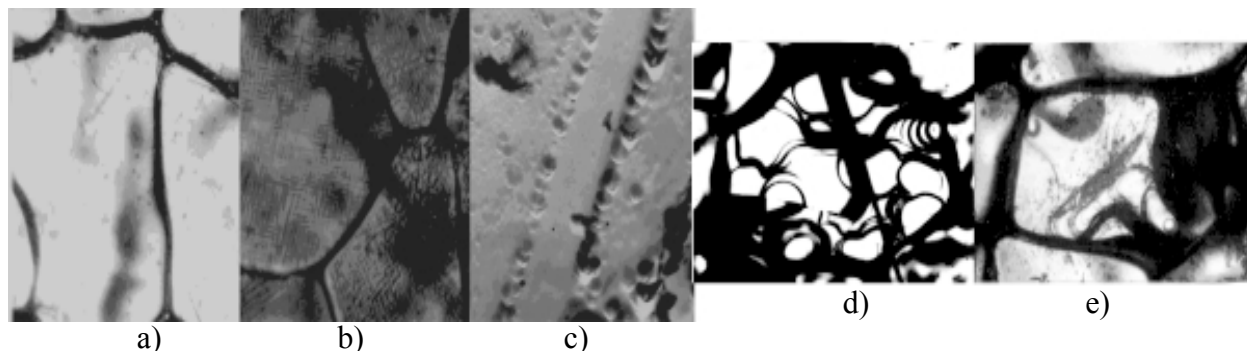

a)   b)   c)   d)   e)

Fig. 1. The microstructure of samples of cerium dioxide, received of tempering from temperature: a) – 1800 °C, X 340; b) – 1900 °C, X340; c) – 1900 °C, X17000; d) – 2000 °C, X340; e) – 2000 °C (3 hour), X340 – evaporation of cerium dioxide.

solution with increasing stress in the lattice, which lead to the formation of edge and screw dislocations.

The experimental results showed, that at: 1800 °C ($x = 0.202$); 1900 °C ($x = 0.308$); 2000 °C – $x = 0.500$), where x – a deviation from regular order in structure.

The microstructure of these samples showed, that in cerium dioxide there is a certain complex defects at each temperature. Probably, these processes have the property of the ordinary and can be consistently investigate.

CALCULATE OF THE ENERGY OF MIGRATION BOUNDARY OF THE GRAIN

Perhaps, the energy of formation of the anion vacancy, the centers of paints, the dislocations, the migration boundary grain and the mobility of defects in the structure determined by the Boltzmann equation for various states of the system: $p[A(T)] = A_0 \cdot \exp(-u/kT)$, where A_0 is about – the total frequency of the oscillations of atoms starting positions of the lattice, and A is a function of the physical parameters of the system depending on the temperature. For two states of a solid at temperatures $T_1; T_2$, use the relative probability of finding the energy states of a rigid body can be determined:

$$p[A(T_1)]/p[A(T_2)] = \exp(-u/kT_1)/\exp(-u/kT_2), \quad (1)$$

where: u – the energy state of a solid; k – Boltzmann constant; that K – temperature solid state.

$$v_1 = v_0\exp(-u/kT_1); \quad v_2 = v_0\exp(-u/kT_2), \quad (2)$$

where v_0 – the common velocity of movement of defects, performed with the initial position; $A(T) = v_1; v_2$ – the rate of the migration boundary grain at different temperatures; u – the energy of the migration boundary grain.

Relation:

$$v_1/v_2 = \exp\left[-\frac{u}{k}(1/T_1 - 1/T_2)\right], \quad (3)$$

or $\quad \ln\dfrac{v_1}{v_2} = \dfrac{u}{k}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right); \quad$ then

$$u = \frac{T_1 T_2}{T_2 - T_1} k \ln\frac{v_1}{v_2}. \quad (4)$$

The energy of migration of grain can to determine at the change of values of the grain of samples at different temperatures or the velocity of the migration boundaries of grain over a wide temperature range of annealing.

The energy of migration boundaries of grain in of cerium dioxide, determined by this method is: $u_g \sim 0.65$ eV at $1800 - 1900$ °C. The activation energy of the process recovery in cerium dioxide is $u_v \sim 0.9$ eV. Since these processes are interrelated, it is obvious, can assume that the difference in $u_v - u_g \sim 0.25$ eV, and to obtain the energy formation of centers of paints (anion vacancy + electron) in the structure of cerium dioxide equal 0.25 eV. These relations, energy (migration of the grains; these centers of paints) are connected with elastic stresses in the lattice of cerium dioxide.

The energy of migration boundaries of grain in of cerium dioxide at temperatures $1900 - 2000$ °C it equal $u_g \sim 0.85$ eV. This value is comparable with the activation energy of the formation of anion vacancies, which indicates a significant change in the chemical composition of the cationic and anionic sub lattices of cerium dioxide, and the presence of edge and screw dislocations in these samples indicate significant plastic deformation.

Increased energy of migration of grains and the presence of screw dislocations at 2000 °C is the evidence about of evaporation cerium dioxide, which proceeds with the transition in Ce_2O_{3-x} and its evaporation by screw dislocations.

According to [10], cerium oxide melts at about ~2150 °C. These data indicate that before melting cerium oxide evaporates in the form of non regular order in structure of oxides.

CALCULATE OF THE ENERGY OF FORMATION EDGE AND SCREW DISLOCATIONS

On the deviation from regular order in structure at temperatures of $1800° - 1900° - 2000$ °C define the magnitude of the formation energy edge and screw dislocations, the density of defects determined from the experiment (fig. 1).

By formula (1) in the cerium dioxide can determine the energy of formation of line defects, where the quantity $A(T) - x$ – deviation from regular order in structure of cerium dioxide at a suitable temperature, u – formation energy of the dislocation.

The energy of formation of an edge dislocation in cerium dioxide in 1800 – 1900 °C, $u_\perp \sim 1.67$ eV and the energy of a screw dislocation in the interval 1900 – 2000 °C: $u_в \sim 2.08$ eV.

The magnitude of the formation energy of the dislocation in the grains of cerium dioxide can be estimated directly from the experience. Since the experimentally observed shift of the unit cell parameter for short distances, for small shear strain, Hooke's law is valid. Poisson's coefficient $v = 0.515$, the module shear for cerium dioxide, according to [11] can be determined at different temperatures by extrapolating the straight-line relationship to the desired temperature set point. Using these data can be to estimate the energy of formation of edge dislocations on the formula, as follows:

$$u_d = \int f \cdot \beta dS, \tag{5}$$

where f – average power (per unit area of S), which is attached to a point on the surface of the crystal during the process of displacement; β – Burger vector of the dislocation [12 – 14].

As a result of these shifts occur in the crystal lattice strain, which under certain values lead to plastic deformation. The stresses in the crystals, which are a function of bias, that leaded to the formation of certain concentrations of dislocations and may be determined by X-ray method using the following equation:

$$\sum \sigma = E \Big/ v\left(\frac{a-a_0}{a_0}\right) = 2\mu\left(1 + 0.515\left(\frac{a-a_0}{a_0}\right)\right), \tag{6}$$

where σ – stress in the crystal, E – Young's modulus; v – Poisson's ratio; μ – shear modulus, a – setting the unit cell strained cubic crystal, a_0 – the lattice parameter of the unstressed crystal. Force f can be determined depending on:

$$f = \sum(\sigma_2 - \sigma_1)/\rho, \tag{7}$$

where σ_1; σ_2; σ_3 – stress in the crystal at different temperatures; ρ – density of dislocations.

The energy of formation of dislocations is determined consistently by the formula:

$u_d \sim f \cdot (a_2 - a_1)$ – for an edge dislocation, (8)
$u_d \sim f \cdot (a_3 - a_2)$ – for a screw dislocation,
where $a_{1;2;3}$ – the lattice strain of a cubic crystal.

In this way the energy of formation have been defined edge and screw dislocations, which occur at 1900; 2000 °C, respectively.

The presence of screw dislocations in the structure of cerium dioxide indicates the destruction of the cationic in sub lattice and the beginning of evaporation. The evaporation takes place on the following reaction: solid solution based on F^1 with a certain amount of Ce^{3+} enters Ce_2O_{3-x}, which evaporates on the screw dislocations. In this form the dislocation pipes of various diameters in height of the dislocation (fig. 1e) and the length of the tube on both sides can see the process of evaporation of cerium oxide, as well as glide of the dislocations.

Table 1

T, K	α^*, nm	σ, H/m^2	ρ, m^{-2}	U, eV
2073	0,5417	15·10^7	–	–
2173	0,5425	17·10^7	6·10^{13}	1,67 $\perp$ – edge dislocation
2273	0,5435	27·10^7	3·10^{13}	2,08 s - screw dislocation

$^*\alpha_0 = 0,5409$ nm. – phase type F^1 unstressed crystal.

OXIDATION OF SAMPLES OF CERIUM DIOXIDE AT LOWER TEMPERATURES IN AIR

1) Samples of cerium dioxide, obtained at 1800 – 1900 – 2000 °C temperatures, were subjected to oxidative annealing at lower temperatures in air (1600 – 1400 °C – 20 hours).

It was found that the samples obtained at 1800 °C are oxidized. This process is accompanied by a decrease in the lattice parameter and the transition phase of type $F^1 \rightarrow F$.

By changing the unit cell parameter were determined residual deviation from regular order in structure at 1600 – 1400 °C and with help of formula (1) is defined by the migration energy of anion vacancies equal $u_d \sim 1.8$ eV at phase transformation $F^1 \rightarrow F$.

The free energy migration of defect determined by the relationship:

$$F \sim (u_d - TS_d), \tag{9}$$

where u_d – energy migration of defects, T – temperature K; S_d – entropy.

The frequency of transition determined by:

$$v_d \sim Bv_0\exp(-u_d/kT), \tag{10}$$

where (10) is B – factor $\sim \exp(S_d/k) > 1$.

A defect in the crystal is moving in the direction of the force, the rate of this drift is described by the Einstein relation

$$v_d = D_d F/kT, \tag{11}$$

where $D_d \sim D_0\exp(-Q/kT)$ – (the law of Flick), (12)

where is D_0 – called the frequency factor; $Q = (u_v + u_d)$ – the energy of activation.

The heterogeneity in the solid phase at temperatures leads to the formation of gradients concentration of defects, it cause of force. Thus, the Einstein relation leads to the flow of defects:

$$v_d \sim D_d \cdot \text{grad} n, \qquad (13)$$

where D_d – is the coefficient diffusion of defects; n – concentration of anion vacancies and for cerium dioxide is: $n \sim x/4$, coefficient $D_0 \sim 9.5 \cdot 10^{-5}$.

We find the parameters of the unit cell and values x at the temperatures: x – at 1600 °C and 1400 °C and determine the velocity of flow:

at 1600 °C: $v_d \sim 2 \cdot 10^{-13}$ m²/s and velocity of movement boundaries of grain $\sim 2.2 \cdot 10^{-10}$ m/s;

at 1400 °C: $v_d \sim 2.5 \cdot 10^{-15}$ m²/s, velocity of movement boundaries of grain $\sim 1.4 \cdot 10^{-10}$ m/s.

2) The samples, cerium dioxide, obtained at 1900 °C and with consisting of the borders dislocations investigated by high-temperature X-ray at 1500 °C in air with different exposures (tabl. 2).

The exposures of simple at 1500 °C (30 – 240 minutes) observation a jump of parameter of the phase cubic type F^1 and appear on X-ray lines characteristic for Ce_2O_3 (fig. 2). The intensity of these lines increases with increasing exposure time to 360 minute, indicating a significant concentration of this phase.

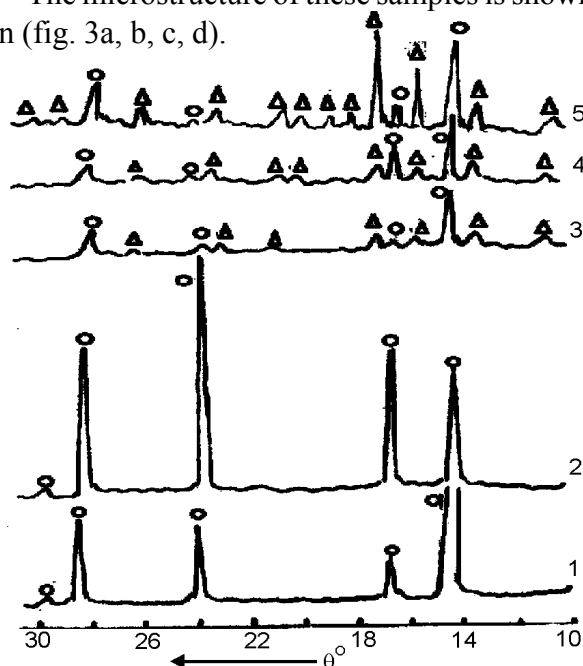The microstructure of these samples is shown in (fig. 3a, b, c, d).

Fig. 2. X-ray diffractions of phase transformation F^1-type fluorite of cerium dioxide at 1500 °C in air, received at: 1 – 60; 2 – 120; 3 – 240; 4 – 600; 5 – 1200 minutes, ≈ – the phase of F^1-type, ▲ – the phase C-type.

Table 2

The values of parameters of phase F^1-type fluorite of cerium dioxide at 1500 °C in air

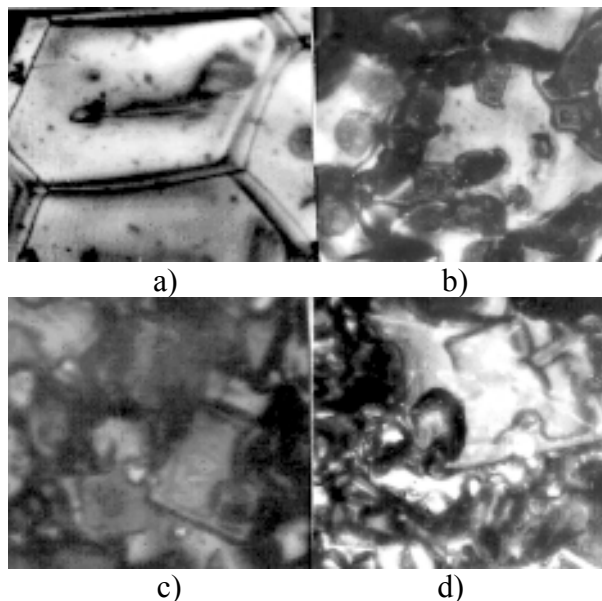| Tame exposures, min	a, nm at direction [311]
30	0,5528
60	0,5528
120	0,5526
180	0,5525
240	0,5521
300	0,5521
360	0,5521

Fig. 3. The microstructure samples of phase F¹ type fluorite of cerium dioxide at 1500 °C in air: a) – 120; b) – 240; c) – 600; d) – 1200, (tame exposures, minutes), X340.

After holding of the samples in during 120 minute was drift on the grain boundaries, and the shift in one direction. Further holding of the samples at this temperature leads to a square plate on these borders and these crystals can be seen as the lists an open book. Then there is a marked increase in individual of the phase cubic type C of cerium dioxide and the velocity increase equal $\sim 1.1 \cdot 10^{-9}$ m/s. This value is an order of magnitude greater than the rate of migration of grain boundaries of cerium dioxide at temperatures of 1400 – 1600 °C, that indicates a large rate of formation of free complexes containing Ce^{3+}, the decay of solid solutions based on F^1, which the grating was very tense, and the microstructure contains mixed the phases: F^1 and C-type of cerium oxide.

3) The samples, cerium dioxide, obtained at 2000 °C and with consisting of the screw dis-

locations which was obtained at 2000 °C and then annealed at 1500 °C in air with different exposures (fig. 4). The oxidation process is accom-panied by the gradual disappearance of the rotation and screw dislocations, increasing the width of the cracks and chips. Isolation of *C*-type cubic phase of cerium oxide in these samples is considerably less, indicating that evaporation of the cubic phase of *C*-type on the screw dislocations at 2000 °C.
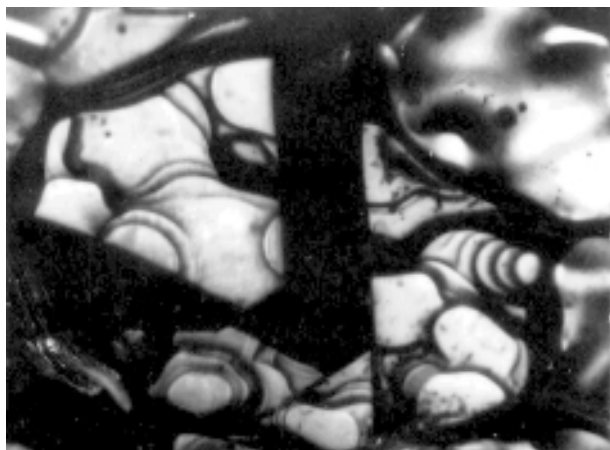
a)

b)

Fig. 4. The microstructure of samples of cerium dioxide, which obtained at 2000 °C, and then annealed at 1500 °C in the air: a) – 600, b) – 1200, (tame exposures, minutes), X340.

CONCLUSION

Modeling the mechanism of interaction of defects is in CeO$_{2-x}$ at high temperatures in air, was founded on the mathematical models with elements of theory probability, which use for the formation of the structural defects in cerium dioxide and interaction between them.

The evaporation of cerium dioxide in interval of temperatures 1800 – 2000 °C in air be accompanied appearance definite complex of defects (the boundary of grain – anions vacancy, center of paint; the boundary of grain - border and spiral dislocations).

The mathematical calculations and experimental results, realization on the by high-temperature X-ray diffraction – the change of parameters in the unit cell, composition of phases and the microstructure of samples of cerium dioxide as at evaporation, so and at oxidation per missed to define the correctly methods at of interaction of defects in structure of cerium dioxide.

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