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THERMODYNAMIC-DIAGRAM ANALYSIS OF Fe-Ni-C-O SYSTEM

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The paper presents the results of calculation of thermodynamic parameters of compounds formed between the system components. Complete thermodynamic-diagram analysis of the Fe-Ni-C-O system has been carried out taking into consideration the congruent compounds. The diagram of the four-component system Fe-Ni-C-O and mathematical model of its phase structure were constructed on the basis of full thermodynamic-diagram analysis and reference thermodynamic data.

Keywords: nickel-containing alloy, Fe-Ni-C-O system, thermodynamic-diagram analysis, triangulation, tetrahedration

INTRODUCTION

So-called thermodynamic-diagram method of analysis is known in the practice of complex theoretical studies of multicomponent systems. This method greatly simplifies the study of phase transformations in multicomponent systems by dividing them into thermodynamically stable elementary partial subsystems of the same dimensionality as the basic one. Thermodynamic diagram analysis combines thermodynamic assessment of chemical interaction of components in the system under study with geometrical diagram. Such combination, as shown by studies of physical and chemical bases of refractories and ferroalloys production, is productive in interpretation of chemical interactions in complex systems [1-3].

RESEARCH METHODOLOGY

This method is particularly effective in terms of application to metallurgical technology, as it allows identifying the features of the phase state of raw materials involved in metallurgical processing.

The final result of such research is phase diagram of a single system with composition which is the closest to that of alloys and compounds. The phase diagram allows to determine without much difficulty the equilibrium relations of phases in any area of the considered system and for each of its polytopes, and thus to implement a differentiated approach in the construction of various models of the behavior of melts properties [4-7]. This work considers the possibility of constructing a diagram for the Fe-Ni-C-O system characterizing the composition of metal products of nickel-containing alloys melting in the processes of nickel reduction from nickel feedstock.

RESULTS RESEARCH AND DISCUSSION

When studying the Fe-Ni-C-O metal system by thermodynamic-diagrammatic analysis it is necessary to proceed from the breakdown of boundary subsystems into elementary tetrahedrons. This requires, first of all, describing the metallic compounds of different complexity that make up the system under the study. Table 1 characterizes the accepted coordinates (based on mass fraction *1000) of Fe-Ni-C-O system's congruent com-

Table 1 **Congruent and incongruent compounds in the Fe-Ni-C-O system and their coordinates on the quadruple concentration simplex (tetrahedron)**

№	Com-pounds	Coordinates based on mass composition			
		Ni	Fe	C	O
1	Ni	1000	0	0	0
2	Fe	0	1000	0	0
3	C	0	0	1000	0
4	O	0	0	0	1000
5	NiO	786	0	0	214
6	FeO	0	778	0	222
7	Ni_2O_3	710	0	0	290
8	Fe_2O_3	0	700	0	300
9	Fe_3O_4	0	724	0	276
10	Ni_3Fe	759	241	0	0
11	Ni_3C	936	0	64	0
12	Fe_3C	0	933	67	0
13	Co	0	0	428	572
14	Co_2	0	0	273	727
15	$NiCO_3$	495	0	101	404
16	$FeCO_3$	0	483	103	414

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pounds that are used in further study of their crystallization fields. Sixteen simple compounds are formed in the system.

Based on the results, a three-component diagram of Fe-C-O system was constructed (Figure 1).

Triangulation of the Fe-C-O system (Figure 1) clearly showed 7 regions: Fe_2O_3-O-CO_2; Fe_2O_3-CO-CO_2; Fe_2O_3-C-CO; Fe_3O_4-C-Fe_2O_3; Fe_3O_4-C-Fe_3C; Fe_3O_4-Fe_3C-FeO; Fe_3C-Fe-FeO. The existence of intermediate phases such as: vustite (close to FeO), magnetite (Fe_3O_4), hematite (Fe_2O_3), iron carbide (Fe_3C) and iron carbonate ($FeCO_3$) has been established as a result of Fe-C-O system study. Vustite is a compound of variable composition, close to FeO and stable in excess of oxygen [8]. It is formed at 1 430 - 1 435 °C by peritectic reaction l+ Fe_3O_4↔vustite and has an incongruent state. The composition of the vustite phase at 560 - 580 °C is described by the formula $Fe_{0,945}O$ or $FeO_{1,058}$. As it is known, in [8] hematite (Fe_2O_3) is formed by reaction Fe_3O_4+O_2↔Fe_2O_3 at 1 457 °C. It exists in two forms: stable α-Fe_2O_3 and metastable γ-Fe_2O_3. Magnetite (Fe_3O_4) melts with an open maximum at 1 600 °C. According to thermodynamic calculations, the melting temperature of cementite is quite accurately found to be 1 226 °C.

As a result of studies of the Ni-C-O system we constructed a three-component diagram. The triangulation of this system (Figure 2) clearly showed 6 coexisting areas: Ni_2O_3-O-CO_2; Ni_2O_3-CO-CO_2; Ni_2O_3-C-CO; Ni_2O_3-C-NiO; NiO-C-Ni_3C; Ni_3C-Ni-NiO.

Nickel forms oxides NiO and Ni_2O_3 with oxygen. The oxide Ni_2O_3 dissociates almost completely when heated by the reaction $2Ni_2O_3 \rightarrow 4NiO + 3O_2$ (at 1 097 °C). Nickel oxide NiO is of great interest for nickel-containing alloys electrothermy, its standard formation heat is ΔH^o_{298K} = - 239,74 kJ / mol. According to the author of work [9], melting temperature of NiO is equal to 1 984 °C and it has stable congruent state. Also, in

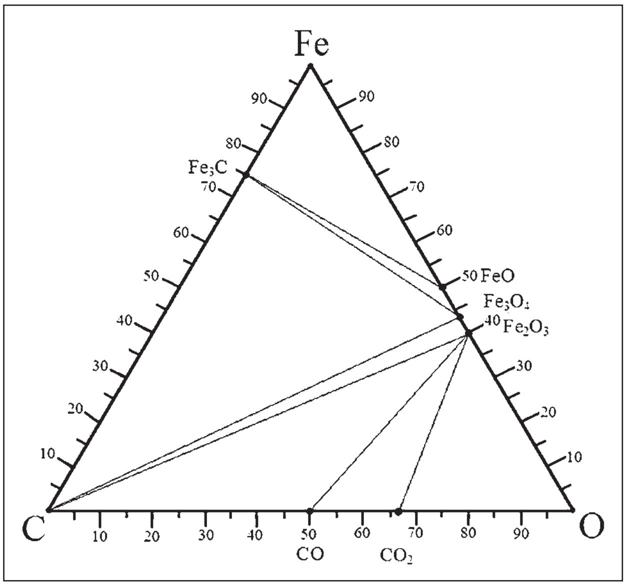

Figure 1 The Fe-C-O system

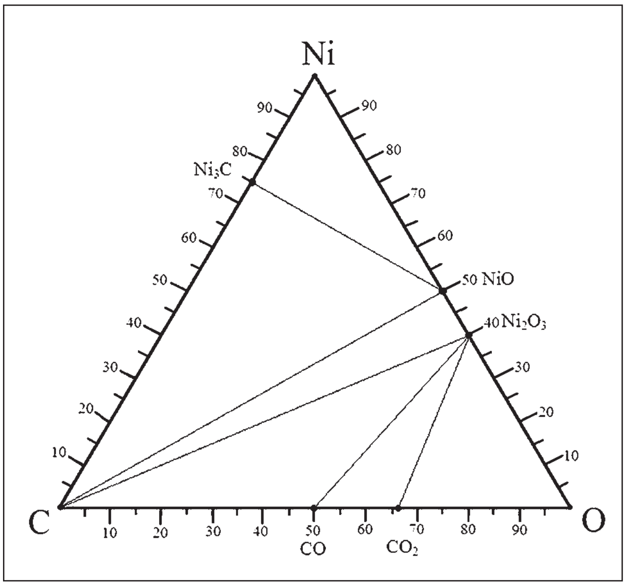

Figure 2 The Ni-C-O system

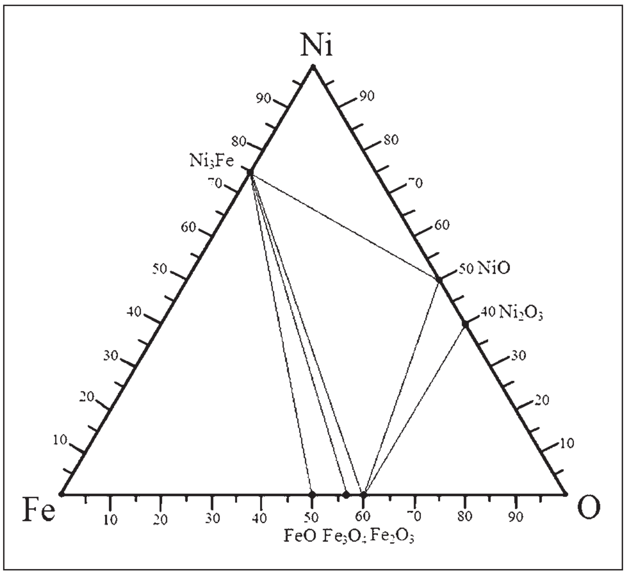

Figure 3 The Ni-Fe-O system

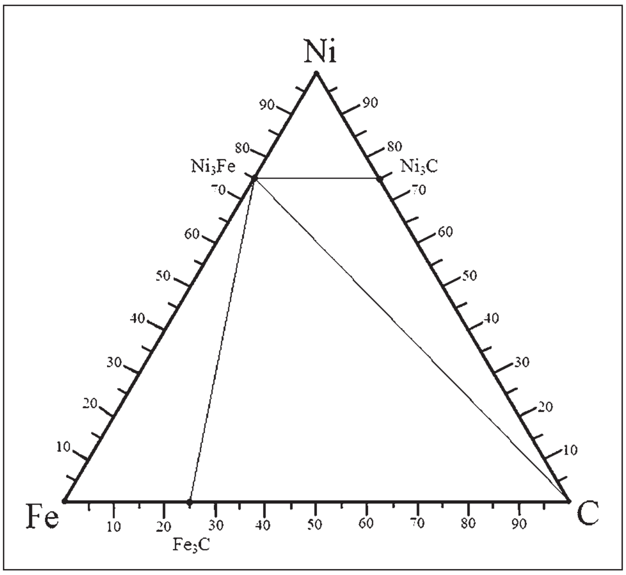

Figure 4 The Ni-Fe-C system

addition to the mentioned nickel oxides, there is little-known oxide NiO_2. Complete decomposition to NiO is fixed at temperatures below 1 100 °C. In addition to the above oxides, in the Ni-O-C system there is metastable carbide Ni_3C, which has simple eutectic form. The eutectic temperature is 1 326 °C.

Study of the Ni-Fe-O system (Figure 3) revealed 7 areas: Ni_2O_3-O-Fe_2O_3; Ni_2O_3-Fe_2O_3-NiO; Ni_3Fe-Fe_2O_3-NiO; Ni_3Fe-Ni-NiO; Ni_3Fe-Fe_3O_4-Fe_2O_3; Ni_3Fe-FeO-Fe_3O_4; Ni_3Fe-Fe-FeO. In addition to the above phases, there is one double compound Ni_3Fe in Ni-Fe-O system. This compound is practically not studied in the Ni-Fe-O ternary system. It was found that the eutectoid reaction takes place at 345 °C: $\gamma=\alpha+Ni_3Fe$. The eutectoid point is located at 52 % (at.) of nickel. Solid solution based on the compound Ni_3Fe has a wide area of homogeneity: ~ 20 % (at.) at 300 ° C.

Triangulation of the Ni-Fe-C system (Figure 4) revealed 4 regions: Ni_3Fe-Ni-Ni_3C; Ni_3Fe-C-Ni_3C; Ni_3Fe-C-Fe_3C; Ni_3Fe-Fe-Fe_3C, which could well describe the existence of several phases, such as: Ni_3Fe, Ni_3C and Fe_3C. Many different iron carbides are mentioned in the literature, but only two of them have been studied under normal pressure and metastable equilibrium conditions: cementite Fe_3C, which crystallizes forming rhombic structure and compound $Fe_{2,2}C$, commonly called Haag carbide [10], formation of which takes place in temperature range from room temperature to 230 °C. Carbide with composition Fe_7C and carbon in the form of diamond are observed only at high pressures and carbon concentrations above 30 - 35 % (at.).

In addition to the above iron carbides, there are different types of carbides, the so-called higher carbides Fe_2C and FeC. Also nickel carbide Ni_3C was found in the Ni-Fe-C system, it has a rhombic lattice like Fe_3C. Ni_3C is most likely stable above 1 600 °C and below 300 °C. Rapid cooling from 2 000 °C to 1 000 °C is required to produce this carbide. The interaction of nickel with CO at about 250 °C reveals another carbide NiC. Its decomposition temperature is about 700 °C, which is higher than that of Ni_3C that decomposes at 380 - 420 °C.

The tetrahedration of the Fe-Ni-C-O system is further performed (Figure 5). Figure 5 shows a general view of the analyzed system.

The partitioning of general system was carried out taking into account the congruent compounds. The sum of relative volumes of elementary tetrahedrons is equal to one (1,000), which confirms the correctness of the performed tetrahedration. The transformation coefficients calculated by the Heath method [11], designed to determine the phase composition by primary components, as well as the volumes of elementary tetrahedrons of the Fe-Ni-C-O system are shown in Table 2.

The application of thermodynamic-diagram analysis results regarding the compositions of nickel-containing alloys, comes down to finding elementary tetrahedrons, inside 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 tetrahedron characterizing nickel-containing alloy composition, it is necessary to know chemical compositions of the initial nickel ores. Chemical analysis of the Batamshinskoye nickel ore (Kazakhstan) is presented in Table 3.

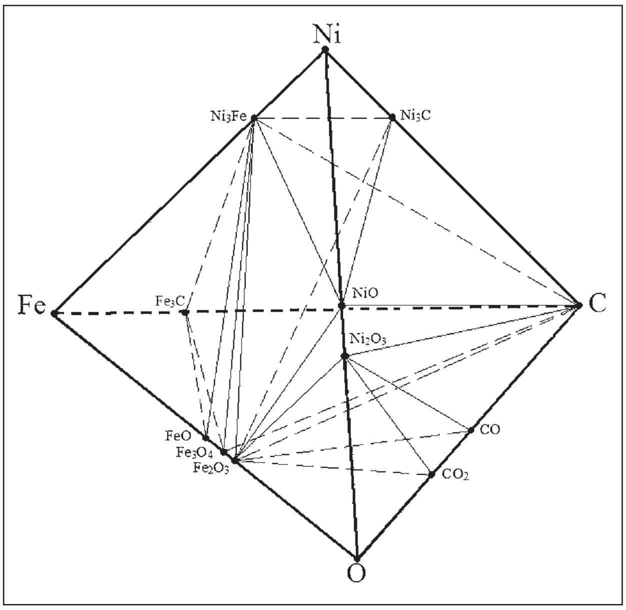

Figure 5 Tetrahedration of the Fe-Ni-C-O system

Table 2 **List of tetrahedrons of the Fe-Ni-C-O system**

№	Tetrahedrons	Elementary volumes
1	Fe_2O_3-Ni_2O_3-O-CO_2	0,135681
2	Fe_2O_3-Ni_2O_3-CO-CO_2	0,077035
3	Fe_2O_3-Ni_2O_3-C-CO	0,284284
4	Fe_2O_3-Fe_3O_4-Ni_3Fe-C	0,018216
5	Fe_3O_4-Ni_3Fe-Fe_3C-C	0,195449
6	Fe_3O_4-Ni_3Fe-FeO-Fe_3C	0,002746
7	Fe-Ni_3Fe-FeO-Fe_3C	0,011289
8	Ni_2O_3-Fe_2O_3-NiO-C	0,053200
9	NiO-Ni_3Fe-Ni_3C-C	0,048273
10	Ni_3C-NiO-Ni-Ni_3Fe	0,003301
11	Ni_3Fe-NiO-Fe_2O_3-C	0,170526
The sum		1,000000

Further, nickel ore was melted and the principal possibility of obtaining nickel-containing alloy from Batamsha nickel ores was established under semi-industrial conditions [12-14]. Results of chemical analysis of nickel-containing alloy are given in Table 4.

CONCLUSION

The results showed that the subsystem characterizing composition of the obtained alloy by the content of Ni is in the region of Fe-Fe_3C-Ni_3Fe compounds (Figure 6).

Thus, the presented information and the calculation results confirm the reliability of the tetrahedration of the Fe-Ni-C-O system phase diagram. This will subsequently make it possible to determine the phase compo-

Table 3 **Chemical composition of nickel ore of Batamshinskoye field [12-14]**

Materials	Samples	$Ni_{general}$	$Fe_{general}$	Cr_2O_3	SiO_2	MgO	Al_2O_3
Nickel ore	№1	0,90	16,39	2,55	45,74	3,70	2,32
Nickel ore	№2	1,23	14,38	1,69	51,57	3,52	1,87

Table 4 **Chemical composition of alloy [12-14]**

Material	Content / %							
Alloy	Ni	Cr	Fe	Si	C	S	P	Co
Sample 1	3,68	4,50	73,8	7,21	4,38	0,022	0,08	0,290
Sample 2	3,2	4,4	62,50	21,58	2,.51	-	0,21	0,15

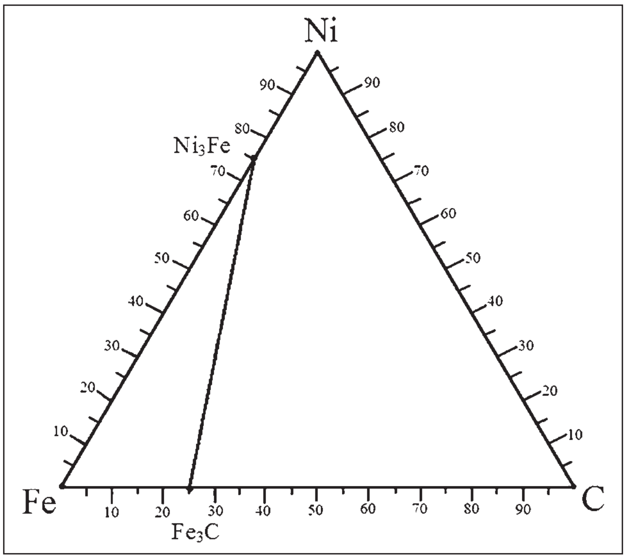

Figure 6 Derived phase area modeling the compositions of the obtained alloy

sition of metal products during melting of nickel alloys using domestic nickel-containing ores.

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