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THERMODYNAMIC DIAGRAM ANALYSIS (TDA) OF MnO–CaO-Al_2O_3-SiO_2 AND PHASE COMPOSITION OF SLAG IN REFINED FERROMANGANESE PRODUCTION

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The research presents the calculations of the analytical expressions of the oxide system MnO-CaO-Al_2O_3-SiO_2 and the phase compositions of the slags from the production of refined ferromanganese. It is determined that the system under consideration is divided into 19 elementary quasi-systems consisting of incongruently melting and congruently melting compounds. The sum of the relative volumes of the elementary tetrahedron of the MnO-CaO-Al_2O_3-SiO_2 system equals one (1,000000), which confirms the accuracy of the performed calculations. Quasi-volumes in the system MnO-CaO-Al_2O_3-SiO_2, simulating the composition of the resulting slag in the process of metallothermic recovery of manganese concentrates are found.

Key words: thermodynamic-diagram analysis, refined ferromanganese, phase composition, oxide system, metallothermy

INTRODUCTION

In metallurgy it's important to study the state of materials that involve in metallurgical conversion, depending on temperature and pressure. However, the classical thermodynamic study of processes in complex systems is rather lengthy and requires using complex mathematical calculations and it's associated with the need to determine the thermodynamic parameters of a large number of independent reactions. Often data on variety of substances that are necessary to determine changes in Gibbs free energy, are limited or absent, which in such cases exclude the thermodynamic analysis possibility of multicomponent system. Moreover, the latter does not consider the particular intermediate stages of the process, since it only operates with input and output parameters of the process.

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 is particularly effective in terms of application to metallurgical technologies, since it allows to reveal the features of the phase state of the raw materials involved in the metallurgical conversion. However, the final result of such researches is a diagram of the phase composition of a single system that is closest to the composition of metallurgical products. Using this diagram, the evolution of phase transformations in slags and metal systems can be visually traced and predict their final state.

RESEARCH METHODOLOGY

In this work, an attempt has been made to create a mathematical model for estimating the type and number of forming phases in the slag system of refined ferromanganese production. It's well known the technology of refined ferromanganese production characterized in the initial periods of melting by slags of the FeO-MnO-CaO-Al_2O_3-SiO_2 system to the final period – by the same system without iron oxide (II).However the physico – chemical properties of the latter system have crucial Impact on value outputs of the technology as a whole. [1]. In order to determine the tetrahedron in the MnO-CaO-Al_2O_3-SiO_2 system to the refined ferromanganese slags, first of all, it is necessary to find those elementary tetrahedrons in which they are located. Then, focusing on the location of slags in one or another tetrahedron, as well as on the normative distribution of their main components between the compounds (secondary phases) located on the tops of this tetrahedron, it is possible to give a qualitative and quantitative technological assessment of the materials under study. Then, focusing on the location of slags in one or another tetrahedron, as well as on the normative distribution of their main components between the compounds (secondary phases)

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located on the vertex corners of this tetrahedron, it is possible to give a qualitative and quantitative technological assessment of the being studied materials. For this we have organized complete TDA of the MnO-CaO-Al_2O_3-SiO_2 system.

The four-component MnO-CaO-Al_2O_3-SiO_2 system is assembled from the individual ternary systems MnO-CaO- SiO_2, MnO-Al_2O_3-SiO_2, MnO-CaO-Al_2O_3 and CaO-Al_2O_3-SiO_2. Based on the calculated thermodynamic data, a diagram of the four-component system MnO-CaO-Al_2O_3-SiO_2 was constructed and a mathematical model of its phase structure was created [2]. Unknown thermodynamic constants of binary compounds are calculated by using the models available in the literature [3–5]. 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 [6] are intended to determine the phase composition of the primary components (by chemical composition). Analysis of the phase equilibrium of the compounds of the MnO-CaO-Al_2O_3-SiO_2 quadruple system, which simulate the phase compositions of the remaining slags of the silicothermic, aluminothermic, alumino-silicothermic (metallothermy) ferromanganese, leads to the conclusion that we considering that four-component system consists of 19 elemental tetrahedrons, volumes (relative to the volume of the general system equal to 1 in terms of the units) are presented in Table 1. 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.

Table 1 **The list of elementary tetrahedrons MnO-CaO-Al_2O_3-SiO_2**

No.	Tetrahedrons	Elementary volumes
1	C-$C_{12}A_7$-C_2S-M	0,179735
2	$C_{12}A_7$-AC-C2S-M	0,045719
3	AC-C_2AS-C_2S-M	0,045848
4	AC-A_2C-C_2AS-M	0,030441
5	M-MA-A_2C-C_2AS	0,027780
6	MA-A_2C-A-C_2AS	0,019305
7	A-C_2AS-CAS_2-MA	0,054394
8	A-A_3S_2-CAS_2-MA	0,023240
9	A_3S_2-MA-M_3AS_3-CAS_2	0,031131
10	S-A_3S_2-CAS_2-M_3AS_3	0,062057
11	MA-M_3AS_3-CAS_2-M	0,043167
12	C_2AS-CAS_2-MA-M	0,078275
13	S-M_3AS_3-M_2S-CAS_2	0,029108
14	M_2S-M_3AS_3-M-CAS_2	0,012298
15	M-M_2S-CAS_2-C_2AS	0,022373
16	CS-CAS_2-C_2AS-M_2S	0,054655
17	CS-C_2S-M_2S-C_2AS	0,043935
18	C_2S-C_2AS-M-M_2S	0,071925
19	S-CS-M_2S-CAS_2	0,124614
Total		1,000000

In work [6] 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 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, coefficients were tabulated in Table 2, which had been calculated by us by the procedure [6] for each secondary component of 19 congruently melting quasi-systems of the basic tetrahedron.

RESULTS RESEARCH

The practical using of the TDA results specifically to the slags from the production of refined ferromanganese 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 for them is equal to 100% of the considered tetrahedron. To determine the technological effectiveness of the generating slags during the smelting process, it is necessary to recalculate average weighted material compositions into four main oxides of the MnO-CaO-Al_2O_3-SiO_2, system, which are listed in Table 3 [7]. 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.

Using silicomanganese as reducing agent in production of refined ferromanganese in the analysis of slag compositions it was established that:

• Slag composition of low carbon ferromanganese (14,0% MnO; 46,0% CaO; 31,0% SiO_2; 2,15% Al_2O_3) simulated by tetrahedron $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$-$CaO{\cdot}SiO_2$-$2MnO{\cdot}SiO_2$-$2CaO{\cdot}SiO_2$ (relative volume $V = 0.043935$), for which transformation equations to calculate the equilibrium ratios of the secondary components through primary component are written in the form of system of four linear expressions:

$C_2AS = 2{,}68817{\cdot}A;$

$CS = -1{,}63709{\cdot}M - 2{,}07738{\cdot}C + 3{,}87500{\cdot}S + 0{,}00275{\cdot}A;$

$M_2S = 1{,}42248{\cdot}M;$

$C_2S = 1{,}21462{\cdot}M + 3{,}07738{\cdot}C - 2{,}87500{\cdot}S - 1{,}69092{\cdot}A.$

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 MnO-CaO-Al_2O_3-SiO_2 system**

components	coefficients	Quasi-quad systems, their volumes and transformation coefficients									
		1	2	3	4	5	6	7	8	9	10
		C_2S-	C_2S-	C_2AS-	A_2C-	M-	A-	A-	A-	CAS_2-	S-
		C-	AC-	M-	AC-	C_2AS-	C_2AS-	C_2AS-	A_3S_2-	A_3S_2-	A_3S_2-
		$C_{12}A_7$-	$C_{12}A_7$-	AC-	C_2AS-	A_2C-	A_2C -	CAS_2-	CAS_2-	M_3AS_3-	CAS_2-
		M	M	C_2S	M	MA	MA	MA	MA	MA	M_3AS_3
Volumes		0,179735	0,045719	0,045848	0,030441	0,02778	0,019305	0,054394	0,02324	0,03113	0,062057
Al_2O_3	a_1	0	0	2,69469	2,54676	-0,69492	1	1	1	0	-0,39276
	a_2	-0,94175	3,70229	0	-1,54676	0	0	0	0	0,96358	1,39276
	a_3	1,94175	-2,70229	-0,00375	0	0	0	0	0	-0,74651	0
	a_4	0	0	-1,69094	0	1,69492	0	0	0	0,78293	0
MnO	b_1	0	0	0	0	1	-1,43902	-1,43902	-1,43902	0	-0,65835
	b_2	0	0	1	0	0	0	0	0	-1,3866	-0,66723
	b_3	0	0	0	0	0	0	0	0	1,07425	0
	b_4	1	1	0	1	0	2,43902	2,43902	2,43902	1,31237	2,32558
SiO_2	c_1	2,86533	2,86533	9,17262	4,35354	-3,55811	5,12021	-0,56781	-2,5461	0	1
	c_2	-1,86533	7,33316	0	-7,91975	4,56621	4,56621	-1,51505	3,5461	1,09271	0
	c_3	0	-9,19849	-5,28207	4,56621	-8,68642	-8,68642	3,08286	0	1,9007	0
	c_4	0	0	-2,89055	0	8,67832	0	0	0	-1,99341	0
CaO	d_1	0	0	-4,91742	-4,64748	2,53725	-3,65116	-0,6055	3,64634	4,97512	-1,43213
	d_2	1	-3,9313	0	5,64748	0	0	3,25622	-7,62147	-4,10791	-2,543
	d_3	0	4,9313	2,8317	0	4,65116	4,65116	-1,65072	4,97513	-2,72204	4,97513
	d_4	0	0	3,08572	0	-6,18841	0	0	0	2,85483	0
		11	12	13	14	15	16	17	18	19	
Volumes		0,043167	0,078275	0,029108	0,012298	0,022373	0,054655	0,043935	0,071925	0,12461	
Al_2O_3	a_1	-0,69492	-0,69492	-0,88512	2,09509	4,16864	1,34719	2,68817	2,68817	-0,59087	
	a_2	0	1,69492	4,85437	-5,94946	-5,92979	-1,70644	0,00275	-0,00168	-1,1339	
	a_3	0	0	-2,96924	4,85437	5,42937	0	0	0,00239	0	
	a_4	1,69492	0	0	0	-2,66822	1,35925	-1,69092	-1,68888	2,72479	
MnO	b_1	1	1	-0,42248	1	1	0,96324	0	0	-0,42248	
	b_2	0	0	0	0	0	-0,40935	-1,63709	1	0	
	b_3	0	0	1,42247	0	0	1,42248	1,42248	0	1,42248	
	b_4	0	0	0	0	0	-0,97637	1,21461	0	0	
SiO_2	c_1	-0,78804	0,39458	1	-2,367	-2,367	-2,28	0	0	1	
	c_2	-0,95921	-0,96239	0	3,367	3,367	0,96894	3,875	-2,367	0	
	c_3	2,74725	3,08286	0	0	0	0	0	3,367	0	
	c_4	0	-1,51505	0	0	0	2,31106	-2,875	0	0	
CaO	d_1	2,96253	0,42077	-0,53313	1,26192	-2,5241	2,4405	0	0	-1,07039	
	d_2	-1,03311	-1,02627	-8,86345	3,6264	3,59048	1,03325	-2,07738	1,26895	2,07039	
	d_3	-5,90454	-1,65072	5,42146	-8,86345	-4,93821	0	0	-1,80504	0	
	d_4	4,97512	3,25622	4,97512	4,97513	4,87183	-2,47375	3,07738	1,53609	0	

*Note. The following abbreviations are used in the table: M-MnO; C-CaO; A-Al_2O_3; S-SiO_2

This implies that, a slag in the subsolidus state includes itself, % 6,20 C_2AS; 1,71 CS; 21,34 M_2S; 70,64 C_2S.

• Composition of highly basic ore-lime melt (12% MnO; 48% CaO; 25,2% SiO_2; 2,5% Al_2O_3) simulated in tetrahedron $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$-MnO-$Al_2O_3{\cdot}$CaO-$2CaO{\cdot}SiO_2$ (relative volume V=0,04585),the given tetrahedron is characterized by a high content of calcium oxide and ratio of CaO/SiO_2 = 1,8-2,2.

Analytical expressions of secondary phases are written as:

C_2AS=-4,91742·C+9,17262·S+2,69469·A;

M = 1,00000·M;

AC = 2,83170·C-5,28206·S-0,00375·A;

C_2S = 3,08572·C-2,89055·S-1,69094·A.

Producing melt will include, %: 27,45 C_2AS; 12,00 M; 2,80 AC; 71,05 C_2S.

The slags from the production of refined ferromanganese are reduced by the aluminosilicothermy method that have the following property. Slag compositon шлака (13,0% MnO; 45,6% CaO; 26,0% SiO_2; 10,0% Al_2O_3) simulated in tetrahedron $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$–MnO-$2MnO{\cdot}SiO_2$-$2CaO{\cdot}SiO_2$ with large relative volume V=0,071925. The transformation equations for the abovementioned quasi-system are written as:

C_2S= 1,53610·C-1,68888·A

C_2AS= 2,68817·A

M=1,00000·M+1,26895·C-2,36700·S-

-0,00168·A

M_2S=-1,80504·C+ 3.36700·S+ 0,00239·A

Table 3 **The weighted average chemical composition of slags from the production of refined ferromanganese smelted by the methods: silicothermy, metallothermy and tetrahedron where they are located**

Material	MnO	CaO	SiO_2	Al_2O_3	Tetrahedron
Silicothermy process					
Slag refined ferromanganese	14,0	46,0	31,0	2,15	C_2AS-CS-M_2S-C_2S
Ore-lime melt	12,0	48,0	25,2	2,50	C_2AS-M-AC-C_2S
Metallothermy process					
Slag refined ferromanganese	13,0	45,6	26,0	10,0	C_2AS-M-M_2S-C_2S

The regulatory phase composition of this slag includes, %: 44,65 C_2S; 38,65 C_2AS; 11,2 M; 5,5 M_2S.

It has been established that the slag composition of the refined ferromanganese reduced by the metallothermy method, alumina secondary compounds based on calcium dominate in slag $2CaO{\cdot}SiO_2{\cdot}Al_2O_3$ (to 45 %, instead 6,0 %), which explains the significant decrease in the concentration of $2CaO{\cdot}SiO_2$ (two-calcium silicate) (from 75 % to 45 %), which diffuses into powder when cooled. The displacement the remaining slag composition to the side of gehlenite by loading an aluminum-silicon-manganese-containing alloy as a reducing agent into furnace-charge does not negatively affect on technology of refined ferromanganese smelting. Including the fact that this displacement raises the melting point of the slag and therefore the whole process, contributes the complete reduction of manganese and silicon from their silicates, notably from tephroite ($2MnO \cdot SiO_2$) [8]. However, due to the limited content of silicon in the ferromanganese according to GOST 4755-91, an excessively high content of alumina in the slag is undesirable, since this contributes to a deeper recovery of silicon.

CONCLUSIONS

From the above mentioned theoretical data follows validaton of the fact that the TDA, in which neglecting the complex mathematical apparatus, allows using the phase diagrams of multicomponent systems to establish the optimal range of slag compositions. Furthermore, according to the data on the melting points of the secondary components of the elementary volume, it is possible to determine the relative melting points of the researched slag.

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