INFLUENCE OF DOPANT AMOUNT ON EVOLUTION OF ZIRCONIA CRYSTAL ENERGY

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Abstract: *Tetragonal crystals were formed at addition of yttrium oxide on concentration range from 2 to 4 mol. %. It was estimated the thermodynamic functions of these systems, in particular on values of free surface energy (G_s) and elastic energy (G_e) of crystals and their ability to respond on change of external conditions – temperature. It was shown for range of small sizes (size decreases at temperature growth) the concentration of dopants practically doesn't influence on dynamic of change of G_s then as for range of particles size of 15-35 nm the concentration of dopant more significantly influence on the G_s. Analysis of dynamic of change of G_s and G_e values shows that for systems which have been formed at heat treatment before 700°C the change of these thermodynamics functions is bigger. In this time the dynamic of change of total G_s + G_e value for systems which was synthesized at different temperatures shows the influence on yttria concentration.*

Keywords: METASTABLE NANOPARTICLES, SURFACE FREE ENERGY, SURFACE ELASTIC ENERGY

1. Introduction

The feature of zirconia is polymorphism [1-3] and its polymorphic forms (monoclinic, tetragonal or cubic) are stable in different ranges of the temperature and pressure. For un-doped zirconia at atmospheric pressure monoclinic phase is stable up to 1000^{o}C and above this temperature it transforms to tetragonal which is stable up to 2500^{o}C, cubic crystals of zirconia form only after 2500^{o}C. With another side the range of stability of the phase can be change by introducing of different dopants (for example, yttrium ions) [4] to zirconia or as result of decreasing of particles to nanosizes (NPs) [5]. The introduction of adding ions to zirconia lattice allow forming the solid solution at its future calcination and formed phase depend on amount and nature of dopants [6]. Usually the formation of metastable phase is realized at a small concentration of dopants and calcination of low temperatures. For Y doped ZrO_2 NPs the tetragonal phase is stable at yttrium ions concentration from 2 to 4 mol. % in zirconia. These zirconia NPs are metastable objects not only due to nanodimension but also due to tetragonal phase. The properties of these objects are labile to external action, in particular temperature, pressure, dopant concentration. The properties of nanosized particles are determined by a large share of surface atoms in system [7] and their behavior as NPs systems (ability to aggregation, consolidation processes other) depends on thermodynamical properties of surface. In this work we estimated the influence of yttrium ions concentration in tetragonal zirconia on thermodynamical properties of surface NPs which was formed at temperature region of 500-1000^{o}C for prediction of behavior of NPs under pressure.

2. Preconditions and means for resolving problems

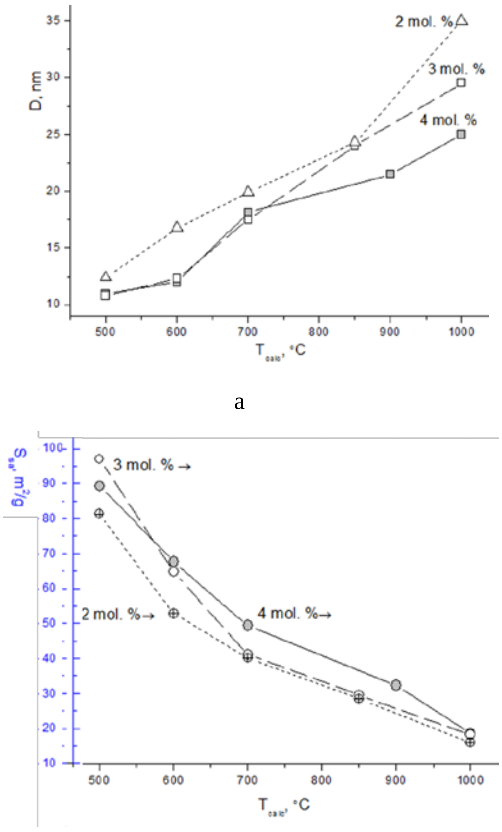
2.1 Synthesis and characterization of zirconia metastable NPs

Co-precipitation method was choosing for synthesis of zirconia NPs. The forming of Y doped zirconia occurs due to decomposition of amorphous xerogel – dehydration of NPs (physical and chemical adsorbed water lost in temperature range of 20-300^{o}C) and crystallization in temperature range 400-500^{o}C. The growth of NPs was observed at follow heat-treatment of NPs at temperature region of 500-1000oC. It was shown phase composition and size of NPs depend on amount of yttrium ions which was introducing in zirconia and calcination temperature of crystals, see table 1. According to presented data the introduction of yttrium ions in zirconia in amounts of 2-4 % led to forming of tetragonal crystals and the increasing of dopant concentration increase the stability of tetragonal phase in synthesized NPs. The increasing of yttrium oxide amount from 2 to 4 mol. % lead to decreasing of amount of monoclinic phase in system from 5% to 1%.

Table 1 *–Phase composition of doped zirconia NPs*

Y_2O_3, mol. %	Phase, % / D, nm, / S_{sa} m^2/mol				
	T_{calcin}, °C				
	500	600	700	850	1000
2	95T-5M	94T-6M	93T-7M	94T-6M	94T-6M
3	96T-4M	98T-2M	97T-3M	97T-3M	95T-5M
4	99T-1M	98T-2M	99T-1M	99T-1M	99T-1M

Fig.1 shows the change of NPs size which was estimated by XRD experience and specific surface area with temperatures rise.



a

b

Fig.1 *Influence temperature on parameters of doped NPs a) size, b) specific surface area*

It was noted the temperature practically doesn't influence on phase composition of synthesized system at same dopant amount. At the same time the NPs size increases and specific surface area of NPs decreases with calcination temperature rise. Thus all investigated systems can be described as tetragonal crystals but their different structural characteristics do not allow considering them as thermodynamical equivalent systems.

2.2 Scheme of calculation of surface free energy (G^S) and elastic free energy (G^E)

According to Gibbs thermodynamics all over characteristics of nanosystems have been seen as surface characteristics. The value of over free energy (G^S) another words a surface free energy is

$$G^s = \gamma \cdot A \tag{1}$$

where γ - specific surface energy; *A*- surface of tension – for nanoparticles with size above 1 nm the surface tension is equal the geometric surface (further specific surface area).

The surface of real crystals contains different planes with different surface energy and so surface free energy of NP is sum of energies of all planes. For tetragonal phase is 5 non-equivalent directions whereas monoclinic phase has 9 non-equivalent directions [8]. For simplification of calculations at estimation of surface free energy the quasi-isotropic approximation for each phase usually was used, in particular, for zirconia case, γ^t is 1,52 J/mol, a γ^m is 1,70 J/mol [8]. For crystal phase two independent ways of increasing of energy are the increasing of surface atoms or changing of elastic deformation of crystals. For this case total free energy of dispersive systems can be noted as

$$G = G^V + G^S + G^E , \tag{2}$$

where G^V is a Gibbs free energy , G^E is elastic free energy.

According to [9] the elastic free energy may be estimated as

$$G^E = PV = (P_i + P_e) \cdot V = (4f / D + P_e) \cdot V , \tag{3}$$

where V is molar volume (m^3/mol) D is particles size (м); P_e is external pressure; P_i is internal pressure, f is parameter which describes the surface stress that it is necessary for increasing of surface unit. In work [9] they are 5,71 J/m^2 for tetragonal phase and 5,30 J/m^2 for monoclinic phase.

The surface free energy and elastic free energy for nanoparticles with different amounts of dopant were calculated by equations (2) and (3). It is necessary noted the same values, in particular surface tension (σ) depend on nanoparticles size [10]. The dependence of surface tension from nanoparticle size The Gibbs- Tolman -Kenig-Buffs equation (GTKB) described a dependence of surface tension from nanoparticle size. The work [11] presented the exact solution of this equation and shown that particular solutions of GTKB equation are Rusanov (4), Tolman (5) and Gibbs (6) equations:

$$\sigma = 0.304\sigma^{\infty} \frac{r}{\delta} , \tag{4}$$

$$\sigma = \frac{\sigma^{\infty}}{1 + \frac{2\delta}{r}} , \tag{5}$$

$$\sigma = \sigma^{\infty} \exp(-\frac{2\delta}{r}) , \tag{6}$$

where δ is Tolman length; *r* is particle size, nm.

These equations have a determined boundary conditions, thus the Rusanov equation was used at condition of $r \le \delta$, Tolman equation was used for calculation when $r > 10\delta$ and Gibbs equation is valid for big particles radius. We used the Tolman equation in our calculation because the typical values (δ) lie in range from 0.1 to 1 nm.

In framerwork of Debay theory the Tolman length was described by next equation [11]:

$$\delta = r\left[\left(\frac{r^2 - (6h - \eta) \cdot r + 9h^2}{r^2 - (6h + 2\eta) \cdot r + 9h^2}\right)^{1/3} - 1\right], \tag{7}$$

where $\eta = 3h(a - 1)/2$; *h* is height of atomic layer, *a* is shown how much the standard deviation of atoms on surface is different on standard deviation of atoms in bulk (usually this values change from 2 to 4); r is nanoparticles radius.

The height of atomic layer is calculated in according to equation [12]

$$h = (\frac{V}{N_A})^{1/3} . \tag{8}$$

The molar volumes of monoclinic and tetragonal phases are 7.39 cm^3/mol and 6.73 cm^3/mol, accordingly. According to (8) *h* was estimated as 0.333 and 0.322 for monoclinic and tetragonal phases, accordingly. The value of *a* was calculated with using of data about the diffusion of atoms in bulk and surface (coefficient of atom diffusion was took from [13]) and a is equal 2.4. The values of η is estimated as 0.6762 and 0.6993 for monoclinic and tetragonal phases, accordingly.

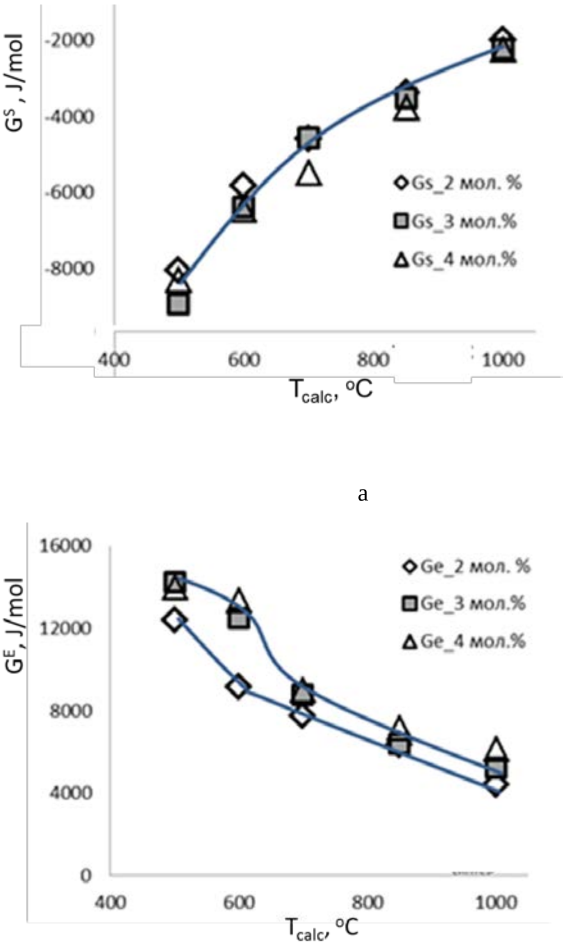
2.3 Change of surface free energy (G^s) and elastic free energy (G^E) at dopant concentration act

The estimated Tolman length, surface tension, internal energy, molar surface, internal energy and amount of surface atoms are presented in tabl. 2.

Table 2 – *NPs characteristics of ZrO_2-Y_2O_3 with different concentration of Y_2O_3 and calcination temperatures*

T, °C	δ, nm	σ, J/m^2	$S_{sa,}$ m^2/mol	U^s, J/mol	Surface atoms, %
2 мол. % Y_2O_3					
500	1,143	0,804	10035	8064	14,7
600	0,970	0,894	6527	5833	11
700	0,909	0,930	4962	4614	9,4
850	0,857	0,964	3522	3395	7,7
1000	0,793	1,008	1973	1990	5,4
3 мол. % Y_2O_3					
500	1,272	0,747	11970	8949	16,8
600	1,149	0,801	7992	6398	14,9
700	0,954	0,903	5071	4579	10,6
850	0,859	0,962	3657	3519	7,8
1000	0,818	0,999	2232	2232	6,4
4 мол. % Y_2O_3					
500	1,252	0,756	11007	8319	16,5
600	1,208	0,774	8347	6465	15,9
700	0,963	0,897	6107	5482	11,9
850	0,887	0,944	3989	3766	8,7
1000	0,851	0,968	2302	2229	7,5

Fig.2 shows the dependence of ZrO_2-Y_2O_3 crystal energies from changing of Y_2O_3 amount and calcination temperature, in particular G^s, G^e. It was shown that the decreasing of NPs size led to rise of surface free energy of investigated systems. Analyses of dynamics of changing of surface free energy (G^s) from NPs size (D) shows that two regions with different behavior of $G_s(D)$ can be marked for investigated NPs size diapason. For diapason of small NPs sizes up to 15 nm the quick growth of G^S was observed when the NPs size decreases and for diapason of sizes bigger than 15 nm the G^S shows more slow growth at decreasing of NPs sizes.



a

B

Fig.2 *The dependence of ZrO_2-Y_2O_3 crystal energies on calcination temperature a)G^S, b) G^E*

Analyses of data (tabl.2, fig.2 and fig.1) shows that the difference of dynamics of changing of $G^s(D)$ between systems with different concentration of Y_2O_3 for NPs sizes of 15-30 nm was caused by some factors. It is size factor (at rise of Y_2O_3 concentration the growth of NPs is slowly at high temperature range) and factor of decreasing of aggregation of nanoparticles to each other. The inflection point on $G^s(D)$ curve corresponds to NPs which were synthesized by heat treatment at 700°C. According to principles of size and structural states at forming crystal under heat treatment the phase must be formed such that sum of surface and elastic energy is minimized.

Fig 3 shows the dependence of $G^S + G^E$ from changing of Y_2O_3 amount and calcination temperature. Analyses of calculations of G^S and G^E values show a bigger change in energetic characteristics of NPs systems at forming of NPs in temperature diapason up to 700°C. At the same time the dynamics of change of sum G^S+G^E shows to dependence on Y_2O_3 concentration for systems which were synthesized at different temperatures. The reduction of G^E with temperature increases is monotonic but for systems with Y_2O_3 concentrations of 3-4 mol. % curves G^E-T has a step in the temperature range of 500-600°C. For system ZrO_2-2 mol.% Y_2O_3 the sum of G^S+G^E monotonic decrease at calcination temperature rise, see fig.1. For systems with Y_2O_3 concentrations of 3 and 4 mol. % the sum of G^S+G^E has a complex character. In this case two systems which were synthesized by heat treatment at 600°C and 850°C deviated from monotonic curves. There are especial points.

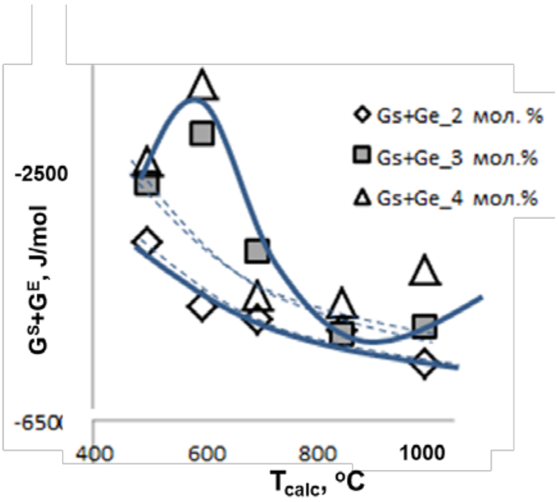


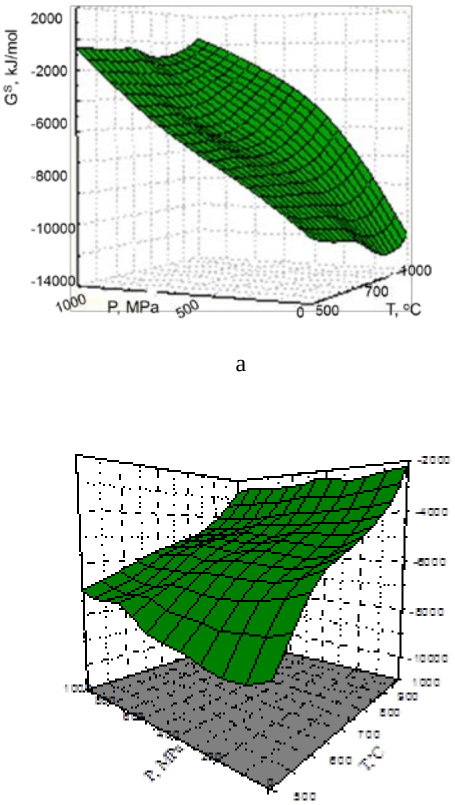
Fig. 3 *The dependence G^S+G^E on calcination temperature*

What are reasons of these deviations? The answer may be connected with the processes which take place at forming NPs in these conditions. The nucleation of crystals take place at crystallization in temperatures range of 400-500°C, the growth of crystals takes place at heat treatment above 500°C. Mechanism of NPs formation is oriental connection [14]. It was known that together with growth of NPs the water loss from NPs surface was observed at heat treatment at 500-700°C. For example, for ZrO_2-3 мол. % Y_2O_3 a water loss is about 33% at heat treatment up to 500°C, and at next temperature rise on 100°C the system lose additionally 3% and 8% water component. The water loss above 700°C practically has not observed.

When water are removed from NPs surface the forming of oxygen vacancies takes place it is possible reason for appearance of elastic deformation on NPs surface. Therefore a rise of NPs size happens slowly at heat treatment in range 500-600°C and contribution of $G^S + G^E$ sum in Gibbs free energy of such systems is a bigger. In this temperature range NPs surface has a big amount of oxygen vacancies but at heat treatment under more high temperatures the oxygen vacancies disappear during the annealing under air. Another reason of such deviation may be dehydration process which also occurs in this temperature range and which led to creation of non-relaxing or non-reconstruction surface. These facts may be connected with the decreasing of NPs growth in this temperature range because the processes of surface rebuilding carried out. In the range of more high temperatures of 800-1000°C the deviation of $G^S + G^E$ sum from monotonic characters may be connected with rebuilding of surface structure of NPs which appearance due to remove of occluded chloride ions or atoms on NPs surface.

Such complex behavior of surface thermodynamical functions may be reasons of complex behavior of NPs with different calcination temperatures under pressure [15]. Fig.4 shows the surface of $G^S(T)$ from external pressure changing. It was shown that the systems have a complex relief of surface of surface free energy. The presence of local minimums and maximums on surface of surface free energy shows on minimization of system energy due to reorganization of its surface state.

It was noted that the increasing of dopant amount in zirconia led to rise of terminal OH groups. It is promoted the creation of oxygen vacancies at removing of these kinds of hydroxyl under heat treatments of NPs. The NPs surface state can be change by their reconstruction or relaxing as results of removing of OH groups, residual chloral, oxygen vacancies creation and their annealing by oxygen at NPs synthesis.



a

b

Fig. 4 Surface of $G^S(T)$ from external pressure changing

a) ZrO_2- 3 mol. %Y_2O_3, b) ZrO_2-4 mol. %Y_2O_3

Non stechiometric of surface which was creations under doping and temperatures actions led to form different defective plans of tetragonal plane and more developed energetic relief of surface of such NPs. Pressure action on these systems changes the phase composition [15] and as results the system energies due to its reorganization. For doped zirconia at increasing of dopant more developed relief of surface of surface free energy $G^S(P,T)$ was observed. It may be evidence about more big labilities for systems with bigger dopant amount which can restrain T-M martensitic T-M transition

Conclusion

Thus influence of Y_2O_3 dopant concentration up to 2 mol. % on surface state and crystal energy is monotonic and point about 700°C on curve G^S+G^E versus T is inflection point. The increasing of dopant up to 4 mol. % led to realize of complex dependence on crystal energy from calcination temperature. It is also influence on complex behavior that these NPs show under pressure [15].

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