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*A. Zhakan¹, A. Zhunusov², A. Akhmetov³, S. Kabylkanov⁴, O. Yucel⁵

^{1,2}Toraighyrov University, Republic of Kazakhstan, Pavlodar
^{1,3,4}Zh. Abishev Chemical and Metallurgical Institute, Republic of Kazakhstan, Karaganda
⁵Istanbul Technical University, Turkey, Istanbul
¹ORCID <u>https://orcid.org/0009-0002-3810-0528</u>
²ORCID <u>https://orcid.org/0000-0001-9119-9737</u>
³ORCID <u>https://orcid.org/0000-0002-1606-838X</u>
⁴ORCID <u>https://orcid.org/0000-0002-1272-2065</u>
⁵ORCID <u>https://orcid.org/0000-0002-3879-0410</u>
*e-mail: <u>armat.01.01@mail.ru</u>

THERMODYNAMIC MODELING OF THE PROCESS OF SMELTING A COMPLEX CHROMIUM-MANGANESE-SILICON-CONTAINING FERROALLOY

This article presents the results of thermodynamic modeling of the process of smelting chromium-manganese-silicon-containing ferroalloy from technogenic raw materials of Kazakhstan. Thermodynamic modeling of chromium-manganesesilicon-containing ferroalloy was carried out using the HSC Chemistry 6 software package (Outokumpu, Finland), based on the principles of minimizing the Gibbs energy and thermodynamic variational principles. Thermodynamic analysis for modeling the process of smelting a complex alloy was carried out in the temperature range from 500 to 2000 °C for four real charge compositions (with a 5% deficiency of solid carbon, with a normal course of the regime, and with an excess of solid carbon of 5% and 10% of the stoichiometry). The mechanism of combined carbothermic reduction of silicon, manganese, chromium and iron was studied using the Fe-Cr-Mn-Si-Al-Ca-Mg-C-O system. The calculations performed allowed us to fully study all the physicochemical processes occurring during smelting of chromium-manganese-silicon-containing ferroalloy using the carbothermic method. Based on the thermodynamic data, the optimum consumption of solid carbon per 100 kg of charge (chromium and manganese dust) was determined to be 10.75 kg. The chemical composition of the ferroalloy at 1800 °C is, %: Cr - 35.84; Mn - 24.47; Si - 16.25 and Fe - 22.63.

Keywords: complex ferroalloy, carbothermic process, chromium-manganesesilicon-containing ferroalloy, thermodynamics, reduction.

Introduction

Complex alloys are primarily composed of elements such as iron, chromium, manganese, silicon, aluminum, and others [1-2].

In the theory and practice of producing chromium-manganese-silicon (Cr-Mn-Si) ferroalloys, the contributions of I. P. Kazachkov and N. P. Melikaev are particularly

significant. Their research led to the development of a one-stage alloy smelting process, which is based on the reduction of iron, chromium, manganese, and silicon oxides from a mixture of chromium and manganese ores using carbon [3-6].

According to [7-9], the reduction of chromium ores begins with the reduction of chromite $\text{FeCr}_{2}O_{4}+C$ according to the reaction:

$$FeCr_2O_4 + C = FeCr_2O_3 + CO$$
(1)

The temperature at which the reduction begins is 1010 °C.

The reduction of magnochromite $MgCr_2O_4$ can proceed according to the reactions:

$$MgCr_{2}O_{4} + \frac{13}{3}C = \frac{2}{3}Cr_{3}C_{2} + MgO + 3CO$$
(2)

$$MgCr_{2}O_{4} + 27/7C = 2/7Cr_{7}C_{3} + MgO + 3CO$$
(3)

$$MgCr_{2}O_{4} + 81/23C = 2/23Cr_{23}C_{6} + MgO + 3CO$$
(4)

$$MgCr_2O_4 + 3C = 2Cr + MgO + 3CO$$
(5)

For a rough estimate of the temperatures at which the reduction of magnochromite begins, the value of the change in the Gibbs energy of the reaction was adopted

$$MgO + Cr_2O_3 = MgCr_2O_4$$
 (6)

within the temperature range of 0 - 1535 °C, i.e. the same 1225, 1265, 1310 and 1385 °C, respectively.

In the reduction of manganese, special attention is paid to the reduction reactions from MnO and rhodonite $MnSiO_3$, since higher manganese oxides tend to dissociate at high temperatures with the release of oxygen. This means that as the temperature increases, manganese oxides such as Mn_2O_3 and MnO_2 can decompose, releasing oxygen and turning into lower oxides, which plays a key role in the reduction process. The reduction reactions of these compounds can significantly affect the efficiency of manganese reduction in metallurgical processes. The following reactions are possible:

$$MnO + \frac{10}{7C} = Mn_7C_3 + CO$$
(7)

$$MnO + 4/3C = 1/3Mn_3C + CO$$
(8)
MnO + C = Mn + CO (9)

$$MnSiO_{2} + 10/7C = 1/7Mn_{7}C_{2} + SiO_{2} + CO$$
(10)

$$MnSiO_3 + 4/3C = 1/3Mn_3C + SiO_2 + CO$$
(11)

$$MnSiO_3 + C = Mn + SiO_2 + CO$$
 (12)

When considering the mechanism of silicon reduction, we note two important reactions:

$$SiO_2 + 3C = SiC + 2CO$$
(13)

$$\mathrm{SiO}_2 + 2\mathrm{C} = \mathrm{Si}_{\mathrm{liquid}} + 2\mathrm{C} \tag{14}$$

Based on reliable experimental data [6], N.V. Tolstoguzov et al. demonstrated that silicon carbide (SiC) can exist in equilibrium with a metal containing more than 22% silicon. In the case of smelting a chromium-manganese-silicon-containing ferroalloy with a silicon content of 10%, the probability of reaction (13) is negligible. For reaction (14), the temperature at which reduction begins is 1665 °C [10-11].

Materials and methods

Thermodynamic modeling of the Cr-Mn-Si ferroalloy production process encompasses all thermodynamic principles related to chemical reactions, phase equilibria, and heat exchange within the system [12].

The production of Cr-Mn-Si ferroalloys is achieved through the reduction of Cr, Mn, and Si oxides with carbon.

Thermodynamic simulations of the Cr-Mn-Si ferroalloy process were conducted using the HSC Chemistry software, which provides extensive thermochemical data on enthalpy (H), entropy (S), and heat capacity (C) for over 29 000 chemical compounds. This software follows the methodology of the SGTE (Scientific Group Thermodata Europe) consortium, which consists of scientific institutions engaged in developing 58 thermodynamic databases for inorganic and metallurgical systems. The consortium includes organizations from Germany, Canada, France, Sweden, the UK, and the USA, and applies this data to solve practical engineering challenges. The work utilized the Equilibrium Compositions module, which is based on the equilibrium calculation method relying on the minimization of Gibbs free energy [12-13].

The principles for thermodynamic modeling of Fe-Cr-Mn-Si-Al-Ca-Mg-C-O systems were established for the thermodynamic analysis [12-13].

The analysis was performed within a temperature range from 500 to 2000 °C. The lower limit represents the standard state, and temperature variations up to 900 °C result in minimal changes, while the upper limit corresponds to the final state, characterized by the melting points of the components and the formation of the final reaction products. This range defines the initial and final equilibrium states of the system. In all calculations, a pressure of 0.1 MPa was assumed, which roughly corresponds to one physical atmosphere, commonly used in most metallurgical processes, including those involving the interaction of solid phases with carbon. The system's volume is determined by its thermodynamic state, and the system is considered to be in a closed state [12-16].

To establish the optimal consumption of solid carbon in the smelting of Cr-Mn-Si ferroalloy, a thermodynamic analysis of four variants of the charge mixture composition was carried out (Table 1).

Charging options	Cr ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	С	O/C*
Nº 1	12.66	7.84	8.50	37.55	6.31	1.39	15.37	9.85	3,90
Nº 2	12.44	7.71	8.33	37.88	6.39	1.37	15.07	10.33	3,71
Nº 3	12.18	7.59	8.18	38.16	6.46	1.35	14.81	10.75	3,56
<u>№</u> 4	11.40	7.44	8.51	38.90	6.42	1.40	14.29	11.13	3,44

Table 1 – Chemical composition of the charge mixture, kg

* - ratio of the sum of oxides to solid carbon

The following phases were adopted for the metallic phase: MnC₂, Cr, Fe, Mn, Cr₄C, Fe₃C, C, Cr₃C₂, Cr₇C₃, FeSi, Cr₃Si, CrSi, Fe₃Si, Cr₅Si₃, Si, CrSi₂, SiC, FeSi₂, Fe₅Si₃, MnSi, MnSi_{1.72}, MnSi_{1.72}, Mn₅Si₃, Mn₃Si;

The following phases are adopted for the slag phase:Cr₂FeO₄, Cr₂O₃, SiO₂, FeO_{1.056}, MgSiO₃, FeAl₂O₄, Al₂O₃, CaO*Al₂O₃*2SiO₂, MgO*Al₂O₃, $CaO*MgO*2SiO_2$, $CaMgSi_2O_6$, CaSiO₃, $MgCr_2O_4$, Mg_2SiO_4 , $(CaMg)_{0.5}SiO_3$, $(CaFe)_{0.5}SiO_3$, $Mg_2Al_4Si_5O_{18}$, Cr_2MgO_4 , $FeSiO_3$, MgO_4 , Al₄Mg₂Si₅O₁₈, CaAl₂SiO₆, CaO*MgO*SiO₂, FeO, *3Al₂O₃*2SiO₂, CaO*Al₂O₃*SiO₂, CaO*Cr₂O₃, Mg₃Al₂Si₃O₁₂, CaMgSiO₄, CaO*Al₂O₃, *2CaO*MgO*2SiO₂, *2CaO*SiO₂, *2FeO*SiO₂, $CaO*2Al_2O_3$, *2CaO*Al₂O₃*SiO₂, FeO*SiO₂, CaO. Al₂O₃*2SiO₂, Ca₃Si₂O₇, *3CaO*2SiO₂, CaO*MgO, *3CaO*MgO*2SiO₂, *3CaO*Al₂O₃*3SiO₂, $CaO*6Al_2O_3$, $Fe_2Al_4Si_5O_{18}$, $Ca_2MgSi_2O_7$, Ca₃SiO₅, $Fe_3Al_2Si_3O_{12}$, *3CaO*SiO₂, *2CaO*Al₂O₃, MgCO₃, CaFeSiO₄, Fe₂MgO₄, *3CaO*Al₂O₃, $CaO*Fe_2O_3$, $Ca_3Fe_2Si_3O_{12}$, $*2CaO*Fe_2O_3$, $MgFe_{1.415}Cr_{0.632}O_{4.07}$, $CaMg(CO_3)_2$, $Mg_7Al_9O_4*Al_9Si_3O_{36}$, $Mg_2Al_4SiO_{10}$, $Ca_3(Al_2Si_2O_8)_3*CaCO_3$, Mn_{0.9554}Ca_{0.0446}SiO₃, Ca₃Cr₂(SiO₄)₃, CaFe₃O₅, MnO*Al₂O₃, MnO, MnSiO₃, $CaFe_5O_7$, Fe_2MnO_4 , $MnO^*Fe_2O_3$, $CaMg_3(CO_3)_4$, $*2Ca_2SiO_4*CaCO_3$, $Ca_3Si_2O_7*2CaCO_3$, *12CaO*7Al₂O₃, Fe₃(CO)₁₂, *4CaO*Al₂O₃*Fe₂O₃, Cr_5O_{12} , $Fe_2(CO)_9$, $Ca(MnO_4)_2$, Mn_2SiO_4 .

The following phases are adopted for the gas phase: $CO_{(g)}$, $CO_{2(g)}$, $SiO_{(g)}$, $Mg_{(g)}$, $Al_{(g)}$, $Si_{(g)}$, $AlO_{(g)}$, $MgO_{(g)}$, $Al_2O_{(g)}$, $MnO_{(g)}$, $MnO_{(g)}$.

Results and discussion

Results of modeling the process in the condensed phase.

As a result of the modeling (Fig. 1 - 12), it was established that during the smelting of Cr-Mn-Si ferroalloy by the carbothermic method up to 2000 °C, the formation and some change of elements occurs, accompanied by their transition to a condensed phase.



Figure 1 – Dependence of the change in slag phases on the temperature of the charge mixture (Deficiency of 5% of stoichiometry)



Figure 2 – Dependence of the change in metal phases on the temperature of the charge mixture (Deficiency of 5% of stoichiometry)

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Figure 3 – Dependence of the change in slag phases on the temperature of the charge mixture (Stoichiometry)



Figure 4 – Dependence of the change in metal phases on the temperature of the charge mixture (Stoichiometry)



Figure 5 – Dependence of the change in slag phases on the temperature of the charge mixture (Excess of 5% of stoichiometry)



Figure 6 – Dependence of the change in metal phases on the temperature of the charge mixture (Excess of 5% of stoichiometry)



Figure 7 – Dependence of the change in slag phases on the temperature of the charge mixture (Excess of 10% of stoichiometry)



Figure 8 – Dependence of the change in metal phases on the temperature of the charge mixture (Excess of 10% of stoichiometry)



The results of modeling the process in the gas phase.

Figure 9 – Dependence of the change in gas phases on the temperature of the charge mixture (Deficiency of 5% of stoichiometry)



Figure 10 – Dependence of the change in gas phases on the temperature of the charge mixture (Stoichiometry)

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Figure 11 – Dependence of the change in gas phases on the temperature of the charge mixture (Excess of 5% of stoichiometry)



Figure 12 – Dependence of the change in gas phases on the temperature of the charge mixture (Excess of 10% of stoichiometry)

The following are the results of the analysis of the simulation and data presented in Figures 1-12.

Charge mixture with a reducing agent deficiency of 5%. The amount of the MgSiO, phase in the temperature range from 500 to 2000 °C is 23-26 kg. The SiO, phase at 500 °C is 16 kg, and at 2000 °C it decreases to 9 kg. The reduction processes leading to the formation of metal begin at a temperature of 1200 °C, while the content of Fe and Mn in the metallic phase reaches 5-6 kg at a temperature of 1300 °C. The amount of the Cr₂FeO₄ phase begins with 11 kg at 500 °C and decreases to 1 kg at 1100 °C. The Cr₂FeO₄ phase decomposes into Cr₂O₃, reaching 10 kg at 1100 °C. In the temperature range from 1100 to 1300 °C, the Cr₂O₃ phase decreases in the slag mixture, while the amount of Cr in the metallic phase increases to 4 kg. The amount of MnC, is 8.5 kg in the temperature range of 500-1200 °C, after which it decreases, and the amount of manganese in the metallic phase reaches 5.92 kg. Starting from a temperature of 1100 °C, the amount of solid carbon and oxide compounds decreases, and in the temperature range of 1700 °C they reach minimum values. At the same time, as the amount of solid carbon decreases, the content of COgas increases. The content of Fe in the temperature range from 900 to 1300 °C is 2-5 kg, and at 2000 °C it reaches 4.38 kg. Silicon in the metal is present in the form of phases Cr₅Si₃, FeSi, CrSi, Fe₃Si, Cr₃Si, CrSi₂.

The charge mixture according to stoichiometry. In this case, no significant changes are observed between the phases. The SiO₂ phase at 500 °C is 17 kg, and at 2000 °C it decreases to 8 kg. The reduction processes leading to the formation of metal begin at a temperature of 1200 °C, while the content of Fe and Mn in the metallic phase is 5-6 kg at a temperature of 1300 °C. The amount of the Cr_2FeO_4 phase begins with 11 kg at 500 °C and decreases to 1 kg at 1100 °C. The Cr_2FeO_4 phase decomposes into Cr_2O_3 , which at 1100 °C is 10 kg. In the temperature range from 1100 to 1300 °C, the Cr₂O₂ phase decreases in the composition of the slag mixture, and the amount of Cr in the metallic phase increases to 3 kg. The amount of MnC2 in the temperature range of 500-1200 °C is 8.33 kg, after which it decreases, and the manganese content in the metallic phase reaches 5.80 kg. Starting from the temperature of 1100 °C, the amount of solid carbon and oxide compounds decreases, and in the temperature range of 1700 °C they reach minimum values. As the amount of solid carbon decreases, the content of COgas increases. The content of Fe in the temperature range from 900 to 1300 $^{\circ}$ C is 2–5 kg, and at 2000 °C it reaches 4.10 kg. Si in the metal is present in the form of the phases Cr₅Si₃, FeSi, CrSi, Fe₃Si, Cr₃Si, CrSi₂.

The charge mixture with a 5% excess of reducing agent. In this case, there were no significant changes between the phases. The amount of the MgSiO₃ phase in the temperature range from 500 to 2000 °C is 22–26 kg. The SiO₂ phase at 500 °C is 17 kg, and at 2000 °C it decreases to 7 kg. The amount of MnC2 in the temperature range from 500 to 1200 °C is 8.18 kg, after which it begins to decrease, and the Mn content in the metallic phase reaches 5.69 kg. Starting from a temperature of 1100 °C, the amount of solid carbon and oxide compounds decreases, and in the temperature range of 1700 °C it reaches minimum values. As the amount of solid carbon decreases, the COgas content increases.

The charge mixture with a 10% excess of reducing agent. The amount of the $MgSiO_3$ phase in the temperature range from 500 to 2000 °C is 21–25 kg. The SiO– phase at 500 °C is 18 kg, and at 2000 °C it decreases to 7 kg. The amount of MnC2 in the temperature range from 500 to 1200 °C is 8.51 kg, after which it begins to decrease, and the Mn content in the metallic phase reaches 5.92 kg. Starting from a temperature of 1100 °C, the amount of solid carbon and oxide compounds decreases, and in the temperature range of 1700 °C they reach minimum values. As the amount of solid carbon decreases, the COgas content increases.

Based on thermodynamic data, the change in the composition of metal and slag for each charge mixture was calculated in the temperature range from 1000 to 2000 $^{\circ}$ C (Table 2).

Charge mixture \mathbb{N}_{2} 1 – 5 % solid carbon deficiency										
t °C	N	Aetal con	nposition	, %	Slag composition, %					
ι, υ	Cr	Mn	Si	Fe	Cr ₂ O ₃	FeO	SiO ₂	Al ₂ O ₂	3 MgO	
1000	0.13	0.00	0.00	37.15	17.14	2.57	50.97	8.56	20.76	
1100	1.95	0.00	0.00	43.64	17.08	1.01	51.99	8.73	21.18	
1200	18.61	30.73	0.00	26.30	11.07	0.56	56.09	9.42	22.85	
1300	34.78	26.63	0.02	24.22	2.26	0.12	61.96	10.41	25.25	
1400	37.70	25.91	0.27	23.77	0.13	0.06	63.27	10.67	25.87	
1500	37.76	25.80	2.20	23.78	0.01	0.03	62.73	10.87	26.36	
1600	37.40	25.54	9.65	23.53	0.01	0.03	60.11	11.64	28.21	
1700	37.45	25.57	12.02	23.49	0.01	0.04	58.89	12.00) 29.07	
1800	37.82	25.83	12.16	23.63	0.01	0.07	58.06	12.25	5 29.61	
1900	38.60	26.39	10.89	23.90	0.04	0.13	57.11	12.53	30.20	
2000	39.85	27.34	8.41	24.32	0.13	0.22	55.73	12.92	2 30.98	
	Charge mixture № 2 - stoichiometry									
+ °C	N	Metal con	npositior	ı, %	Slag composition, %					
l, C	Cr	Mn	Si	Fe	Cr ₂ O ₃	FeO	SiO ₂	Al ₂ O ₃	MgO	
1000	0.14	0.00	0.00	25.04		I		0 - 0		
1100	0.04		0.00	33.84	16.91	2.32	51.62	8.70	20.44	
	2.24	0.00	0.00	41.54	16.91 16.75	2.32 0.88	51.62 52.65	8.70 8.88	20.44 20.85	
1200	2.24 20.96	0.00 28.91	0.00	33.84 41.54 25.14	16.91 16.75 9.54	2.32 0.88 0.47	51.62 52.65 57.51	8.70 8.88 9.70	20.44 20.85 22.78	
1200	2.24 20.96 34.74	0.00 28.91 25.57	0.00 0.00 0.03	33.84 41.54 25.14 23.41	16.91 16.75 9.54 1.54	2.32 0.88 0.47 0.10	51.62 52.65 57.51 62.85	8.70 8.88 9.70 10.60	20.44 20.85 22.78 24.90	
1200 1300 1400	2.24 20.96 34.74 36.71	0.00 28.91 25.57 25.09	0.00 0.00 0.03 0.34	33.84 41.54 25.14 23.41 23.16	16.91 16.75 9.54 1.54 0.07	2.32 0.88 0.47 0.10 0.05	51.62 52.65 57.51 62.85 63.73	8.70 8.88 9.70 10.60 10.80	20.44 20.85 22.78 24.90 25.35	
1200 1300 1400 1500	2.24 20.96 34.74 36.71 36.69	0.00 28.91 25.57 25.09 25.00	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.03\\ 0.34\\ 2.87\end{array}$	33.84 41.54 25.14 23.41 23.16 23.15	16.91 16.75 9.54 1.54 0.07 0.01	2.32 0.88 0.47 0.10 0.05 0.02	51.62 52.65 57.51 62.85 63.73 62.95	8.70 8.88 9.70 10.60 10.80 11.06	20.44 20.85 22.78 24.90 25.35 25.96	
1200 1300 1400 1500 1600	2.24 20.96 34.74 36.71 36.69 36.28	0.00 28.91 25.57 25.09 25.00 24.70	$\begin{array}{c} 0.00\\ 0.00\\ 0.03\\ 0.34\\ 2.87\\ 11.58\end{array}$	33.84 41.54 25.14 23.41 23.16 23.15 22.86	16.91 16.75 9.54 1.54 0.07 0.01 0.00	2.32 0.88 0.47 0.10 0.05 0.02	51.62 52.65 57.51 62.85 63.73 62.95 59.80	8.70 8.88 9.70 10.60 10.80 11.06 12.00	20.44 20.85 22.78 24.90 25.35 25.96 28.17	
1200 1300 1400 1500 1600 1700	2.24 20.96 34.74 36.71 36.69 36.28 36.36	0.00 28.91 25.57 25.09 25.00 24.70 24.75	0.00 0.00 0.03 0.34 2.87 11.58 14.22	33.84 41.54 25.14 23.41 23.16 23.15 22.86 22.85	16.91 16.75 9.54 1.54 0.07 0.01 0.00	2.32 0.88 0.47 0.10 0.05 0.02 0.03	51.62 52.65 57.51 62.85 63.73 62.95 59.80 58.32	8.70 8.88 9.70 10.60 10.80 11.06 12.00 12.45	20.44 20.85 22.78 24.90 25.35 25.96 28.17 29.20	
1200 1300 1400 1500 1600 1700 1800	2.24 20.96 34.74 36.71 36.69 36.28 36.36 36.36 36.81	0.00 28.91 25.57 25.09 25.00 24.70 24.75 25.06	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.03\\ 0.34\\ 2.87\\ 11.58\\ 14.22\\ 14.37\\ \end{array}$	33.84 41.54 25.14 23.16 23.15 22.86 22.85 23.08	16.91 16.75 9.54 1.54 0.07 0.01 0.00 0.00 0.00	2.32 0.88 0.47 0.10 0.05 0.02 0.02 0.03 0.05	51.62 52.65 57.51 62.85 63.73 62.95 59.80 58.32 57.24	8.70 8.88 9.70 10.60 10.80 11.06 12.00 12.45 12.79	20.44 20.85 22.78 24.90 25.35 25.96 28.17 29.20 29.92	
1200 1300 1400 1500 1600 1700 1800 1900	2.24 20.96 34.74 36.71 36.69 36.28 36.36 36.81 37.72	0.00 28.91 25.57 25.09 25.00 24.70 24.75 25.06 25.69	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 0.03\\ 0.34\\ 2.87\\ 11.58\\ 14.22\\ 14.37\\ 12.84\\ \end{array}$	33.84 41.54 25.14 23.41 23.15 22.86 22.85 23.08 23.49	16.91 16.75 9.54 1.54 0.07 0.01 0.00 0.00 0.00 0.01	2.32 0.88 0.47 0.10 0.05 0.02 0.02 0.02 0.03 0.05 0.09	51.62 52.65 57.51 62.85 63.73 62.95 59.80 58.32 57.24 56.07	8.70 8.88 9.70 10.60 10.80 11.06 12.00 12.45 12.79 13.17	20.44 20.85 22.78 24.90 25.35 25.96 28.17 29.20 29.92 30.66	

Table 2 – Chemical composition of metal and slag

Charge mixture № 3 – 5% solid carbon excess										
+ °C	Ν	Aetal con	nposition	ı, %	Slag composition, %					
ι, υ	Cr	Mn	Si	Fe	Cr_2O_3	FeO	SiO ₂	Al ₂ O ₃	MgO	
1000	0.15	0.00	0.00	34.67	16.62	2.14	52.23	8.84	20.18	
1100	2.46	0.00	0.00	39.76	16.38	0.78	53.25	9.01	20.57	
1200	22.51	27.52	0.00	24.21	8.25	0.40	58.73	9.94	22.69	
1300	34.26	24.78	0.03	22.79	1.13	0.09	63.50	10.75	24.54	
1400	35.69	24.44	0.39	22.63	0.05	0.04	64.11	10.90	24.90	
1500	35.62	24.34	3.48	22.62	0.00	0.02	63.15	11.21	25.62	
1600	35.19	24.03	12.97	22.30	0.00	0.02	59.68	12.25	28.05	
1700	35.30	24.10	16.06	22.32	0.00	0.02	57.88	12.77	29.32	
1800	35.84	24.47	16.25	22.63	0.00	0.03	56.57	13.15	30.25	
1900	36.87	25.18	14.49	23.18	0.01	0.07	55.23	13.52	31.18	
2000	38.40	26.24	11.39	23.86	0.03	0.15	53.57	13.97	32.28	
Charge mixture № 4 – 10% solid carbon excess										
	N	Aetal con	nposition	ı, %	Slag composition, %					
t, °C	Cr	Mn	Si	Fe	Cr ₂ O ₃	FeO	SiO ₂	Al ₂ O ₃	MgO	
1000	0.15	0.00	0.00	33.34	15.70	2.03	53.75	8.87	19.65	
1100	2.45	0.00	0.00	37.96	15.43	0.73	54.78	9.04	20.03	
1200	22.34	28.45	0.00	22.17	7.14	0.35	60.44	9.97	22.10	
1300	32.12	25.60	0.03	22.17	0.90	0.07	64.68	10.68	23.66	
1400	33.27	25.31	0.45	22.06	0.04	0.03	65.14	10.82	23.97	
1500	33.17	25.19	4.16	22.04	0.00	0.02	63.99	11.19	24.80	
1600	32.76	24.86	13.90	21.75	0.00	0.01	60.40	12.31	27.28	
1700	32.90	24.96	17.56	21.80	0.00	0.01	58.16	13.03	28.80	
1800	33.54	25.45	17.79	22.21	0.00	0.02	56.37	13.62	29.99	
1900	34.69	26.33	15.72	22.91	0.00	0.05	54.60	14.25	31.10	
2000	36.30	27.57	12.27	23.74	0.01	0.12	52.63	14.97	32.27	

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Table 2 shows that the composition of the alloys obtained at temperatures of 1600–2000 °C typical for pyrometallurgical processes is satisfactory and is characterized by a fairly high content of leading elements. Some change in them is expectedly observed depending on the content of solid carbon in the initial charge.

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Conclusions

A thermodynamic analysis of the Cr-Mn-Si ferroalloy smelting process using the carbothermal method was conducted within the Fe-Cr-Mn-Si-Al-Ca-Mg-C-O system. For comparative analysis, a temperature of 1800 °C was chosen, corresponding to the temperature of tapping the alloy from the ore-smelting furnace. The Mn content in all charge mixtures is almost the same - 24.47-25.83%. A high Cr content (37.82%) in the alloy is observed in charge mixture \mathbb{N}_2 1, however, a high silicon content in the slag indicates an obvious deficiency of the reducing agent. For a complex ferroalloy, the

Si content in the alloy plays an important role, since Si, forming Mn and Cr silicides, contributes to a higher extraction of the leading elements into the alloy and facilitates the tapping of the alloy from the furnace. In this regard, the preferred composition of the charge mixture is N_{2} 3. The temperature range of metal formation is 1500–1800 °C. The predicted composition of the Cr-Mn-Si containing ferroalloy at a temperature of 1800 °C, %: Cr – 35.84; Mn – 24.47; Si – 16.25; Fe – 22.63.

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*А. М. Жақан¹, А. К. Жунусов², А. С. Ахметов³, С. К. Кабылканов⁴, О. Үисеl⁵

^{1,2}Торайғыров университеті, Қазақстан Республикасы, Павлодар қ.

1,3,4 Ж. Әбішев атындағы Химия-металлургия институты,

Қазақстан Республикасы, Қарағанды қ.,

5Стамбул техникалық университеті, Стамбул, Түркия қ.

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ХРОМ-МАРГАНЕЦ-КРЕМНИЙ ҚҰРАМДАС ФЕРРОҚОРЫТПАНЫ БАЛҚЫТУ ҮРДІСІН ТЕРМОДИНАМИКАЛЫҚ МОДЕЛЬДЕУ

Бұл мақалада Қазақстанның техногендік шикізатынан хром-марганецкремний құрамдас ферроқорытпаны балқыту үрдісін термодинамикалық құрамдас модельдеу нәтижелері берілген. Хром-марганец-кремнийі феррокорытпаны термодинамикалық модельдеу Гиббс энергиясын минимизациялау және термодинамикалық вариациялық принциптерге негізделген HSC Chemistry 6 багдарламалық кешенін (Outokumpu, Финляндия) қолдану арқылы жүзеге асырылды. Күрделі қорытпаны балқыту үрдісін модельдеу үшін термодинамикалық талдау шикіқұрамның төрт нақты құрамы үшін 500-ден 2000 °C дейінгі температура аралығында жүргізілді (қатты көміртегінің 5% жетіспеушілігімен, режимнің қалыпты ағымымен және қатты көміртегінің 5% және 10% стехиометриялық артықшылығымен). Fe-Cr-Mn-Si-Al-Ca-Mg-C-О жүйесі арқылы кремний, марганец, хром және темірдің бірлескен қарботермиялық тотықсыздану механизмі зерттелді. Жүргізілген есептеулер хром-марганец-кремний құрамдас феррокорытпаны карботермиялық әдіспен балқыту кезінде болатын барлық физикалықхимиялық үрдістерді толық зерттеуге мүмкіндік береді. Термодинамикалық мәліметтер негізінде 100 кг шикіқұрамға (хром және марганец шаңы) қатты көміртектің оңтайлы шығыны 10,75 кг деп анықталды. 1800 °С температурада ферроқорытпаның химиялық құрамы, %: Сr - 35,84; Мп -24,47; Si - 16,25 және Fe - 22,63.

Кілтті сөздер: күрделі ферроқорытпа, карботермиялық үрдіс, хром-марганец-кремний құрамдас ферроқорытпа, термодинамика, тотықсыздандыру.

*A. М. Жақан¹, А. К. Жунусов², А. С. Ахметов³, С. К. Кабылканов⁴, О. Yucel⁵ ^{1,2}Торайгыров университет, Республика Казахстан, г. Павлодар ^{1,3,4}Химико-металлургический институт имени Ж. Абишева, Республика Казахстан, г. Караганда ⁵Стамбульский технический университет, Стамбул, г. Турция Поступило в редакцию 12.11.24. Поступило с исправлениями 20.11.24. Принято в печать 25.11.2024.

ТЕРМОДИНАМИЧЕСКОЕ МОДЕЛИРОВАНИЕ ПРОЦЕССА ВЫПЛАВКИ КОМПЛЕКСНОГО ХРОМ-МАРГАНЕЦ-КРЕМНИЙСОДЕРЖАЩЕГО ФЕРРОСПЛАВА

В данной статье приведены результаты термодинамического моделирования выплавки хром-марганец-кремнийсодержащего процесса ферросплава из техногенного сырья Казахстана. Термодинамическое моделирование хром-марганец-кремнийсодержащего ферросплава было проведено с использованием программного комплекса HSC Chemistry 6 (Outokumpu, Финляндия), основанного на принципах минимизации энергии Гиббса и термодинамических вариационных принципах. Термодинамический анализ для моделирования процесса выплавки комплексного сплава осуществлялся в

температурном интервале от 500 до 2000 °С для четырех реальных составов шихты (с недостатком 5 % твердого углерода, с нормальным ходом режима и с избытком твердого углерода 5% и 10 % от стехиометрии). Механизм совместного карботермического восстановления кремния, марганца, хрома и железа изучали по системе Fe-Cr-Mn-Si-Al-Ca-Mg-C-O. Проведенные расчеты позволяют полноценно изучить все физико-химические процессы, происходящие при выплавке хром-марганец-кремнийсодержащего ферросплава карботермическим методом. На основе термодинамических данных был определен оптимальный расход твердого углерода на 100 кг шихты (хромовой и марганцевой пыли), составивший 10,75 кг. Химический состав ферросплава при 1800 °С составляет, %: Cr – 35,84; Mn – 24,47; Si – 16,25 и Fe – 22,63.

Ключевые слова: комплексный ферросплав, карботермический процесс, хром-марганец-кремнийсодержащий ферросплав, термодинамика, восстановление. Теруге 05.12.24 ж. жіберілді. Басуға 30.12.24 ж. қол қойылды. Электрондық баспа 5,07 Mb RAM Шартты баспа табағы 1,09 Таралымы 300 дана. Бағасы келісім бойынша. Компьютерде беттеген: Е. Е. Калихан Корректор: А. Р. Омарова, Д. А. Кожас

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> «Toraighyrov University» баспасы Торайғыров университеті 140008, Павлодар қ., Ломов к., 64, 137 каб. 67-36-69

> > e-mail: kereku@tou.edu.kz nitk.tou.edu.kz