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THERMODYNAMIC AND EXPERIMENTAL SIMULATION OF THE SMELTING PROCESS OF MEDIUM CARBON FERROMANGANESE WITH THE USE OF ZHEZDINSKY MANGANESE ORES

This article presents the results of a complete thermodynamic modeling and experimental study of the process of smelting medium-carbon ferromanganese using Zhezdinsky manganese ores. Full thermodynamic modeling of the process of smelting medium-carbon ferromanganese was carried out in the HSC Chemistry 6 software package. Thermodynamic modeling of the smelting process was carried out in the temperature range of 898–1989 K. Thermodynamic analysis for modeling the smelting process was carried out for four real charge compositions depending on the basicity of the slag (CaO/SiO_2 – 1,4; 1,6; 1,8; 2,0). Based on the obtained thermodynamic data, an experimental study was carried out on the smelting of medium-carbon ferromanganese in a Tamman laboratory high-temperature furnace. Manganese ore MnTot. was used as charge material – 48,23 %, SiO_2 – 12.48 %, Al_2O_3 – 2,76 %, Fetot. – 3,45 %, ferrosilicomanganese grade SMn-17, not less than 90 % lime CaO. According to thermodynamic data, the optimal composition of the slag was established, which provides the highest extraction of manganese into the alloy and metal-slag separation. The chemical composition of the metal obtained in the laboratory is as follows, %:Mn – 83–84; Si – 1,5–3; C – 0,95–1,68; P –0,13–1,6; which corresponds to GOST 4755-91. Slag chemical composition, %: MnO – 10,92–17,90; SiO_2 19,02–21,45; CaO 36,92–40,43; FeO – 0,33–0,77.

Keywords: ferromanganese, ferrosilicomanganese, thermodynamics, manganese ore, laboratory smelting, slag basicity.

Introduction

The main direction in the development of ferrous metallurgy is to improve the quality and increase the output of new highly efficient types of metal products, including alloy steels, the production of which is impossible without the use of refined manganese ferroalloys.

Despite significant advances in the development of ferroalloy production, the problem of the rational use of manganese has acquired particular importance in recent years. The main reason for this is the constantly deteriorating quality of mined manganese ores, as well as the high cost of raw materials and electricity. In this regard, the issues of improving the technology for the production of refined manganese alloys continue to be relevant and require further theoretical, laboratory and industrial research.

One of the main determining factors in the development of the mining and metallurgical complex of a country is a high-quality ore and raw material base and its impressive reserves. Kazakhstan has large reserves of manganese raw materials and is among the top ten leading countries in terms of its production. Information about the manganese ore reserves of Kazakhstan is given in many open sources [1, 2]. The reserves of manganese ores in the country are sufficient in absolute terms to provide for the metallurgical enterprises of the Republic of Kazakhstan, however, their unsatisfactory quality served as an obstacle to the use of ores [3]. Along with ore quality requirements for phosphorus and silica content, there is also a restriction on iron content. This moment is absent in the universal integrated technology for the processing of manganese ore, which could provide the country's operating enterprises with high-quality raw materials. At the moment, Kazakhstan produces only ferrosilicomanganese, and there is no production of refined ferromanganese at all. This is primarily due to the lack of high-quality initial charge materials, as well as the lack of theoretical and applied research adapted to new production conditions.

In our country, the reserves of manganese ores are concentrated in Central Kazakhstan. Kazmanganets Mining Administration is the country's main enterprise for the extraction of manganese ore. In 2021, the mining department will produce 0.9 million tons of ore and 0.2 million tons. The main fields of management are the Dzhezdinskoye deposit and the Zhairemskoye GOK [4].

Kazakhstani sources of manganese raw materials are beneficial for Russia by the relative cheapness of the supplied products, the absence of interaction of import duties (like the countries of the Customs Union) and low transport costs for delivery to the place of consumption [5].

Ferrosilicomanganese is a deoxidizer in steel production. The largest producer of ferrosilicomanganese in the Republic of Kazakhstan is Aksu Ferroalloy Plant JSC, a branch of TUK Kazchrome JSC (ERG Eurasian Group). The plant has four main melting shops with 26 powerful electric furnaces, as well as auxiliary facilities. The production capacity is more than 1 million tons of ferroalloys per year, of which 200,000 tons of ferrosilicomanganese. The enterprise manufactures the following products: high-carbon ferrochrome, ferrosilichrome, ferrosilicon, ferrosilicomanganese. The company's products are exported to the markets of Western Europe, USA, Japan, China, Russia [4–6].

Based on the above requirements, it is clear that the production of medium-carbon ferromanganese in the country is the most promising. It is necessary to carry out experimental and theoretical work to determine the optimal basicity of the slag during the smelting of medium-carbon ferromanganese. Information obtained from laboratory studies is important in assessing the possibility of certain chemical interactions. The main raw materials for smelting medium-carbon ferromanganese are manganese ore, ferrosilicomanganese, and lime. The study of the main reactions in the Mn-Fe-Si-Al-Ca-Mg-O system is necessary to create a mechanism for the joint metallothermic reduction of manganese, iron, silicon, aluminum in the alloy and to study the process of slag formation [7,8].

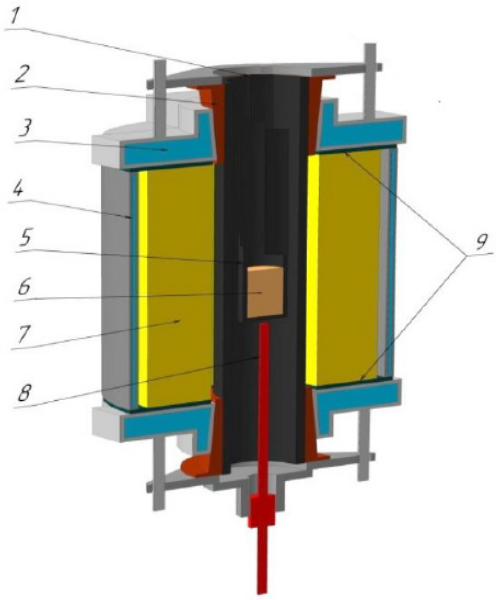
Materials and methods. Full thermodynamic modeling (FTM) is widely used in research and production practice in the study of chemically complex systems at high temperatures, when chemical and phase transformations play an important role.

FTM of the process of smelting complex master alloys was carried out using the HSC Chemistry software package [9,10] containing an extensive thermochemical database of enthalpy (H), entropy (S) and heat capacity (C) for more than 29,000 chemical compounds. The HSC Chemistry software package includes more than 10 modules. The article used the Equilibrium Compositions module using the equilibrium calculation method using the Gibbs minimum energy principle. To analyze the metallurgical reduction of manganese, the method of full thermodynamic modeling of the metallurgical process (TTM) was implemented using the HSC Chemistry 6 complex software package. Experimental studies were carried out on the smelting of medium-carbon ferromanganese in the Tamman high-temperature resistance furnace (Figure 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 control 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 busbars at low voltage (in the range from 0.5 to 15V). The temperature in the Tammann furnace was measured with a VR-5/20 tungsten-rhenium thermocouple in a corundum housing [11, 12].

To determine the optimal mode of the metallurgical process, a complete thermodynamic analysis of the feedstock was carried out (Table 1).

Table 1 – Chemical composition of primary raw materials, %

Material	Mn_{tot}	SiO_2	Al_2O_3	Fe_{tot}	MgO	CaO
Manganese ore	48,23	12,48	2,76	3,45	1,47	1,28
Lime	-	1	0,18	0,62	1,14	90
Reducing agent	Mn	Si	Fe	S	P	**C**
Ferrosilicomanganese	65,54	16,5	9,5	0,05	0,05	2,5



1 – carbon-graphite tube; 2 – copper compression ring;
3 – water-cooled cover; 4 – water-cooled housing; 5 – alundum glass;
6 – investigated charge; 7 – protective lining;
8 – thermocouple; 9 – bottom electrode;

Figure 1– Tamman High Temperature Furnace (sectional view)

To determine the thermodynamic parameters for the composition of the 4 options for raw materials, the composition of the working bodies was calculated in the range of 1.4–2.0, depending on the suitability of the slag (Table 2).

a – manganese ore b – Ferrosilicomanganese

c – lime

Figure 2 – Charge materials

Table 2 – List of raw materials for smelting medium-carbon ferromanganese, in grams

Raw materials, versions	Materials, gr		
	Manganese ore	Ferrosilicomanganese	Lime
1	59	53	38
2	59	53	44
3	59	53	49
4	59	53	55

The equilibrium composition of the multicomponent oxide-metal system was carried out every 100 K in the temperature range 898–1998 K using the Equilibrium Compositions software module. To calculate the silicothermal reduction of medium-carbon ferromanganese, the following phases were taken:

- in molten metal: Mn, Mn_3Si, Fe, Fe_3Si, MnSi, Si, Al, Fe_5Si_3, Mn_5Si_3, FeSi, $FeSi_2$, $MnSi_{1.7}$, $MnSi_{1.727}$;

- in molten slag: $2CaO \cdot SiO_2$, $CaSiO_3$, MnO, $2CaO \cdot Al_2O_3 \cdot SiO_2$, $2CaO \cdot MgO \cdot 2SiO_2$, CaO, $CaMgSiO_4$, MgO, $CaO \cdot Al_2O_3$, $MnO \cdot Al_2O_3$, SiO_2, $MgSiO_3$, Al_2O_3, $MgO \cdot Al_2O_3$, Mn_2SiO_4, Mg_2SiO_4, $CaO \cdot 2Al_2O_3$, $MnSiO_3$, FeO, $FeAl_2O_4$, $FeO \cdot SiO_2$, $3Al_2O_3 \cdot 2SiO_2$, $2FeO \cdot SiO_2$, Mn_3O_4, Mn_2O_3, $Mg_2Al_4Si_5O_{18}$, $Al_4Mg_2Si_5O_{18}$, MnO2, Fe_2O_3, $12CaO \cdot 7Al_2O_3$, Fe_3O_4, $Fe_2Al_4Si_5O_{18}$, $CaFe_3O_5$.

Results and discussion

The results of thermodynamic modeling in 4 versions are presented in fig. 1. As a result, the complete reduction of manganese ends at a temperature of 1598 K. The optimal basicity of the slag composition is determined in the range of 1.6–1.8.

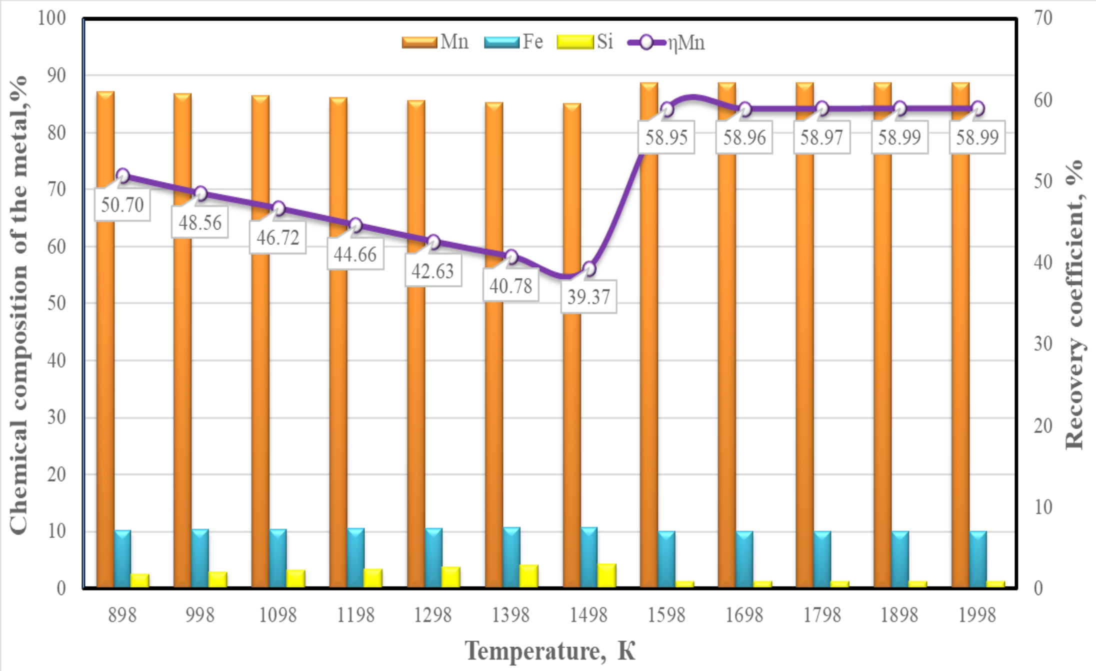


Figure 3 – Full results of thermodynamic modeling B=1.4

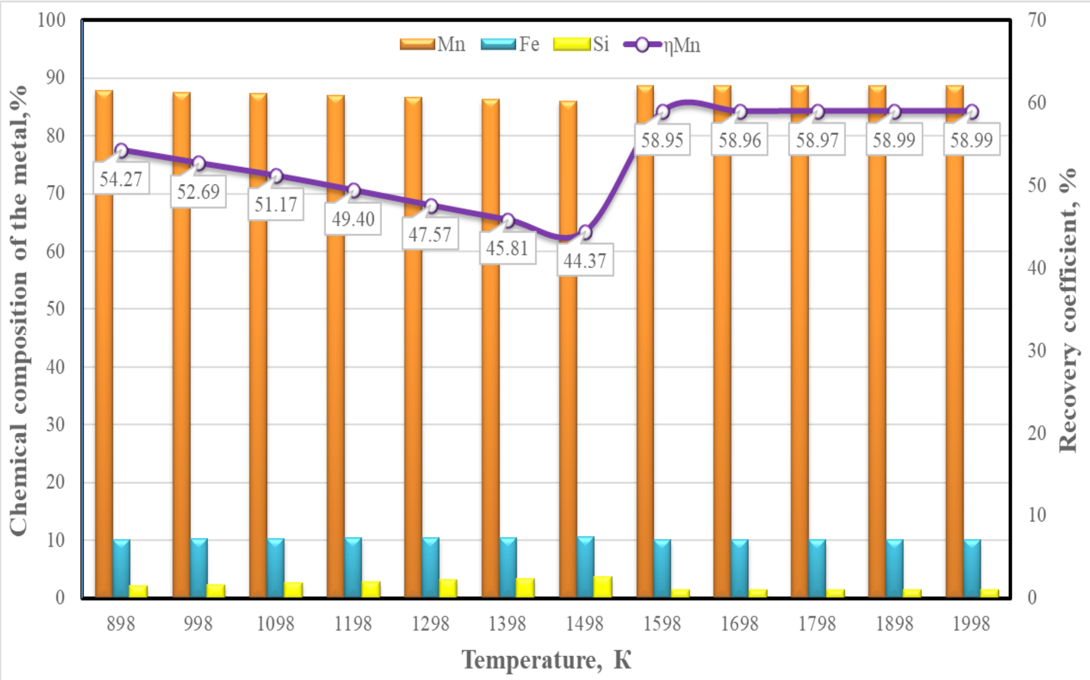


Figure 4 – Complete thermodynamic simulation results B=1,6

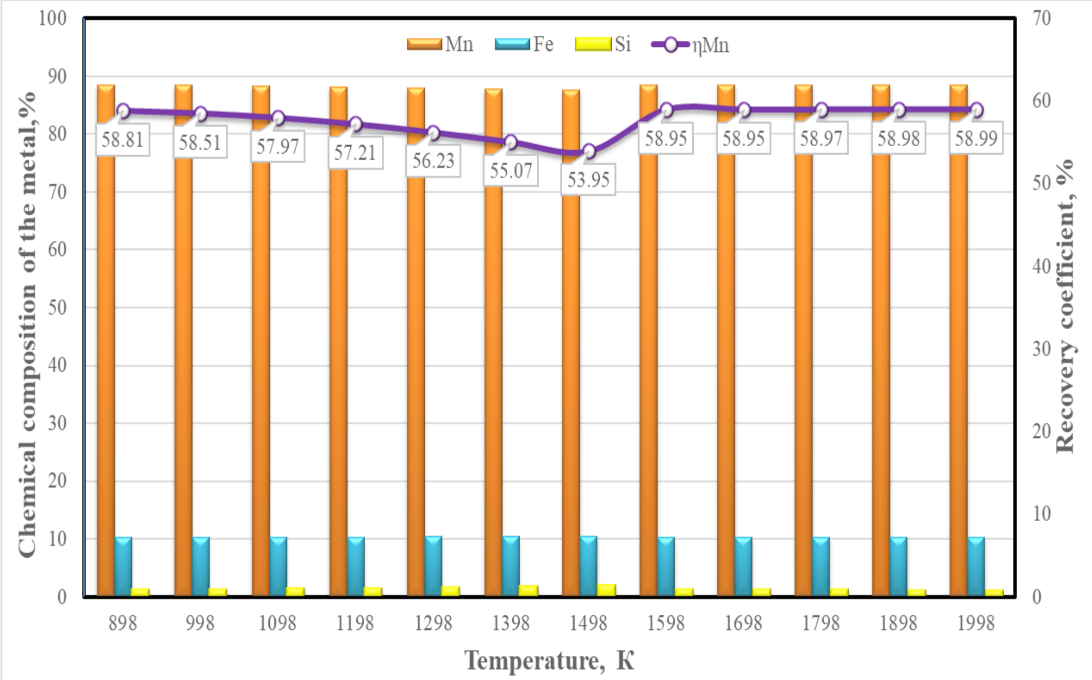


Figure 5 – Complete thermodynamic simulation results B=1,8

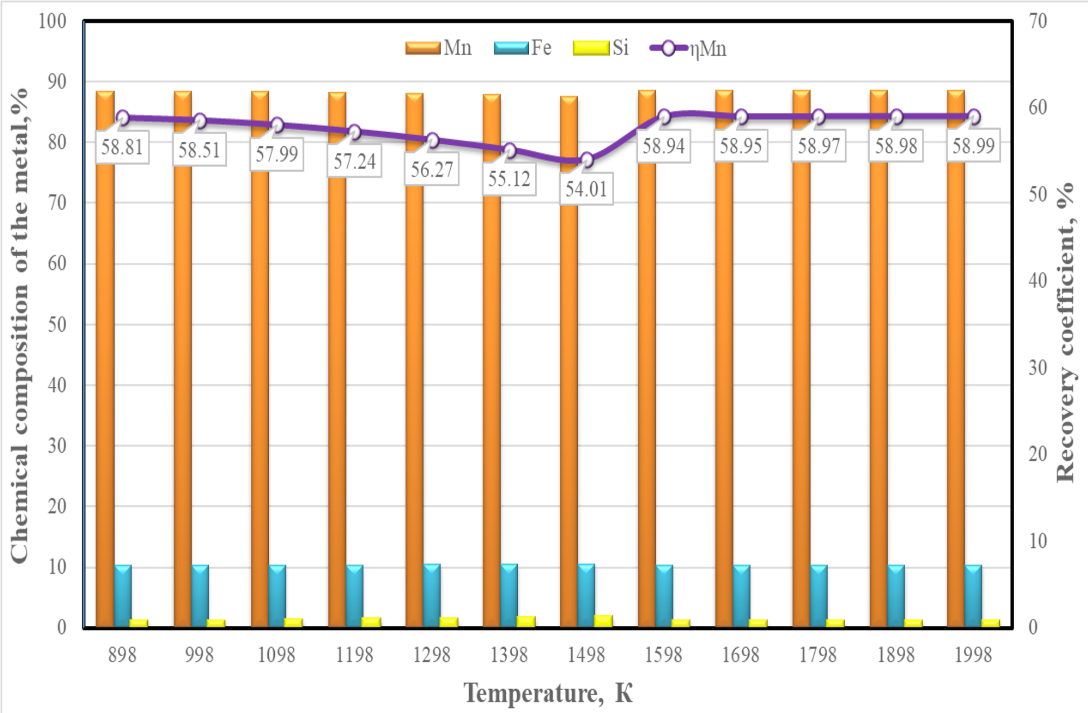


Figure 6 – Full results of thermodynamic simulation B=2.0

As a result of thermodynamic modeling of the process of smelting medium-carbon ferromanganese, a forecast for obtaining a real alloy was determined. Therefore, a number of practical experiments were carried out with various raw materials in order to establish technological and temperature regimes and technical parameters close to the real conditions for carrying out reduction reactions.

Sampling and preparation of samples of manganese ores, ferrosilicomanganese, quartzite and lime were carried out to study the physical and chemical characteristics of raw materials used in laboratory studies.

The chemical composition of raw materials was taken according to table 1, and materials for experimental melting were prepared according to 4 options. The calculation was taken in the range of 1.4–2.0 depending on the basicity of the slag, as indicated above. The raw materials for the Tamman furnace were placed into the furnace space through the crucible.

During the experiment, according to the results of thermodynamic modeling, it was heated to a temperature of 1698 K. As a result of heating, further combustion of silicon in the deoxidizer allows the metal and slag to be completely formed. Figure 7 shows a cross section of a crucible (metal and slag).

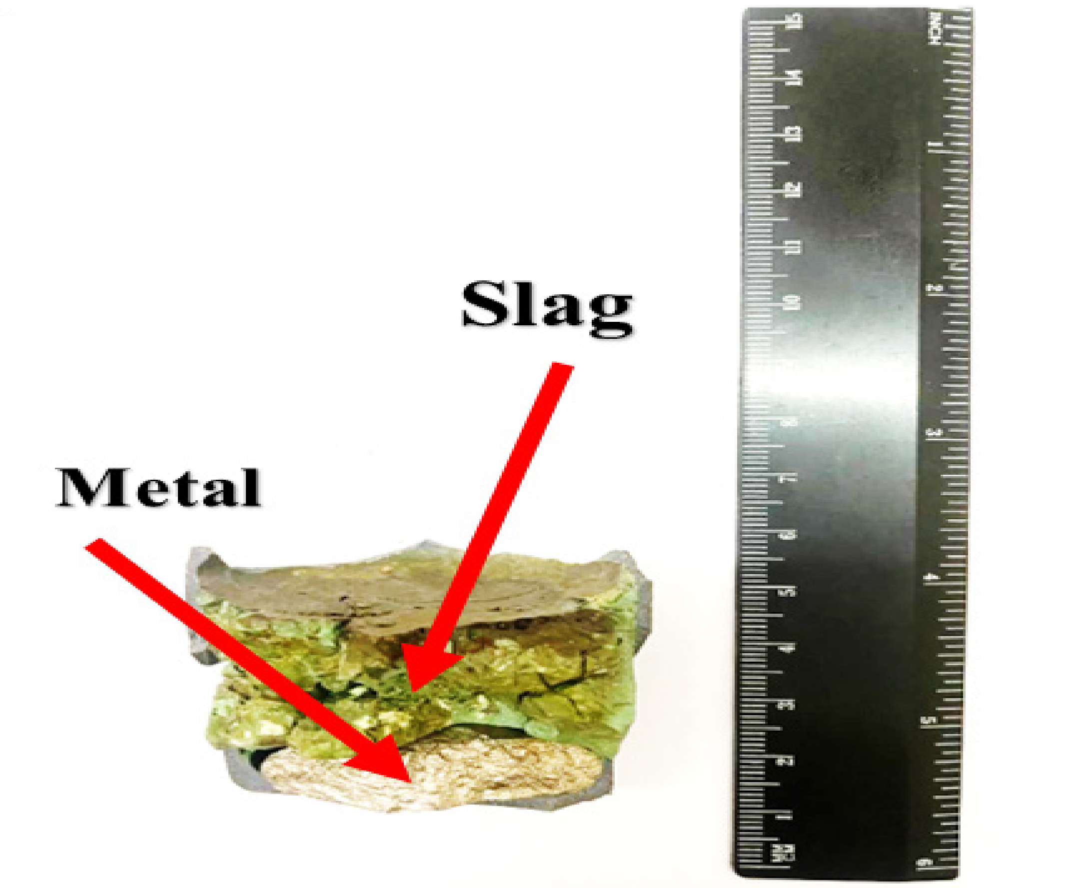


Figure 7 – Sectional crucible (metal and slag)

Tables 3 and 4 show the results of experimental melting in Tamman's laboratory resistance furnace and the chemical composition of the metal and slag. According to the obtained experimental results, the separation of metal and slag is shown in Table 5.

Table 3 – Chemical composition of the metal,%

№	Mn	Fe	Si	C	P
1	83,54	11,36	2,13	0,95	0,161
2	84,81	10,4	0,6	1,46	0,137
3	84,39	11,46	0,23	1,66	0,16
4	84,81	12,23	0,055	1,68	0,155

Table 4 – Chemical composition of slag, %

№	MnO	SiO_2	CaO	MgO	FeO
1	17,90	21,45	36,92	7,94	0,77
2	11,79	22,19	36,92	10,83	0,55
3	10,92	20,51	38,67	9,03	0,73
4	12,22	19,02	40,43	10,11	0,33

Table 5 – Extraction into the alloy, %

Variants	Distribution of elements			
	Metal		Slag	
	Fe	Mn	Fe	Mn
1	99	60	1	40
2	99	61	1	39
3	99	61	1	39
4	99	60	1	40

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Conclusion

Full thermodynamic modeling of medium-carbon ferromanganese and the study of laboratory experiments in the Tamman furnace led to the following conclusions:

- temperature range by thermodynamic simulation

A period of 1598–1698 K was observed. As a result of the study, the optimal slag range of 1.6–1.8 is suitable for melting medium-carbon ferromanganese;

- The process was completely carried out at the working temperature of the Tamman furnace approximately 1598–1698. At a temperature of 1698 K, metal and slag were completely formed during the melting process.

In a word, the optimal requirements for the technological regime of the normal process of smelting medium-carbon ferromanganese, implemented in a refined furnace, were established. It allows you to conduct laboratory and large-scale laboratory tests based on data obtained from thermodynamic and laboratory studies.

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ЖЕЗДІ МАРГАНЕЦ КЕНІҢ ҚОЛДАНА ОТЫРЫП, ОРТА КӨМІРТЕКТІ ФЕРРОМАРГАНЕЦТІ БАЛҚЫТУ ПРОЦЕСІН ТЕРМОДИНАМИКАЛЫҚ ЖӘНЕ ЭКСПЕРИМЕНТТІК МОДЕЛЬДЕУ

Бұл мақалада толық термодинамикалық модельдеу нәтижелері және Жезді марганец кендерін қолдана отырып, орта көміртекті ферромарганецті балқыту процесін эксперименттік зерттеу келтірілген. Орта көміртекті ферромарганецті балқыту процесін толық термодинамикалық модельдеу «HSC Chemistry 6» бағдарламалық кешенінде жасалынды. Балқыту процесін термодинамикалық модельдеу 898–1989 К температуралық интервалда жүргізілді. Балқыту процесін модельдеуге арналған термодинамикалық талдау қождың негізділігіне байланысты шихтаның төрт нақты құрамы үшін жүргізілді (CaO/SiO_2 – 1,4; 1,6; 1,8; 2,0). Алынған термодинамикалық мәліметтерге сәйкес Тамманның Жоғары температуралы зертханалық пешінде орта көміртекті ферромарганецті балқыту бойынша эксперименттік зерттеулер жүргізілді. Марганец кені шикіқұрам материалдары ретінде пайдаланылды Mnобщ. – 48,23 %, SiO_2 – 12.48 %, Al_2O_3 – 2,76 %, Feобщ. – 3,45 %, СМн-17 маркалы ферросиликомарганец, әк CaO 90 % аспауы керек. Термодинамикалық мәліметтерге сәйкес, қождың оңтайлы құрамы анықтай отырвп, марганецтің қорытпаға ең жоғары шығарылуын және металл-қождың бөлінуін қамтамасыз етеді. Зертханалық жағдайда алынған металдың химиялық құрамы келесідей %: Mn – 83–84; Si – 1,5–3; C – 0,95–1,68; P–0,13–1,6; который соответствует ГОСТу 4755-91. Қождың химиялық құрамы, %: MnO – 10,92–17,90; SiO_2 19,02–21,45: CaO 36,92–40,43; FeO – 0,33–0,77.

Кілтті сөздер: ферромарганец, ферросиликомарганец, термодинамика, марганец кені, зертханалық балқыту, қож негізділігі.

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ТЕРМОДИНАМИЧЕСКОЕ И ЭКСПЕРИМЕНТАЛЬНОЕ МОДЕЛИРОВАНИЕ ПРОЦЕССА ВЫПЛАВКИ СРЕДНЕУГЛЕРОДИСТОГО ФЕРРОМАРГАНЦА С ИСПОЛЬЗОВАНИЕМ ЖЕЗДИНСКИХ МАРГАНЦЕВЫХ РУД

В данной статье приведены результаты полного термодинамического моделирования и экспериментальное исследование процесса выплавки среднеуглеродистого ферромарганца с использованием Жездинских марганцевыхруд.Полное термодинамическое моделирования процесса выплавки среднеуглеродистого ферромарганца были произведены в программном комплексе «HSC Chemistry 6». Термодинамическое моделирование процесса выплавки проводили в интервале температуры 898–1989 К. Термодинамический анализ для моделирования процесса выплавки осуществлялся для четырех реальных составов шихты в зависимости от основности шлака (CaO/SiO_2 – 1,4; 1,6; 1,8; 2,0). По полученным термодинамическим данным были проведены экспериментальные исследование по выплавке среднеуглеродистого ферромарганца в лабораторной высокотемпературной печи Таммана. В качестве шихтовых материалов были использованы марганцевая руда Mnобщ. – 48,23 %, SiO_2 – 12.48 %, Al_2O_3 – 2,76 %, Feобщ. – 3,45 %, ферросиликомарганец марки СМн-17, известь CaO не менее 90 %. Согласно термодинамическим данным установлен оптимальный состав шлака, которое обеспечивает наиболее высокое извлечения марганца в сплав и разделение металл-шлак. Химический состав металла полученного лабораторных условиях следующее, %: Mn – 83-84; Si – 1,5-3; C – 0,95-1,68; P – 0,13–1,6; который соответствует ГОСТу 4755-91. Химический состав шлака, %: MnO – 10,92–17,90; SiO_2 19,02–21,45: CaO 36,92–40,43; FeO – 0,33–0,77.

Ключевые слова: ферромарганец, ферросиликомарганец, термодинамика, марганцевая руда, лабораторная плавка, основность шлака.

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