DIAGRAM OF PHASE STRUCTURE OF METALLIC SYSTEM IN LIQUID STATE

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ABSTRACT

An important place in systematization of the results of measuring phase and structural properties of alloys of a specific multicomponent system is taken by its diagrams of the phase structure and state. The existence of the phase structure diagram allows defining without special difficulty the equilibrium ratios of phases in any area of the considered system and for each its polytope and to realize a differentiated approach in the development of different behaviour models of melts properties if there are known the parameters of individual substances (compounds) located at peaks of the appropriate polytopes.

The analysis of the world of the raw materials source for metallurgy shows that there are become less qualitative ore raw materials every year, and the requirements to quality of metal, on the contrary, grow. Present day technologies need the metals possessing a complex of properties. Such complex properties are shown by the complex alloy aluminumsilicochrome, which composition and technology are developed by scientists of the Chemical and Metallurgical Instituten.a.Zh. Abishev. When developing the technology of obtaining aluminumsilicochrome the authors carried out in-depth physical and chemical studies.

The main goal of this work consists in carrying out the thermodynamic assessment of the possibility of smelting a metal of the given composition. For this purpose thermodynamic diagram analysis of Fe-Al-Si-Cr system is carried out with the established list of elementary polytopes. According to this diagram it will be possible to predict the phase composition of chromic complex alloys in case of different weight content of elements, thereby showing at what point of space of these volumes the best grades of aluminumsilicochrome are formed.

1 INTRODUCTION

To obtain a diagram of the phase structure or ratios (DPhS) of the metal Fe-Cr-Si-Al system in all intervals of temperatures of compounds phase transformations, temperature dependences of heat capacity are also needed, as well as enthalpies and entropies of melting these compounds [1-4].

In works [5,6] a number of methods of approximate calculation of heat capacity of solid inorganic compounds is described, however, a large gap of the absence of reliable data of these methods accuracy and boundaries of applicability left. Nevertheless, using different methods we derived an equation of heat capacity dependence on temperature – $C_p = f(T)$, melting enthalpy – ΔH^0_{tr} and melting entropy of melt – ΔS^0_{tr} of compounds are determined which are formed in the metal Fe-Cr-Si-Al system for which there were no reference data.

The full calculation of thermodynamic constants of the reactions proceeding in these systems was carried out using the program Gibbs complex. The PC "Gibbs" developed by scientists of the ChMIn.a. Zh. Abishev enables defining changing enthalpy, entropy, heat capacity, Gibbs energy of any reaction both in heterogeneous, and in homogeneous and liquid-phase states at different temperatures taking into account all phase transitions (allotropic transformations, melting, etc.) for all the components of systems and to calculate a constant of equilibrium of reaction. The algorithm of determining the ΔG value of the reaction according to the "Gibbs" PC is possible to be presented by the following formulas:

1) the values of Gibbs energy $\Delta G^0_{f,298,15}$ of specified compounds are determined by the formula:

$$\Delta G^0_{f,298,15} = \Delta H^0_{f,298,15} - T \cdot S^0_{298,15}, \quad (1)$$

2) the calculation of the reaction enthalpy changing at a set temperature:

$$\Delta H^0_T = \Delta H^0_{298,15} + \int_{298,15}^{T_{tr}} \Delta C_p \, dT + \Delta H^0_{tr} \quad (2)$$

3) determining the reaction entropy changing at a set temperature:

$$\Delta S_T^0 = \Delta S_{298,15}^0 + \int_{298,15}^{T_{tr}} \Delta C_p \frac{dT}{T} + \Delta S_{tr}^0 \quad (3)$$

4) calculating Gibbs energy changing at a set temperature– ΔG_T^0 by the formula of Gibbs-Helmholtz.

After substituting formulae (2) and (3) by formula (1) we obtain the expression:

$$\Delta G_T^0 = \Delta H_{298,15}^0 + \int_{298,15}^{T_{tr}} \Delta C_p dT + \Delta H_{tr}^0 - T \cdot \left(\Delta S_{298,15}^0 + \int_{298,15}^{T_{tr}} \Delta C_p \frac{dT}{T} + \Delta S_{tr}^0 \right), \quad (4)$$

where $\Delta H_{298,15}^0$ is a standard value of the reaction enthalpy, J/mol

$\Delta S_{298,15}^0$ is a standard value of the reaction entropy, J/(mol·K)

ΔC_p is the reaction heat capacity, J/(mol·K)

T_{tr} is the current temperature or the temperature of phase transformation (melting, evaporation, etc.) of the component, respectively, K

T – is the temperature at which the system is in homogeneous liquid-phase state, K

ΔH_{tr}^0 is the phase transformation enthalpy or melting a component, respectively, J/mol

ΔS_{tr}^0 is the phase transformation or melting a component, respectively, J/(mol·K).

2 THERMODYNAMICCAL CULATIONS

To carry out a tetrahedration of the Fe-Cr-Si-Al system by the method of thermodynamic- diagram analysis (TDA) it is necessary to break boundary subsystems of Si-Al-Fe, Si–Cr–Fe, Fe–Al–Cr and Si–Al–Cr into elementary independent triangles. Connodes of the coexisting phases are carried out by the Hess's rule. For the Si-Al-Fe subsystem the value of Gibbs energy (ΔG^0_{2500}) of reactions (calculated by means of the program Gibbs complex) are provided in Table 1. On the basis of the obtained thermodynamic data the Si–Al–Fe subsystem DPhS was constructed up to the temperature of 2500 K (Figure 1).

Table 1: Thermodynamics of reactions in the Si–Al–Fe subsystem (T = 2500K)

Reaction equation	**ΔG^0_{2500}, (J)**
$3Al + FeSi_2 = FeAl_3 + 2Si$	112613.76
$FeAl_3 + FeSi_2 = 3Al + 2FeSi$	-40517.68
$2FeAl_3 + 3FeSi = 6Al + Fe_5Si_3$	-93331.98
$FeAl_3 + Fe_5Si_3 = 3Al + 3Fe_2Si$	-39119

As a result of carrying out triangulation of the Si – Al – Fe system (Figure 1) taking into account all compounds 5 zones are formed. In zones Si – Al – $FeSi_2$ (1), $FeSi_2$ – Al – FeSi (2), FeSi – Al – Fe_5Si_3 (3), Fe_5Si_3 – Al – Fe_2Si (4) there are incongruent compounds. AtthesiteofthediagramFe_2Si – Al – Fe there is one congruent (Fe_2Al_5) and two incongruent compounds: $FeAl_3$, FeAl. These compounds divide this site into four subzones: Fe_2Si – Al – $FeAl_3$ (5^I), Fe_2Si – $FeAl_3$ – Fe_2Al_5 (5^{II}), Fe_2Si – Fe_2Al_5 – FeAl (5^{III}), Fe_2Si – FeAl – Fe (5^{IV}).

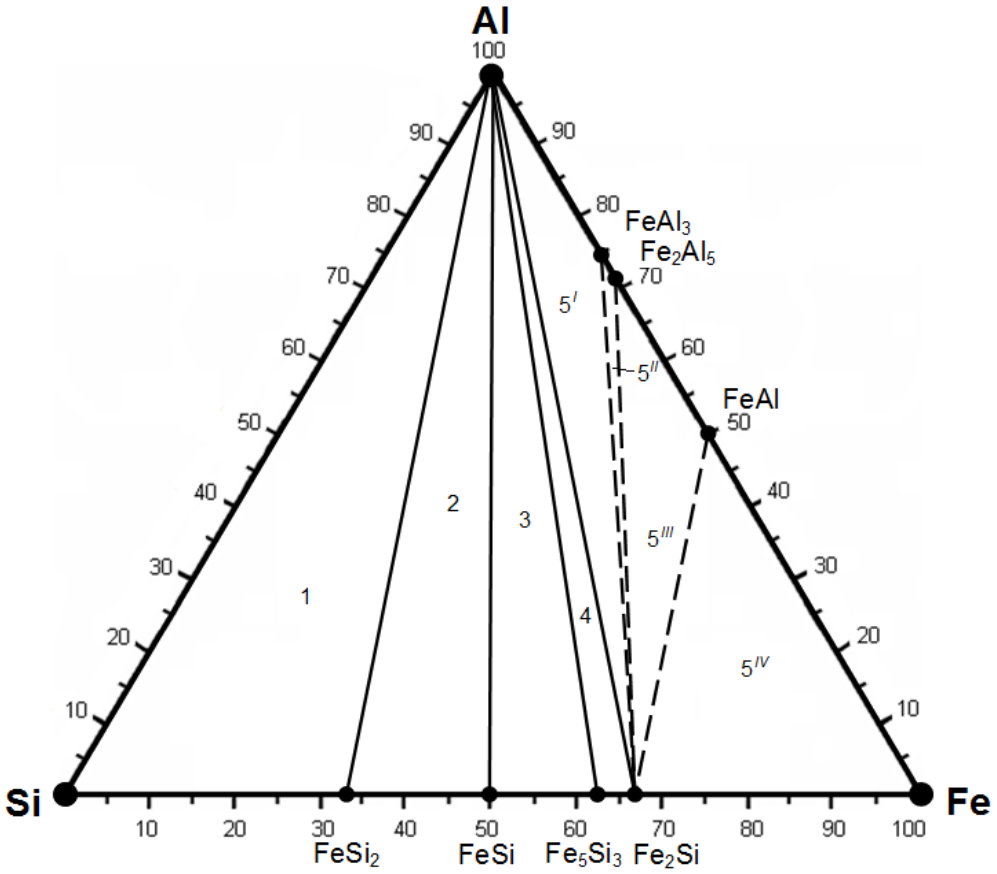

Figure 1: Diagram of the substantial ratios in the Si–Al–Fe system at T = 2500K

The values of changing Gibbs energy of the reactions for the Si-Cr-Fe subsystem are given in Table 2. On the basis of the obtained thermodynamic data the Si-Cr-Fe subsystem DPhS was constructed also up to the temperature of 2500 K (Figure 2).

Table 2: Thermodynamics of reactions in the Si-Cr-Fe subsystem

Reaction equation	**ΔG^0_{2500}, (J)**
$FeSi+CrSi_2=FeSi_2+CrSi$	-45773.4
$2FeSi+5CrSi=2FeSi_2+Cr_5Si_3$	-32065.96
$4FeSi+3Cr_5Si_3=4FeSi_2+5Cr_3Si$	-70950.76
$FeSi+Cr_3Si=FeSi_2+3Cr$	14613.29
$Fe_5Si_3+2Cr_3Si=5FeSi+6Cr$	39786.33
$5Fe_2Si+Cr_3Si=2Fe_5Si_3+3Cr$	7091.3
$2Fe+Cr_3Si=Fe_2Si+3Cr$	41238.29

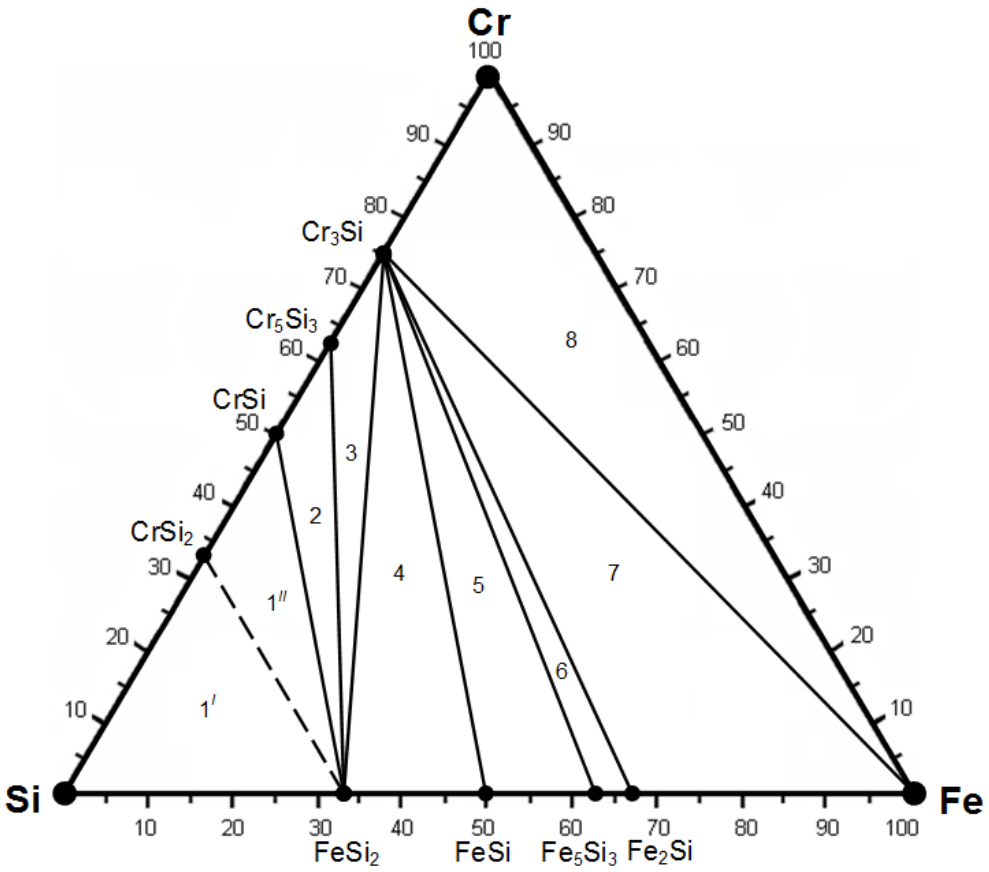

Figure 2: Diagram of the substantial ratios in the Si-Cr-Fe subsystem at T = 2500K

When carrying out triangulation of the triple Si-Cr-Fe system (Figure 2) 8 zones were formed. The Si – CrSi – $FeSi_2$ zone has one congruent compound, $CrSi_2$, as a result of which two subzones were formed: Si-$CrSi_2$-$FeSi_2$ (1^{I})and CrSi-$FeSi_2$-$CrSi_2$ (1^{II}). In the CrSi – Cr_5Si_3 – $FeSi_2$ (2), Cr_5Si_3 – Cr_3Si – $FeSi_2$ (3), Fe_2Si – Cr_3Si – FeSi (4), FeSi – Cr_3Si – Fe_5Si_3 (5), Fe_5Si_3 – Cr_3Si – Fe_2Si (6), Fe_2Si – Cr_3Si – Fe (7) и Cr_3Si – Cr – Fe (8) there are incongruent compounds.

The values of Gibbs energy changing of reactions for the Fe–Al–Cr system are presented in Table 3. Based on the obtained thermodynamic data a DPhS of the Fe–Al–Cr system was constructed for the temperature of 2500K (Figure 3). The Fe–Al–Cr system DPhS is a totality of double compounds found in its binary systems Cr–Fe, Fe–Al, Cr–Al.

Table 3: Thermodynamics of reactions in the Fe–Al–Cr subsystem (T=2500K)

Reaction equation	**ΔG^0_{2500}, (J)**
$Fe + Cr_2Al = FeAl + 2Cr$	- 7161.8
$Fe_2Al_5 + 6Cr = 2FeAl + 3Cr_2Al$	338089.4
$2FeAl_3 + 3Cr = Fe_2Al_5 + Cr_2Al$	- 282521.99
$11FeAl_3 + 2{,}5Cr_2Al = 5{,}5Fe_2Al_5 + Cr_5Al_8$	- 1614651.8
$26FeAl_3 + 4Cr_5Al_8 = 13Fe_2Al_5 + 5Cr_4Al_9$	- 3489900.6
$14FeAl_3 + Cr_4Al_9 = 7Fe_2Al_5 + 4CrAl_4$	- 2194167.3
$3FeAl_3 + CrAl_4 = 1{,}5Fe_2Al_5 + 0{,}5Cr_2Al$	- 388554.25
$3FeAl_3 + 0{,}5Cr_2Al = 1{,}5Fe_2Al_5 + CrAl_7$	- 440552.1

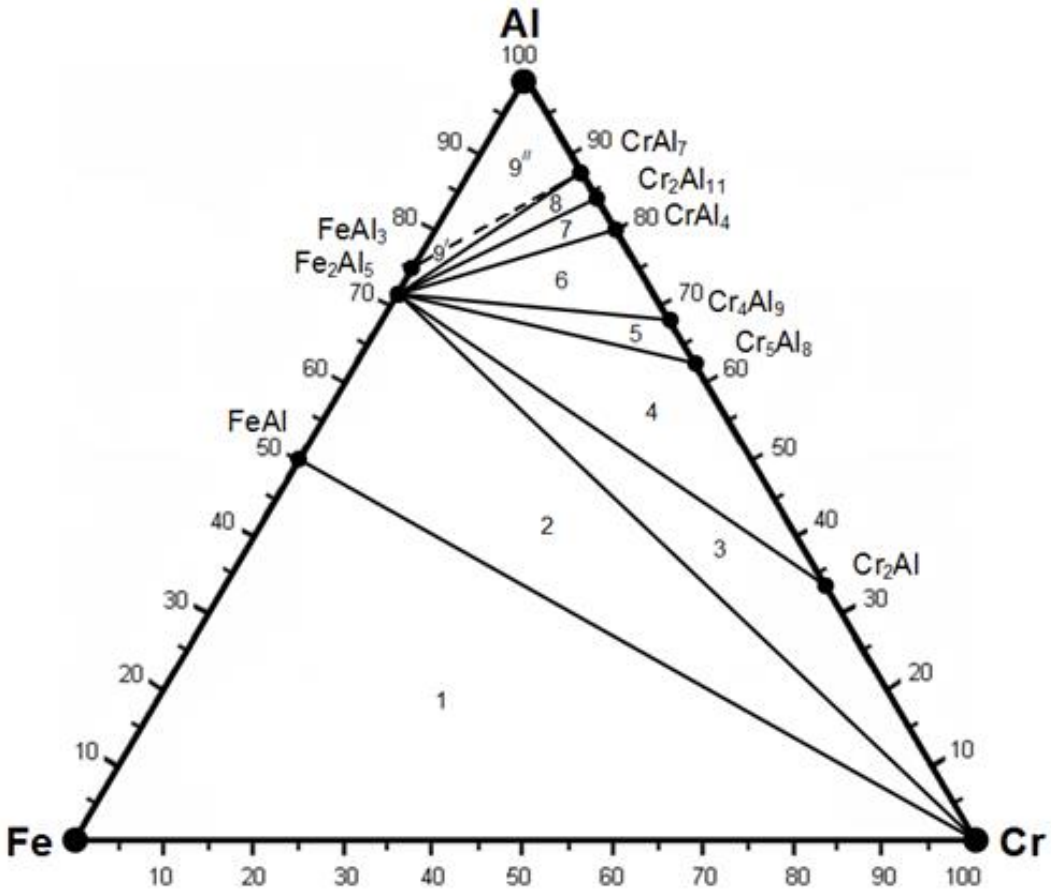

Figure 3: Diagram of substantial ratios in the Fe–Al–Cr subsystem at T=2500 K

When carrying out triangulation of the Fe – Al – Cr triple system (Figure 3) 9 zones were formed. In the Fe – FeAl – Cr (1), Fe_2Al_5 – Cr – FeAl (2), Fe_2Al_5 – Cr_2Al – Cr (3), Fe_2Al_5 – Cr_5Al_8 – Cr_2Al (4), Fe_2Al_5 – Cr_4Al_9 – Cr_5Al_8 (5), Fe_2Al_5 – $CrAl_4$ – Cr_4Al_9 (6), Fe_2Al_5 – Cr_2Al_{11} – $CrAl_4$ (7) иFe_2Al_5 – $CrAl_7$ – Cr_2Al_{11} (8) zones there are no incongruent compounds. At this, the Fe_2Al_5 – Al – $CrAl_7$ zone has one incongruent compound, $FeAl_3$, which divides this zone into two subzones: Fe_2Al_5 – $FeAl_3$ – $CrAl_7$ (9^I) and$FeAl_3$ – Al – $CrAl_7$ (9^{II}).

The values of Gibbs energy changing for the Si–Al–Cr system are presented in Table 4. Based on the obtained thermodynamic data there was built a DPhS for the Si–Al–Cr system at the temperature 2500 K (Figure 4).

Table 4: Thermodynamics of reactions in the Si–Al–Cr subsystem (T=2500K)

Reaction equation	**ΔG^0_{2500}, (J)**
$2Si+CrAl_7=CrSi_2+7Al$	- 190216
$CrSi_2+CrAl_7=2CrSi+7Al$	- 214368
$3CrSi+2CrAl_7=Cr_5Si_3+14Al$	- 339778
$0,5Cr_5Si_3+2CrAl_7=1,5Cr_3Si+14Al$	- 359510

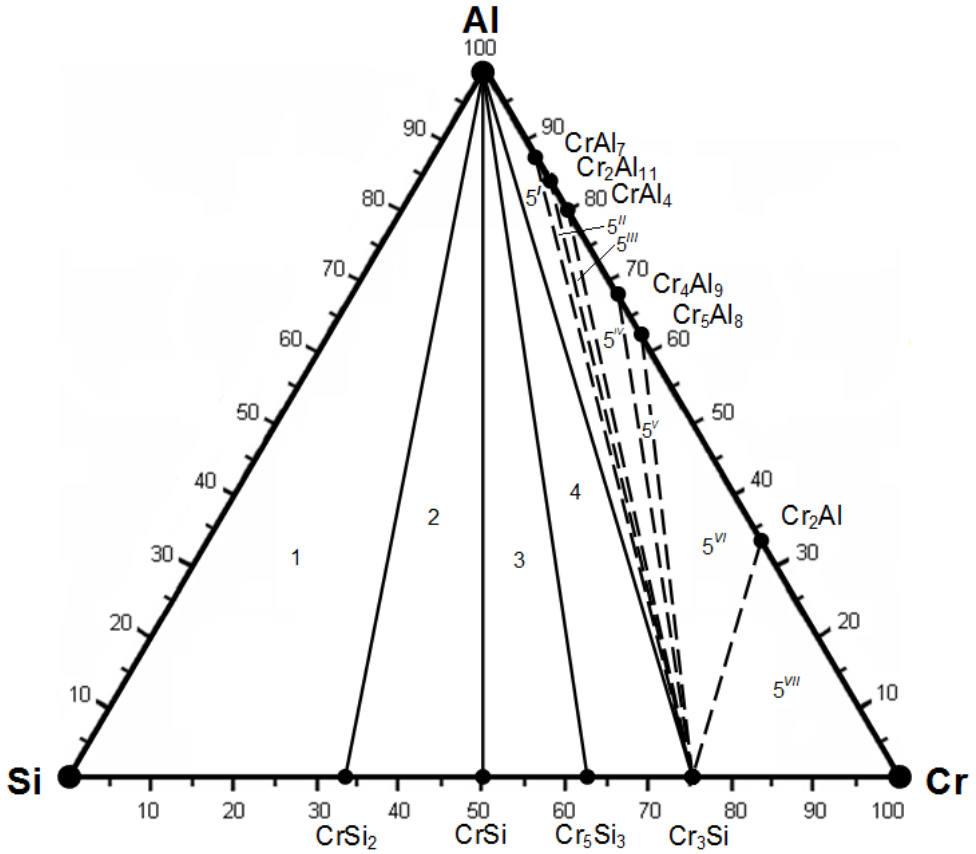

Figure 4: Diagram of the substantial ratios in the Si-Al-Cr subsystem at T=2500 K

When carrying out triangulation of the triple Si – Al – Cr system (Figure 4) there were formed 5 zones. In the Si – Al – $CrSi_2$ (1), $CrSi_2$ – Al – CrSi (2), CrSi – Al–Cr_5Si_3 (3), Cr_5Si_3 – Al – Cr_3Si (4) there are no incongruent compounds. On the diagram site Fe_3Si – Al – Cr there are two congruent (Cr_2Alи$CrAl_7$) and four incongruent compounds: Cr_2Al_{11}, $CrAl_4$, Cr_4Al_9, Cr_5Al_8, as a result of which there are formed seven subzones: Cr_3Si – Al – $CrAl_7$ (5^{I}), Cr_3Si – $CrAl_7$ – Cr_2Al_{11} (5^{II}), Cr_3Si – Cr_2Al_{11} – $CrAl_4$ (5^{III}), Cr_3Si – $CrAl_4$ – Cr_4Al_9 (5^{IV}), Cr_3Si – Cr_4Al_9 – Cr_5Al_8 (5^{V}), Cr_3Si – Cr_5Al_8 – Cr_2Al (5^{VI}), Cr_3Si – Cr_2Al – Cr (5^{VII}).

Table 5: Congruent and incongruent metal compounds in the Cr-Fe-Al-Si system and their coordinates on the quadruple concentration simplex (tetrahedron)

No	Compound	Coordinated based on*1000 mass fraction			
		Cr	Fe	Al	Si
1	Cr	1000	0	0	0
2	Fe	0	1000	0	0
3	Al	0	0	1000	0
4	Si	0	0	0	1000
5	FeAl	0	675	325	0
6	$FeAl_2$	0	509	491	0
7	Fe_2Al_5	0	453	547	0
8	$FeAl_3$	0	409	591	0
9	Fe_2Si	0	800	0	200
10	Fe_5Si_3	0	769	0	231
11	FeSi	0	667	0	333
12	$FeSi_2$	0	500	0	500
13	$CrAl_7$	216	0	784	0

No	Compound	Coordinated based on*1000 mass fraction			
		Cr	Fe	Al	Si
14	Cr_2Al_{11}	259	0	741	0
15	$CrAl_4$	325	0	675	0
16	Cr_4Al_9	461	0	539	0
17	Cr_5Al_8	546	0	454	0
18	Cr_2Al	790	0	210	0
19	Cr_3Si	848	0	0	152
20	Cr_5Si_3	755	0	0	245
21	CrSi	650	0	0	350
22	$CrSi_2$	481	0	0	519

The accepted coordinates (on the basis of *1000 mass fraction) the congruent and incongruent compounds of the Cr-Fe-Al-Si system used further in case of studying their fields of crystallization are specified in Table 5. In the system 22 simple and complex compounds are formed.

In Figure 5 general view of the analyzed Cr-Fe-Al-Si system in liquid state is presented.

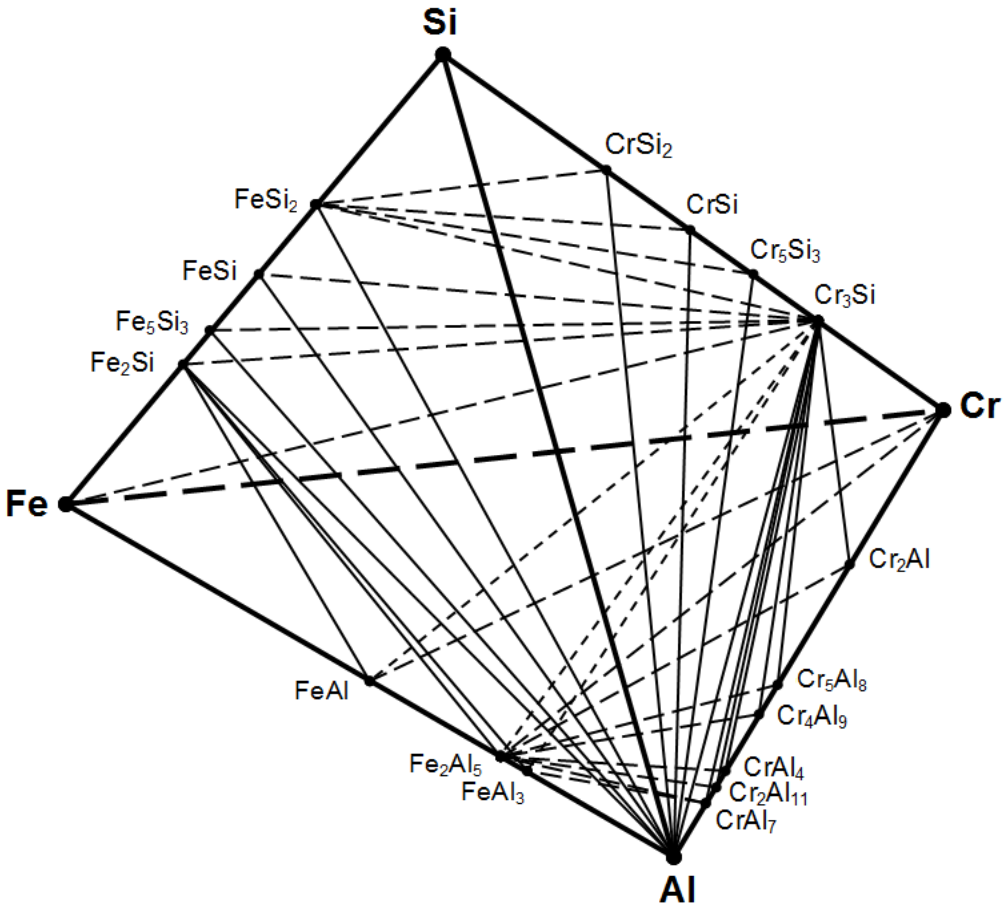

Figure 5: Tetrahedration of the metallic Cr-Fe-Al-Si system

3 CONCLUSIONS

On the basis of the carried-out tetrahedration of the metal Fe-Cr-Si-Al system for the liquid-phase state (T=2500K) it is set that the system consists of 21 elementary independent tetrahedrons, the simulating compositions of different grades of aluminumsilicochrome in the course of reducing the elements from ashes of high-ash coal.

Splitting of the general system is realized taking into account congruent and incongruent compounds. The amount of the relative volumes of elementary tetrahedrons is equal to a unit (0.999999) that confirms the correctness of the carried-out tetrahedration. Fundamental elementary fourfold systems and their volumes are given in Table 6.

Table 6: List of tetrahedrons of the Cr-Fe-Al-Si system

No	Tetrahedrons	Elementary volumes
1	$Si – FeSi_2 – Al – CrSi_2$	0.2405
2	$CrSi_2 – FeSi_2 – CrSi – Al$	0.0845
3	$CrSi – Cr_5Si_3 – Al – FeSi_2$	0.0525
4	$Cr_5Si_3 – Cr_3Si – Al – FeSi_2$	0.0465
5	$FeSi – FeSi_2 – Al – Cr_3Si$	0.141616
6	$Fe_5Si_3 – FeSi – Al – Cr_3Si$	0.086496
7	$Fe_2Si – Fe_5Si_3 – Al – Cr_3Si$	0.026288
8	$FeAl_3 – Al – Cr_3Si – Fe_2Si$	0.069366
9	$FeAl_3 – Fe_2Al_5 – Cr_3Si – Fe_2Si$	0.007462
10	$Fe_2Al_5 – FeAl – Cr_3Si – Fe_2Si$	0.037651
11	$FeAl – Fe – Cr_3Si – Fe_2Si$	0.05512
12	$Fe – Cr – Cr_3Si – FeAl$	0.0494
13	$FeAl – Fe_2Al_5 – Cr – Cr_3Si$	0.033744
14	$Fe_2Al_5 – Cr – Cr_3Si – Cr_2Al$	0.01446
15	$Fe_2Al_5 – Cr_2Al – Cr_5Al_8 – Cr_3Si$	0.016801
16	$Fe_2Al_5 – Cr_4Al_9 – Cr_5Al_8 – Cr_3Si$	0.005853
17	$Fe_2Al_5 – CrAl_4 – Cr_4Al_9 – Cr_3Si$	0.009364
18	$Fe_2Al_5 – Cr_2Al_{11} – CrAl_4 – Cr_3Si$	0.004544
19	$Fe_2Al_5 – CrAl_7 – Cr_2Al_{11} – Cr_3Si$	0.002961
20	$FeAl_3 – Fe_2Al_5 – CrAl_7 – Cr_3Si$	0.001445
21	$Al – FeAl_3 – CrAl_7 – Cr_3Si$	0.013428
Total		**0.999999**

Thus, the data provided and the results of the carried-out calculations confirm reliability of tetrahedration of the diagram of the phase structure (ratio) of the metal Cr-Fe-Al-Si system in liquid state. It will afterwards permit to predict phase compositions of metal products in a subsolidus state when smelting different grades of the complex alloy aluminumsilicochrome.

4 REFERENCES

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