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RESEARCH PAPER

MODELING THE FERROSILICOMANGANESE SMELTING PROCESS USING MANGANESE-RICH SLAG

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ABSTRACT

This article presents the results of complete thermodynamic modeling (TDM) of the smelting process of standard ferrosilicomanganese (FeSiMn) from the slag of refined ferromanganese and manganese ores of Kazakhstan. Complete thermodynamic modeling of the smelting process of standard ferrosilicomanganese was performed in the software package "HSC Chemistry 6". The principle of operation of this software package is based on the principle of maximum entropy and takes into account all known properties of the reacting components that make up the thermodynamic system. The simulation of chemical and phase transformations in the system was studied in the temperature range 500-2200 °C for six real charge compositions with a carbon content of 8-10-12-14-16-18 kg and a pressure of 0.1 MPa. The mechanism of joint carbothermic reduction of manganese, silicon, aluminum, calcium and iron was studied using the Mn-Si-Al-Ca-Mg-O-C system. The calculations carried out make it possible to fully consider all the physicochemical processes occurring during the smelting of standard ferrosilicomanganese by the carbothermic method. During the simulation, it was found that the production of the metal phase of standard ferrosilicomanganese corresponded to GOST 4756-91 at a temperature of 1600-1700 °C with a carbon content of 12-14 kg per 100 kg of charge. With a further increase in temperature, manganese and silicon begin to enter the gas phase. The chemical composition of the alloy at 1700 °C with a content of 12 kg, %: Mn – 73.05; Si – 16.24; Fe – 9.67 and C – 1.03, and with a content of 14 kg is, %: Mn – 73.15; Si – 17.12; Fe – 8.24 and C – 1.48. The thermodynamic modeling of the phase transitions of the manganese charge–reducing agent subsystem made it possible to analyze the possibility of obtaining ferrosilicomanganese from hard-to-recover oxidized manganese ores of the Zhayrem deposit and manganese slag by electric melting. Also presents the results of experimental melting of silicomanganese, carried out in a Tamman laboratory furnace at a temperature of 1650 °C with an exposure of 20 minutes in a graphite crucible (manganese ore - 35%, manganese slag - 35%, Shubarkol coal - 30%).

Keywords: thermodynamic analysis, modeling, manganese slag, manganese ore, carbothermic process, ferrosilicomanganese.

INTRODUCTION

More than 90% of the world's manganese goes to steel production in the form of ferroalloys, so it is not surprising that the demand for manganese is mainly driven by the development of steel production. At present, the consumption of manganese alloys is increasing. China accounts for the lion's share of the increase in production. Manganese ore is the main source of manganese to produce iron and steel. To date, no technology could replace the role of manganese in steel production. Manganese imparts useful mechanical properties to alloys, namely hardness, toughness, and corrosion resistance. Manganese additions to the alloys are carried out in the form of raw ore. As a result, ferromanganese, ferrosilicomanganese, high-carbon ferromanganese, refined medium-low-carbon ferromanganese and metallic manganese are obtained, which serves as a desulfurizer in steel production [1], [2].

Global ferrosilicomanganese production contracted by 7% in 2020 to around 16 million tons, after rising for four consecutive years, due to dwindling demand from the steel sector. Among all major SiMn-producing countries, only Russia recorded a production growth (+10%). China’s FeSiMn output decreased by 4% in 2020 despite rising steel output, because of destocking at both ferroalloy plants and steel mills. Production recorded double-digit decreases in India, Ukraine, Norway, Georgia, and Kazakhstan. As shown in picture 1, China currently accounts for 73% of global FeSiMn production, followed by India with 9% and Ukraine (4%) [3].

In terms of proven reserves of manganese ores, Kazakhstan ranks third in the world, but in terms of their quality, it is significantly inferior to the world's main producers. According to the US Geological Survey, Kazakhstan in 2016 ranked 11th in the world in terms of production and 9th in terms of manganese reserves. The leaders in production were South Africa (4,700 thousand tons), China (3,000 thousand tons), Australia (2,500 thousand tons).

In 2019, the volume of extraction of manganese ores in the Karaganda region (the entire volume of manganese ores was mined here) amounted to 1.14 million tons, 16.5% less than in 2018 [4]. The main reserves of manganese ores in Kazakhstan (about 70%) are represented by iron-manganese varieties. The remaining 30% are difficult-to-enrich oxidized and primary manganese ores. In [5-7], the maturing problem of the shortage of high-quality manganese ores was noted, which is still relevant. At the moment, producers of ferroalloys, such as the Karaganda plant of Asia FerroAlloys LLP and the Aksu Ferroalloy Plant of TNK

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Kazchrome, smelting silicomanganese using traditional technology, are facing problems due to a shortage of rich manganese ores.

The novelty of this work is the production of standard grades of silicomanganese using poor manganese ore and slag of refined ferromanganese replacing rich manganese ore.

The source of manganese slags is the slag heaps of the industrial mini-workshop of the Chemical and Metallurgical Institute named after Z. Abishev. The industrial mini-workshop has been smelting refined ferromanganese since 2018 [8].

There are about 100 tons of manganese slags in the slag heaps. Refined ferromanganese slag is a very pure source of manganese since easily recoverable impurities in the ores were absorbed by the refined ferromanganese metal at the previous stage of the process.

The organization of industrial productions based on the deposits of oxidized manganese ores available in significant quantities to obtain internationally competitive products in the Republic of Kazakhstan is relevant [9].

The study of options for obtaining ferrosilicomanganese from ferromanganese ore and manganese slag opens prospects for science and industry, opening the way to innovative approaches in the production and use of metallurgical resources.

MATERIAL AND METHODS

As part of the study, thermodynamic modeling and experimental electric melting of charge materials using a high-temperature Tamman furnace were carried out. The HSC-9.0 (Outokumpu) software package [10] based on the Gibbs minimum energy principle was used for thermodynamic modeling. Previously, the authors used the HSC Chemistry program to study various ferroalloys, and their results were confirmed during the data collection process [11-13].

Manganese ore, slag of refined ferromanganese and Shubarkol coal were used as the initial charge materials for TDM. When working with the HSC Chemistry software package, the initial information was presented in the form of a quantitative (kg) distribution of substances in the system under study (Table 1).

For thermodynamic analysis, the principles that formed the basis of thermodynamic modeling of Mn- Ca-Si- Mg-Al- O-C systems were formulated.

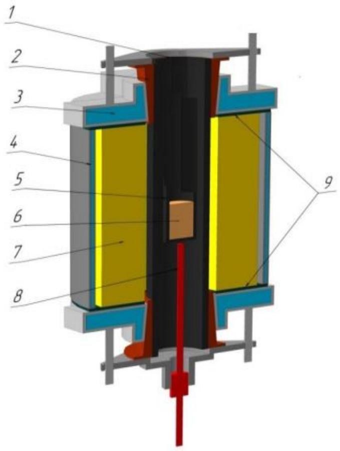
1. Temperature. Thermodynamic analysis was carried out in the temperature range from 500 to 2200 °C. The lower limit characterizes the standard state, changes are insignificant up to a temperature of 500 °C, the upper limit is the final state, the melting point of the components, the formation of the final reaction products, that is, the initial and final equilibrium states of the system.
2. In all calculations, the pressure was chosen to be 0.1 MPa, which approximately corresponds to a pressure of 1 physical atm. typical for most metallurgical processes, including processes of solid-phase carbon thermal interaction.
3. Volume. The volume is determined by the thermodynamic state of the system.
4. The system is closed, there is no exchange with the environment.
5. According to the thermodynamic calculations of the manganese charge–reducing agent system (carbon with a content in the system was considered as a reducing agent 8, 10, 12, 14, 16, 18 kg) for smelting standard ferrosilicomanganese from manganese ore and refined ferromanganese slag, in order to determine the optimal mode of the carbothermic process (**Table 1**).
6. The following substances were selected as associates for calculations:

- the metal phase: C, Mn_3Si, Mn_5Si_3, MnSi, Fe, FeSi, Fe_3Si, Si, $MnSi_{1.7}$, $MnSi_{1.727}$, Fe_5Si_3, $FeSi_2$, Mg_2Si;
- the slag phase: MnO, $CaSiO_3$,Al_2O_3, $Ca3SiO_5$, $Ca_3Si_2O_7$, $MgSiO_3$, FeO, CaO, $FeAl_2O_4$, $CaO·MgO·2SiO_2$, MgO, $3Al_2O_3·2SiO_2$, Mn_3O_4, $CaFe_3O_5$,Al_2SiO_5, $2CaO·MgO·2SiO_2$, $MgO·Al_2O_3$, $MnO·Fe_2O_3$, $3CaO·MgO·2SiO_2$, CaO·MgO, Fe_3O_4, Fe_2O_3, Mn_2O_3, Ca_2SiO_4, $Fe_3Al_2Si_3O_{12}$, $CaO·Fe_2O_3$, MnO_2, $Fe_2Al_4Si_5O_{18}$, $FeO·SiO_2$, SiO_2,$MnO·Al_2O_3$, $FeSiO_3$, $CaO·MgO·SiO_2$, Mg_2SiO_4, $Al_2O_3·2SiO_2$, $CaO·Al_2O_3$, $2CaO·Fe_2O_3$.
- the gas phase: $CO_{(g)}$, $SiO_{(g)}$, $CO_{2(g)}$, $Si_{(g)}$, $Mn_{(g)}$, $MgO_{(g)}$, $O_{(g)}$, $O_{2(g)}$, $Mn_{O(g)}$, $O_{3(g)}$

Table 1 Chemical composition of the charge mixture, kg

Charge mixture	Mn_2O_3	MnO	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	C
№ 1	28	12	4	25	7	13	1	8
№ 2	28	12	4	25	7	13	1	10
№ 3	28	12	4	25	7	13	1	12
№4	28	12	4	25	7	13	1	14
№5	28	12	4	25	7	13	1	16
№6	28	12	4	25	7	13	1	18

Experimental studies have been conducted on the melting of silicomanganese in a high-temperature Tamman resistance furnace (**Fig. 1**). The Tamman furnace is designed to simulate metallurgical processes. The working area of the device is made of a graphite tube, and a thyristor voltage regulator is used to regulate the temperature. Since the thyristor voltage regulator is connected to the primary winding of the power transformer, it is possible to obtain a current of several thousand amperes on the output buses at low voltage (in the range from 0.5 to 15V). The temperature in the Tamman furnace was measured with a tungsten-rhenium thermocouple BP-5/20 in a corundum case.

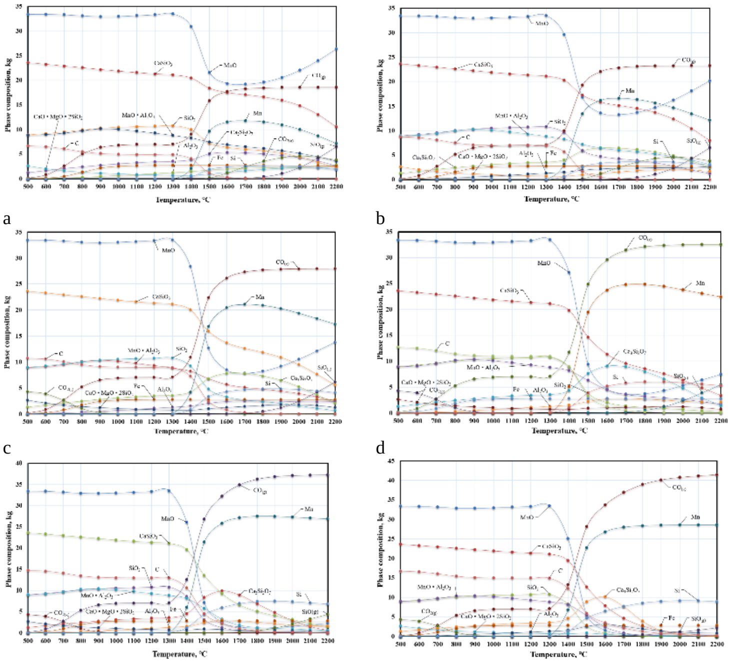


1-carbon-graphite pipe; 2-copper ring; 3,4-water-cooled lid and housing; 5-crucible; 6-charge under study; 7-protective shell; 8-thermocouple; 9-insulating material.

Fig. 1 Tamman Laboratory Furnace (cutout view)

RESULTS AND DISCUSSION

The main purpose of thermodynamic modeling in this work is to establish patterns of distribution of chemical elements between metal, slag and the gas phase during the carbothermic reduction of manganese ore and slag of refined ferromanganese. Data analysis shows that the initial composition of the charge is recovering and undergoing significant changes. As a result of modeling, it was revealed that, during the smelting of standard ferrosilicomanganese by the carbothermic method up to 2200 °C, the formation and some changes of elements (**Fig. 2 (a,b,c,d,e,f)**) into the gas, metal and slag phase are observed.



a b c d e f

Fig. 2 The content of the condensed and gaseous phase composition depends on temperature (a- consumption of solid coal 8 kg per 100 kg of ore mixture, b - a-consumption of solid coal 10 kg per 100 kg of ore mixture, c- a-consumption of solid coal 12 kg per 100 kg of ore mixture, d - consumption of solid coal 14 kg per 100 kg of ore mixture, e - consumption of solid coal 16 kg per 100 kg of ore mixture f- consumption of solid coal 18 kg per 100 kg of ore mixture)

The analysis of the curves shown in the figures shows that:

- charge mixture № 1 (**Fig. 2a**), solid carbon consumption of 8 kg. The reduction processes of metal formation begin at a temperature of 1300 °C, and the content of manganese and silicon at a temperature of 1400-1500 °C intervals is 9.5-15.57 kg in the metallic phase, practical in all solid carbon costs. At a solid carbon consumption of 8 kg per charge mixture, the phase - $CaSiO_3$, MnO Al_2O_3, $Ca_3Si_2O_7$, SiO_2, at a temperature of 1600 °C, will decompose into free MnO, the content of which reaches 33 kg in the slag mixture. As the temperature increases, the MnO content decreases to 19.35 kg. The high content of MnO and SiO_2 in the slag phase indicates a clear lack of a reducing agent. The content of manganese and silicon in the metal phase is very low.
- charge mixture № 2 (**Fig. 2b**), solid carbon consumption of 10 kg. The reduction processes of metal formation begin at a temperature of 1300 °C, and the content of manganese and silicon at a temperature of 1400-1500 °C intervals is 12.35 - 20.67 kg in the metallic phase, practical in all solid carbon costs. At a solid carbon consumption of 10 kg per charge mixture, the phase - $CaSiO_3$, MnO • Al_2O_3, $Ca_3Si_2O_7$, SiO_2, at a temperature of 1600 °C, will decompose into free MnO, the content of which reaches 33 kg in the slag mixture. As the temperature increases, the MnO content decreases to 13.26 kg. The high content of MnO and SiO_2 in the slag phase indicates a clear lack of a reducing agent.
- charge mixture № 3 (**Fig. 2c**), solid carbon consumption 12 kg. The reduction processes of metal formation begin at a temperature of 1300 °C, and the content of manganese and silicon at a temperature of 1400-1500 °C intervals is 15.16 - 25.38 kg in the metallic phase, practical in all solid carbon costs. At a consumption of solid carbon of 12 kg per charge mixture, the phase - $CaSiO_3$, $MnO \cdot Al_2O_3$, $Ca_3Si_2O_7$, SiO_2, at a temperature of 1600 °C, will decompose into free MnO, the content of which reaches 33 kg in the slag mixture. As the temperature increases, the MnO content decreases to 8.48 kg. The high content of SiO_2 in the slag phase indicates a clear lack of a reducing agent.
- charge mixture № 4 (**Fig. 2d**), solid carbon consumption 14 kg. The reduction processes of metal formation begin at a temperature of 1300 ° C, the content of iron, manganese and silicon at a temperature of 1400-1700 °C is 18-33 kg in the metallic phase, practical in all solid carbon consumption. At a solid carbon consumption of 14 kg per charge mixture, starting from a temperature of 1300 to 1500 °C, the phase - MnO, $MnO \cdot Al_2O_3$ in the slag mixture decreases, the content of Mn5Si, Mn_3Si, MnSi and $MnSi_{1.7}$ increases in the metal phase. This value is the formation of the metal phase of the content of iron, manganese and silicon following GOST 4756-91.
- charge mixture № 5 (**Fig. 2e**), solid carbon consumption 16 kg. The reduction processes of metal formation begin at a temperature of 1300 °C, the content of iron, manganese, carbon and sil-

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icon at a temperature of 1400-1700 °C is 20.6-37.9 kg in the metallic phase, practical in all solid carbon consumption. At a solid carbon consumption of 16 kg per charge mixture, starting from a temperature of 1300 to 1500 °C, the phase - MnO, $MnO·Al_2O_3$ in the slag mixture decreases, the content of C, Mn_5Si, Mn_3Si, MnSi and $MnSi_{1.7}$ increases in the metal phase.

- charge mixture № 6 (**Fig. 2f**), solid carbon consumption 18 kg. The reduction processes of metal formation begin at a temperature of 1300 °C, the content of iron, manganese, carbon and silicon at a temperature of 1400-1700 °C is 23.27-39.63 kg in the metal phase, with almost any consumption of solid carbon. At a solid carbon consumption of 16 kg per charge mixture, starting from a temperature from 1300 to 1500 °C, the content of the phase - MnO, $MnO·Al_2O_3$ decreases in the slag mixture, and the content of C, Mn_5Si, Mn_3Si, MnSi and $MnSi^{1,7}$ increases in the metal phase.7. The C_{solid} content in the metal at a temperature of 1600-1700 °C ranges from 5 to 8 % (**Fig. 3**). This does not meet the requirements of GOST.

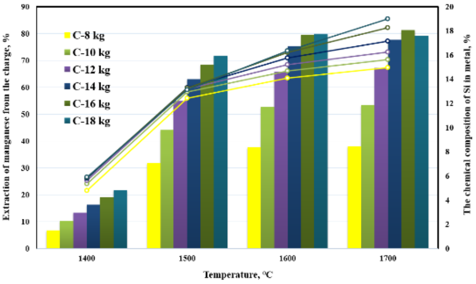

Fig. 3 Changes in the extraction of manganese from the charge and the amount of silicon in the metal in the temperature range of 1400-1700 °C at different carbon contents

Based on thermodynamic modeling, it was revealed that during the smelting of silicomanganese, the distribution of metal and slag occurs at temperatures above 1600 ° C. Further, in the Tamman laboratory furnace (**Fig. 1**) at a temperature of 1650 ° C with an exposure of 20 minutes, experimental smelting of silicomanganese in a graphite crucible was carried out (manganese ore – 35%, manganese slag-35%, Shubarkol coal-30%).

The result of experimental melting (**Fig. 4**) at a temperature of 1650 °C with an exposure time of 20 minutes shows the separation of metal and slag. Small pieces of metal are found in the slag in small volumes. Thus, at temperatures above 1600 °C, the formation and accumulation of metal occurs faster. The data of the experimental melting results are given below.

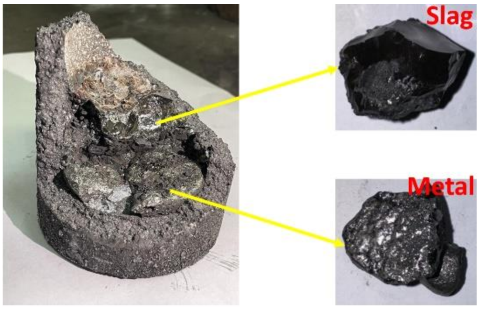

Fig. 4 The product is experimental melting.

Table 2 Chemical composition of the resulting metal, %

Mn	Si	Fe	P	S	C
63.84	18.30	16.10	0.11	0.05	0.80

Table 3 Chemical composition of the resulting slag, %

MnO	SiO_2	CaO	MgO	Al_2O_3	FeO	P_2O_5
5.68	43.72	30.85	2.58	15.60	1,54	0.04

CONCLUSIONS

For the research work, first of all, 100 kg of charge was calculated for the production of ferrosilicomanganese. Zhairem manganese ore, refined ferromanganese slag and carbon of various weights were obtained as a charge. After determining the chemical composition and weight of the charge, a complete thermodynamic simulation was performed with a change in the amount of carbon using the integrated program "HSC Chemistry 6".

Based on the thermodynamic analysis, the following results were obtained:

- The composition of the condensed and gaseous phases depending on the temperature;
- Extraction of manganese from the charge in the temperature range 500-2200 °C at different carbon content;
- Chemical composition of metal and slag;
- Optimal temperature and carbon content for ferrosilicomanganese smelting.

Based on **Fig. 2(a, b, c, d, e, f)**, it can be seen that metal formation occurs at a temperature of 1300 °C and the weight of manganese and silicon increases to 1700 °C, and with further increase in temperatures, manganese and silicon begin to transition into the gas phase. According to **Fig. 3**, it can be concluded that the amount of carbon affects the extraction of manganese from the charge and the transition of silicon to metal at different temperatures. A low carbon content leads to the possibility of silicon deficiency and, conversely, a high carbon content leads to an increase in the carbon content of the metal by more than 2.5%. According to the results of experimental melting, it can be revealed that at a temperature of 1650 °C, the metal accumulates in sufficient volume.

Thus, the most optimal temperature range is the extraction of silicon and manganese 1600-1700 °C with a carbon content of 12-14 kg per 100 kg of charge, which corresponds to the grades according to GOST 4756-91 (ISO 5447-80) ferrosilicomanganese.

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