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ANALYTICAL EXPRESSIONS OF THE Fe -Zr - Si - Al SYSTEM AND PHASE COMPOSITION OF THE COMPLEX ALLOY OF FERRUM-SILICON-ZIRCONIUM

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Preliminary Note – Prethodno priopćenje

The goal there was constructed a diagram of the state of the system Fe-Zr-Al-Si by method of thermodynamic diagram. With the help of modeling, it is possible to track the phase structure a complex alloy of ferrum-silicon-zirconium. As a result of the calculations, it was found that the Fe-Zr-Al-Si metal system consists of 12 elementary tetrahedron. The sum of the relative volumes of elementary tetrahedron of the Fe-Zr-Si-Al, system equals one (1,00000), which confirms the correctness of the tetrahedron. The analytical equation of each tetrahedron is obtained. As a result, the alloy with a content of 25 % Zr is modeled by the Si-Fe_2Al_5-$FeSi_2$-Zr_6Si_5 tetrahedron. The compositions of the alloy with 35 and 50 % Zr are decomposed in the Si-Fe_2Al_5-$FeSi_2$ - Zr_6Si_5 and Zr_5Si_3-Fe - Fe_2Al_5-FeSi tetrahedra.

Keywords: Fe-Zr-Si-Al, thermodynamic-diagram, phase, Heath method, tetrahedron.

INTRODUCTION

As the analytical review of the world market for the extraction of mineral raw materials shows, there is less quality ore raw materials every year, and the demand for high-quality metal is growing. The solution to this problem is the development of a new alloy complex with various physical and chemical properties. One example of such alloys is a complex alloy of ferrum-silicon-zirconium, where does he get alumothermia [1]. To improve the quality of steel and introduce new technologies, it is necessary to study in detail the physical and chemical processes of smelting complex alloys. It should be noted that the known thermodynamic studies of processes in multicomponent systems are quite complex and require huge labor, material and time costs to determine the mathematical calculations of a large number of independent reactions.

An alternative variant to the classical thermodynamic study of processes in metallurgy is method of analyzing geometric thermodynamics - thermodynamic diagram analysis (TDA), developed by the Chemical Metallurgical Institute (CMI).

This method has proven to be the simplest and at the same time one of the most accurate methods in the study of phase transformations of thermodynamic process [2, 3].

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RESEARCH METHODOLOGY

According to the goal, was analyzed TDA of the Fe-Zr-Al-Si metal system. Using this diagram, it is possible to predict the phase composition of a complex ferrum-silicon-zirconium alloy at different element contents. This indicates the tetrahedron where the necessary grades of the resulting alloy are formed. This is the meaning of the calculations f the TDA of a multicomponent system.

The Fe-Zr-Si-Al system consists of a triple system of Fe-Zr-Al, Fe-Si-Al, Fe-Zr-Si and Zr-Si-Al. Based on the calculated thermodynamic data, a diagram of the four-component system Fe-Zr-Si-Al was constructed and a mathematical model of its phase structure was created. Unknown thermodynamic constants of binary compounds are calculated by using the models available in the literature [4-7]. To simplify the comprehension of this diagram and its phase structure, it's moved apart into integral parts. The transformation coefficients calculated by the method of Heath are intended to determine the phase composition of the primary components (by chemical composition).

Analysis of the phase equilibrium of the compounds of the Fe-Zr-Si-Al system, which simulate the phase compositions of the remaining of the complex alloy of ferrum-silicon-zirconium leads to the conclusion that we considering that four-component system consists of 12 elemental tetrahedrons, volumes are presented in Table 1.

In work [8-10] have been explained the easiest and accessible method for manual calculations the derivation of transformation equations, that expresses any secondary system through primary systems of basic

Table 1 **The list of elementary tetrahedrons Fe-Zr-Si-Al**

No.	Tetrahedrons	Elementary volumes
1	$ZrAl_2$-$ZrAl_3$-Fe_2Al_5-Zr_5Si_3	0,008902
2	Zr_3Al_2-$ZrAl_2$-Fe_2Al_5-Zr_5Si_3	0,028636
3	FeSi- $FeSi_2$- Fe_2Al_5- Zr_5Si_3	0,074524
4	Al- Fe_2Al_5-$ZrAl_3$.Zr_5Si_3	0,026813
5	Si-$FeSi_2$-Fe_2Al_5- Zr_6Si_5	0,129580
6	Al- Si-Zr_6Si_5-Fe_2Al_5	0,155870
7	Fe-FeSi-Fe_2Al_5-Zr_5Si_3	0,223125
8	$ZrFe_2$-Zr_3Al_2-Zr-Zr_5Si_3	0,100050
9	Fe-$ZrFe_2$-Fe2Al5-Zr_5Si_3	0,089161
10	$ZrFe_2$-Zr_3Al_2-Fe_2Al_5-Zr_5Si_3	0,101439
11	Zr_5Si_3-Zr_6Si_5-$FeSi_2$-Fe_2Al_5	0,017021
12	Al-Zr_5Si_3-Zr_6Si_5-Fe_2Al_5	0,053120
Total		1,000000

system. Calculated by the Heath equation the positive quantity of all the *n*-th amount coefficients of secondary components of a particular polytope, are the criterion for the location of a given composition of the melt in one of the quasi- systems. From what has been said, coefficient were tabulated in Table 2, which had been calculated by us by the procedure for each secondary component of 12 congruently melting quasi-systems of the basic tetrahedron. The breakdown of the general system is carried out with congruently melting compounds by combining a metastable conod of incongruent secondary components into stable triangles. The total of the relative volumes of elementary tetrahedrons is equal to one (1,000000), which confirms the correctness of the tetrahedration [11-13].

RESULTS RESEARCH

The practical using of the TDA results specifically to the complex alloy of ferrum-silicon-zirconium lies in the fact of finding the elementary tetrahedron, within which their compositions are located, and the normative distribution of primary phases between secondary compounds them is equal to 100 % of the considered tetrahedron. To determine the technological efficiency of the composition of the complex alloy of ferrum-silicon-aluminum-zirconium, the compositions of which are given in Table 3. The phase composition in each of the tetrahedrons in Table 1 can be described by substituting the proper coefficients from Table 2 into the equation:

$$X_i = a_iC_o + b_iM_o + c_iA_o + d_iS_o,$$

which is the transformation equation (according to Heath), where X_i is the amount of the secondary forming phase; a_i, b_i, c_i, d_i - transformation ratios; C_o, M_o, A_o, S_o - the number of primary oxide components in the melt.

When processing the compositions of various ferrum-silicon-zirconium alloys by means of thermodynamic-diagram analysis, it was established:

- The composition of the alloy with 50 % Zr is modeled by the tetrahedron Zr_5Si_3-Fe-Fe_2Al_5-FeSi. The transformation equations for calculating the equilibrium ratios of secondary components

Table 2 **The list of elementary tetrahedrons, their volumes and the coefficients of the equations to calculate the equilibrium ratios of the secondary components of the Fe-Zr-Si-Al system**

Components	Coefficients	Quasi-quad systems, their volumes and transformation coefficients											
		1	2	3	4	5	6	7	8	9	10	11	12
		$ZrAl_2$-	$ZrAl_2$-	Zr_5Si_3-	Al-	Si-	Si -	Zr_5Si_3-	Zr-	$ZrFe_2$-	$ZrFe_2$-	Zr_5Si_3-	Zr_5Si_3-
		Fe_2Al_5-	Fe_2Al_5-	Fe_2Al_5-	Fe_2Al_5-	Fe_2Al_5-	Fe_2Al_5-	Fe-	$ZrFe_2$-	Fe_2Al_5-	Fe_2Al_5 -	Fe_2Al_5 -	Fe_2Al_5-
		$ZrAl_3$-	Zr_3Al_2-	$FeSi_2$-	$ZrAl_3$-	$FeSi_2$-	Al-	Fe_2Al -	Zr_3Al_2-	Fe-	Zr_3Al_2-	$FeSi_2$ -	Al-
		Zr_5Si_3	Zr_5Si_3	FeSi	Zr_5Si_3	Zr_6Si_5	Zr_6Si_5	FeSi	Zr_5Si_3	Zr_5Si_3	Zr_5Si_3	Zr_6Si_5	Zr_6Si_5
Volumes		0,00890	0,02863	0,07452	0,02681	0,12958	0,15587	0,22312	0,10005	0,08916	0,10143	0,01702	0,05312
Fe	a_1	7,51959	-5,6101	0	-2,4965	2,003	0	0	-0,4993	0	1,32288	13,6454	0
	a_2	3,4965	3,4965	0	3,4965	0	0	1	1,49925	0	0,41132	0	0
	a_3	-10,016	3,11362	-2,9940	0	3,003	1	0	0	1	0,7342	3,003	1
	a_4	0	0	3,99401	0	0	0	0	0	0	0	15,6484	0
Zr	b_1	9,03614	-1,4981	1,6	-3	-0,8348	-0,8348	1,6	1	3,003	0,35326	5,6875	5,6875
	b_2	0	0	0	0	0	0	0,6	0	0	-0,8238	0	0
	b_3	-8,0361	2,49813	-1,7964	4	0	0	0	0	-2,003	1,47061	0	0
	b_4	0	0	1,19641	0	1,83486	1,8348	-1,2	0	0	0	-4,6875	-4,6875
Si	c_1	-15,060	2,49688	0	5	1	1	0	-1,6667	-5,005	-0,5887	-6,8125	-6,8125
	c_2	0	0	0	0	0	0	-1	0	0	1,37311	0	0
	c_3	13,3935	-4,1635	2,99401	-6,6667	0	0	0	0	3,33834	-2,4510	0	0
	c_4	2,66667	2,66667	-1,9941	2,6667	0	0	2	2,6667	2,6667	2,666	7,812	7,812
Al	d_1	-3,0125	2,24719	0	1	0,80232	0	0	-1,5	0	-0,5299	-5,4658	0
	d_2	0	0	1,40056	0	1,40056	1,4005	-0,401	0	1,40056	1,2358	1,40056	1,40056
	d_3	4,01205	-1,2479	1,19928	0	-1,2028	-1,4005	1,4005	2,5	-0,4006	0,29409	-1,2028	-0,4006

through the primary component are below, where Si, Fe, Zr, Al are the content of primary metals in the alloy. The relative volume V= 0,223125.

Analytical expressions of secondary phases are written as:

Zr_5Si_3 = 1,60000 · Zr;

Fe = 1,00000 · Fe + 0,60000·Zr –

– 1,00000 · Si-0,40056·Al;

Fe_2Al_5 = 1,40056 · Al;

FeSi = – 1,20000 · Zr + 2,00000 · Si.

It follows from this that an alloy with 50 % Zr in the liquidus temperature range includes phases, in %: (Zr_5Si_3) = 75,20 %; (Fe) =16, 59 %; (Fe_2Al_5) =12,61 % and (FeSi) = – 4,40 %.

- The composition of the complex alloy with 35 % Zr is modeled by tetrahedrons Zr_5Si_3-Fe_2Al_5-$FeSi_2$-FeSi. The relative volume V= 0,074524. The transformation equations for the abovementioned quasi-system are written as:

Zr_5Si_3 = 1,6000·Zr;

Fe_2Al_5 = 1,40056·Al;

$FeSi_2$ = – 2,99401·Fe – 1,79641·Zr +

+ 2,99401·Si+1,19928·Al;

FeSi = 3,99401 · Fe + 1,19641 · Zr –

– 1,99401·Si-1,59984·Al.

The regulatory phase composition of this complex alloy includes, %: (Zr_5Si_3) = 59,20 %; (Fe_2Al_5) = 8,40 %; ($FeSi_2$) = 57,49 % and (FeSi) = -25,09%.

- The composition of the complex alloy of ferrum-silicon-zirconium with 25 % Zr is modeled by tetrahedrons Si-Fe_2Al_5-$FeSi_2$-Zr_6Si_5. The relative volume 0,129580.

Analytical expressions of secondary phases written as:

Si = – 2,00300·Fe – 0,83486·Zr +

+ 1,00000·Si + 0,80232·Al – 53,63446;

Fe_2Al_5 = 1,40056·Al;

$FeSi_2$ = 3,0·Fe-1,20288·Al;

Zr_6Si_5 = 1,83486·Zr.

The composition of the complex alloy of ferrum-silicon-zirconium with 25 % Zr in the temperature liquidus region includes phases, in %: (Si) = - 53,63 %; (Fe_2Al_5) = 7,00 %; ($FeSi_2$) = 108,10 %; (Zr_6Si_5) = 38,53 %.

Table 3 **Average chemical composition of a complex alloy based on Fe-Zr-Si-Al**

Materials	Chemical compositions / %			
	Zr	Al	Si	Fe
FeSiAlZr 50	47	9	26	18
FeSiAlZr 35	36	6	48	9
FeSiAlZr 25	21	5	36	38

CONCLUSION

As a result of modeling with the help of TDA, quasi-volumes of the multicomponent system Fe-Zr-Si-Al, characterizing the compositions of complex alloy of ferrum-silicon-zirconium with various compositions, have been established. As a result, it was found that the alloy with a content of 25 % Zr is modeled by the Si-Fe_2Al_5-$FeSi_2$-Zr_6Si_5 tetrahedron, and the alloy compositions with 35 and 50 % Zr are located in the Si-Fe_2Al_5-$FeSi_2$-Zr_6Si_5 and Zr_5Si_3-Fe-Fe_2Al_5-FeSi tetrahedrons.

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