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Phase Composition of Zirconium Dioxide Stabilized With Yttrium

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Abstract. The results of X-ray and thermodynamic analysis of the phase formation in the system Zr-YO, which is the starting material for the formation of yttrium-stabilized ceramic zirconia. Found that the material is multiphase and contains monoclinic, cubic and tetragonal zirconia weight ratios which vary considerably.

Introduction

Yttrium is a stabilized ceramics based on zirconium dioxide takes a special place in the list of promising types of ceramics and finds a wide application in various industries, as it has a high strength in bending, fracture resistance, acid and corrosion resistance, wear and heat resistance, good biocompatibility and extremely low friction coefficient with metals. The remarkable properties of ceramics based on zirconium dioxide, certainly caused by features and regularities of interatomic interactions and phase formation taking place in the Zr-Y-O system, as evidenced by the results presented in [1,2].

The aim of the work is the analysis of the phase formation regularities in the Zr-Y-O system, which is the initial material for the formation of yttrium-stabilized ceramics on the basis of zirconium dioxide.

Results and Discussion

In the investigated compounds based on ZrO_2-$YO_{1.5}$ zirconium belongs to the transition metals, and is characterized by the presence of two electrons by the unfilled 4d-shell and two electrons by the outer 5s-shell. On the one hand, yttrium recommended to be called as a rare-earth metal (REM), and on the other hand, due to the presence of the electron by the 4d-shell, the properties of yttrium determine it as a transition metal. Herewith, yttrium takes a special place among the REM, and it is because of the fact that Y atoms have no f-electrons. The third component in the compound of ZrO_2-$YO_{1.5}$ is oxygen, which is significantly different in chemical properties in relation to the transition metals, particularly to Zr and Y, and an explanation of this lies in different electronic structure of atoms of these elements. The atomic radius of oxygen is significantly smaller than the sizes of metallic elements ($R_0 = 0.089$ nm with valence -2, $R_{Zr} = 0.1602$ nm). Variable valence of O atoms, an electron attachment ease of other elements, and also the opportunity of release of their electrons in the interaction reactions contributes to the formation of oxygen solid solutions in Zr and Y crystal lattices, and the formation of suboxides [3-5] (Fig. 1). The ultimate solubility of oxygen can vary from thousandths and hundredths to tens of atomic percent. In α-Zr oxygen solubility reaches 29 at. %. In β-Zr of oxygen up to ~10.4 at. % is dissolved. Oxygen is dissolved in yttrium to large values, and this value depends on the crystal modification: 30.4 % [at].% O is held fixed in β-Y; in α-Y – 15,9 % [at.% O [6].

Table 1. Structural data of the compounds formed in the system of Zr-O

№	Compound	Prototype	Pearson symbol, sp. gr	Unit cell parameters, [nm]	Note	Source
Zr–O system						
1	γ-ZrO$_2$	CaF$_2$	*cF*12, $Fm\bar{3}m$	*a*=0.509 *a*=0.5272	T=2400°C	[6]
2	β-ZrO$_2$	HgI$_2$	*tP*6, *P42/nmc*	*a*=0.364 *c*=0.527	T=1250°C	[6]
3	α-ZrO$_2$	ZrO$_2$	*mP12,* *P*2$_1$/c *mP12,* *P*2$_1$/c	*a*=0.51505 *b*=0.52116 *c*=0.53173 β= 99.230°		[6]
				a = 0.51415 *b* = 0.52056 *c* = 0.53128 *β* = 99.30	T<1205°C	[9,10]
4	δ-ZrO$_2$	–	*Pbcm*	*a*=0.5007 *b*=0.5227 *c*=0.5058	At T=600°C and P=6 GPa	[6]
5	δ-ZrO$_2$	–	*oP*16, *Pbcm*	*a*=0.50364 *b*=0.52546 *c*=0.50855	3<P<12.5 GPa	[11]
6	ε-ZrO$_2$	PbCl$_2$	*oP*12, *Pnma*	*a* = 0.562 *b* = 0.3347 *c* = 0.6503	P> 12.5 GPa	[11,12]
7	ω-ZrO$_2$	MnF$_2$	*tP*12 $P\bar{4}m2$	*a* = 0.5046 *c* = 0.5219	3.5 < P < 15 GPa	[11]

Oxygen with transition metals can give compounds with an ordered structure formed from solid solutions; in the systems of metal - oxygen numerous phases of variable composition are formed - from suboxides to peroxide compounds. This phenomenon is clearly seen in Zr and Y. Namely, a great variety of different phases and various polymorphic transformations at different temperatures and pressures is observed [7]. Also, these facts are confirmed by Zr-O systems (Table 1) and Y-O (Table 2), due to the different nature of chemical bond in these compounds. An important point is that typically metallic bond existing in solid solutions of metals with oxygen, in the individual phases and compounds begins to move in a covalent and ionic in the gradual going from one compound to another. The manifestation of intermediate types of bonds (a combination of metallic type of bonding with covalent, and covalent with ionic bonding, etc.) is also possible. The structural parameters of the compounds formed in the systems of Zr-O, Y-O and ZrO$_2$–YO$_{1,5}$ are systematized and presented in Table. 1 and Table 3.

According to the data presented in the reference book [6], phase diagram of Y-Zr system refers to the eutectic type, without the formation of intermetallic compounds and solid solutions. Zirconium decreases transformation temperature α↔β in yttrium to 1063 ° C in temperature by the eutectoid reaction (β-Y) ↔ (α-Y) + (β-Zr). Yttrium increases transformation temperature α↔β in zirconium up to 886°C by the peritectoid reaction (β-Zr) + (α-Y) ↔ (α-Zr). The solubility of yttrium in zirconium is not high ≈0.5 at. % (Fig. 1) [6].

Table 2. Structural data of the compounds formed in the system of Y-O

№	Compound	Prototype	Pearson symbol, sp. gr	Unit cell parameters, [nm]	Note	Source
1	γ-Y_2O_3	Mn_2O_3	*cI*80, *Ia3*	*a*=1,0605		[6]
				a=1,0605 *a*=1,0601 *a*=1,0604	High-temperature	[13]
2	α-Y_2O_3	Sm_20_3	*mC30*, sp.gr. *C2/m*	*a*=1,391, *b*=0,3483 *c*=0,8593 β=100,17°		[6]
3	β-Y_2O_3	La_20_3	*hP5*, $P\bar{3}m1$	*a*=0,3805 *c* = 0,6085	T=2330°C	[6]
				a = 0,381 *c* = 0,608	T∈2445÷2327 °C	[14]

Table 3. Structural data of the compounds formed in the system of ZrO_2–$YO_{1.5}$

№	Compound	Prototype	Pearson symbol, sp. gr	Unit cell parameters, [nm]	Note	Source
1	δ-$Zr_3Y_4O_{12}$	$Zr_3Y_4O_{12}$	*hR*5 $R\bar{3}$	*a* = 0.97345 *c* = 0.91092		[16]
				a = 0.9738 *c* = 0.9115		[17]
				a = 0.9723 *c* = 0.909		[18]
2	ZrY_6O_{11}				At T > 1750°C	[15]
3	$Zr_2Y_2O_7$				T∈1100-2530°C	[15]
4	α-$(Y_{1-x}Zr_x)_2O_{3+x}$	Mn_2O_3	*cI*80, $Ia\bar{3}$		0.85<x<1, T < 2327°C	[19]
				a=1.025+0.352x	0.65 < x < 0.9	[20]
				a = 1.0546	x = 0.835	[21]
				a = 1.058	x = 0.925	[21]
5	β-$Zr_{1-x}Y_xO_{2-x/2}$		*tP*6 $P4_2/nmc$	*a* = 0.36055 c = 0.51797	T=2377-1009°C 0 < x < 0.047	[19]
				a = 0.5106 *c* = 0.51808	3 mol% Y_2O_2	[22]
				a = 0.5095 *c* = 0.5180	2 mol% Y_2O_2	[23]
				a = 0.5098 *c* = 0.5180	4 mol% Y_2O_2	[23]
6	γ-$Zr_{1-x}Y_xO_{2-x/2}$	CaF_2	*cF*12 $Fm\bar{3}m$	*a* = 0.5132	T<2785°C 0 < x < 0,69	[19]
				a=0.5104+0,0204x	0.18 < x < 0.9	[20]
				a=0.511+0,030x	0.08 < x < 0.56	[24]
				a =0.51478	x = 0.182	[25]

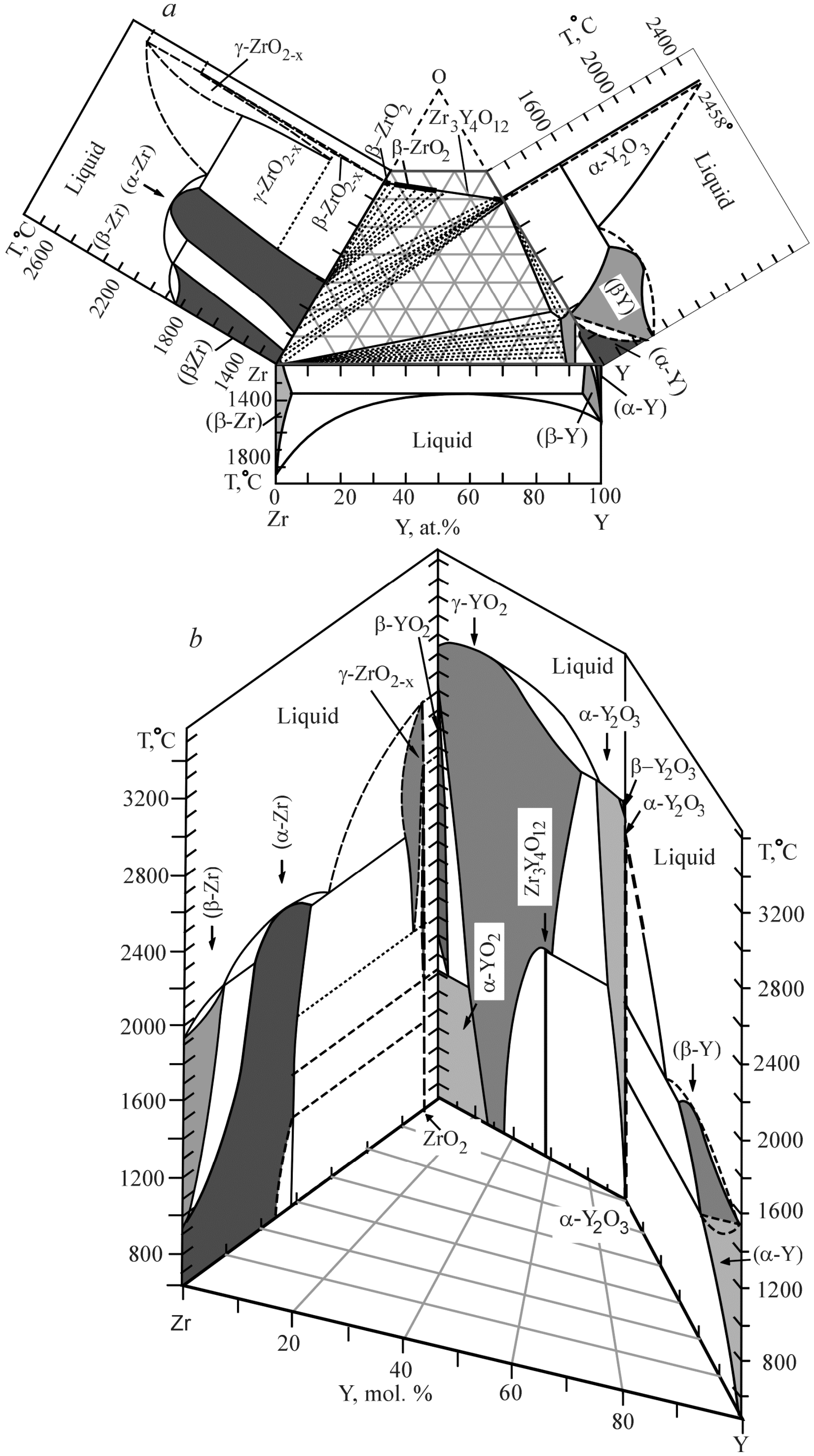

Fig. 1. Binary diagrams of Zr-Y, Zr-O, Y-O systems [6] and isothermal cross-section of the ternary Zr-Y-O system at 1200°C [15,26] (a); a spatial view of the phase diagram of the ternary Zr-Y-O system constructed on the basis of Zr-O, Y-O binary systems [6] and the quasi-binary system of ZrO_2–$YO_{1,5}$ [13,19] (b)

The results of a systematic analysis of the literary sources presented in Tables 1-3 and in Fig. 1, have been confirmed in diffraction studies of ZrO_2 + 3% (mol) Y_2O_3 system. Fulfilled diffraction studies (X-ray diffraction (X-ray phase analysis) and electron beam diffraction (electron microscopic microdiffraction analysis)) have shown that zirconium dioxide powders, partially stabilized with yttrium, are the multiphase material (Table 4). To our mind, the main reason is a heterogeneous distribution of yttrium being a stabilizer of a high-temperature modification of zirconium dioxide. A separation should be given to a heterogeneous distribution of yttrium in the material volume specified by technological factors, taking place in the powder production, and a heterogeneous distribution of yttrium specified by the degree of the powder particles perfection. The availability of the crystal structure defects in the material (vacancies and their complexes, dislocations, intraphase low and high-angle boundary of a general and special type), and this fact has been detected while investigating the powder structure using electron microscopy method, can lead to a redistribution of yttrium ions and their yield of defects. Such yttrium ions remaining in the material volume cease to have a stabilizing effect on the crystal lattice of zirconium dioxide, it leads to a reduction of the stability level of its high-temperature modification [27].

Table 4. The list of reference phases, integral and relative intensities of diffraction lines of phases

№	Phase	Chemical formula	I	I [rel], %	V [wt], %
1	96-230-0297_Mono (m)	O_8Zr_4	567.8	9.2	24.5
2	96-230-0299_Ytry_Tetra (t)	O_2Zr	0.027	4.4×10^{-4}	0.7
3	96-500-0039_Cubic (k)	O_8Zr_4	3.9×10^{3}	63.6	0.8
4	96-900-5834_Mono (m)	O_8Zr_4	890.1	14.4	0.09
5	96-900-7449_Mono (m)	O_8Zr_4	614.9	9.9	73.1
6	96-900-9052_Cubic (k)	O_8Zr_4	1.32	0.02	0.8
7	96-900-9920_Orto (o)	O_8Zr_4	0.49	7.9×10^{-3}	1.6×10^{-4}

Note: I - the calculated values of the integral intensity of the phases; I (rel.) - the relative intensity of the phases in the integral intensity; V(wt) - weight fraction of the phases, taking into consideration the atomic composition of the unit cells.

Conclusion

The systematic analysis of the literary sources has been carried out and the variety of phases formed in the system of Zr-Y-O has been found. It has been shown that multi-phase ceramic material caused by the features of the oxygen interaction with transition metals, which allow to set up compounds with the ordered structure formed from solid solutions; numerous phases of a variable composition - from suboxides to peroxide compounds. The diffraction studies (X-ray phase and electron microscopic microdiffraction analysis) of the phase composition and the state of the ceramic material defect substructure of ZrO_2 + 3% (mol) Y_2O_3 composition have been implemented. It has been established that the test material is multiphase and contains a wide range of modifications of zirconium dioxide and their weight ratios are greatly different.

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