PRODUCTION LOW-CARBON FERROCHROME WITH LOW CONTENT OF PHOSPHORUS USING THE COMPLEX REDUCER

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ABSTRACT

Production of low carbon ferrochrome with low phosphorus content is associated with certain difficulties. Phosphorus, being supplied with the charge materials, almost completely transfers into alloy. The main part of phosphorus which presents in alloy comes with ferrochrome silicon. In order to reduce the phosphorus content in alloy, there are several variants of combined and successive usage of two reducing agents (aluminum and ferrochrome silicon) in the process of low-carbon ferrochrome smelting. Composition of metal and slag phases in dependence on charge of reducing agents and flux (limestone) has been received with thermodynamic analysis.

Industrial smelts with successive usage of the two reducing agents with various charging materials' ratio during different smelt stages have been carried out. The best ratio of usage of charging materials and electric energy has been determined.

The low-carbon ferrochrome with the concentration of phosphorus less than 0.015 % wt has been got. A result of research of electric conductivity of slags with a high concentration of aluminium and chrome oxides is being shown.

KEYWORDS: *Low-carbon ferrochrome, thermodynamic modeling, silico-aluminothermy reduction, electrical conductivity of slags.*

1. INTRODUCTION

In order to improve the qualities of the high-alloy chrome steel it's necessary to use fine charging materials. Decrease of the amount of phosphorus in metal will make it possible to increase the steel's working characteristics; for instance, to reduce the tendency to brittle fracture and increase the resilience to corrosion cracks.

Today the reduction of the phosphorus amount is carried out through the mixture of two melts (the low-phosphorus unalloyed melt and the high-chrome melt with a high concentration of phosphorus), or through the usage of basic charging materials with a very low content of phosphorus. In order to carry out the processing of high-chrome scrap it is convenient to implement the method of remelting of alloy wastes with the successive final stage of chrome concentration's replenishment by the low-carbon ferrochrome with the reduced concentration of phosphorus.

The traditional practice of low-carbon ferrochrome production is based on the reduction of chrome and iron from chromium ore by silicon of the ferrochrome silicon with the usage of flux (lime). The result is the alloy with the constitution that is approved by the Russian Federal Agency on Technical Regulating and Metrology and corresponds to the state standard – GOST 4757-91 (Ferrochromium. Specifications and conditions of delivery); the content of chrome is not less than 65% and the content of phosphorus does not exceed 0.03%.

One of the methods to obtain a low-carbon ferrochrome with a low concentration of phosphorus is the method of selection of the charging materials. The amount of phosphorus that is added by the ferrochrome silicon of the type FKhS–48, does not exceed 60%; that is why it's important to use another reducing agent with the low content of phosphorus, in particular aluminum. Due to the high cost of aluminum, the process of chrome reduction can be carried out using a complex reducing agent, combining both silicon and aluminum.

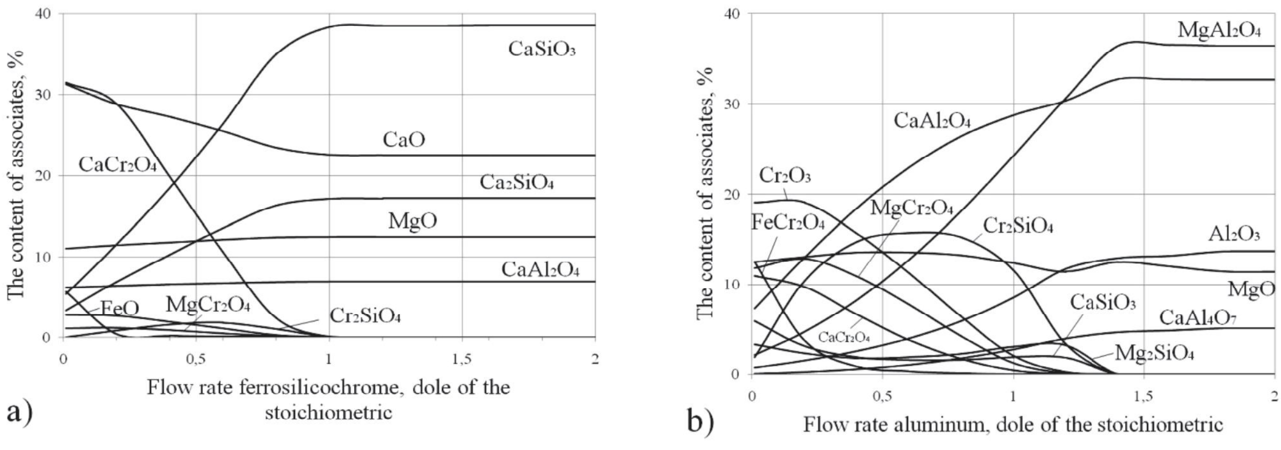
2. THERMODYNAMIC MODELING

In order to explain the processes that can be observed during the complex silicon aluminothermic reduction of chrome it's necessary to forecast the results of chemical interactions and phase transformations in the multicomponent heterophase inorganic systems.

A full thermodynamic modeling was made with help of the software system "TERRA" [1]. Thermo chemical characteristics of the materials were taken from reference books, the missing data was assessed by the authors according to the known methods, the facts are matched and they also match the experimental data about thermodynamic activity of the elements in metallurgic solutions. The constitution of the liquid solution was described within the framework of the model of the association solution [2].

There are results of calculations of changes in the constitution of metal and slag at the temperature 1750°C that depend on the increased usage of the reducing agents (ferrochrome silicon and aluminum) that were used separately. The composition of the charging materials for each reducing agent differs and it reflects the conditions of experimental industrial smelts. Below are the compositions of charge mixtures, for which the calculation was, kg:

Component	**Cr_2O_3**	**FeO**	**SiO_2**	**MgO**	**Al_2O_3**	**CaO**	**P**	**Cr**	**Si**	**Fe**	**Al**
Reduce of ferrosilicochrome	520,2	125,8	72,7	216,2	82,5	887,6	0,16	103,9	201,8	89,9	–
Reduce of aluminum	520,2	125,0	71,9	203,7	81,0	117,3	0,002	–	–	1,9	188,7



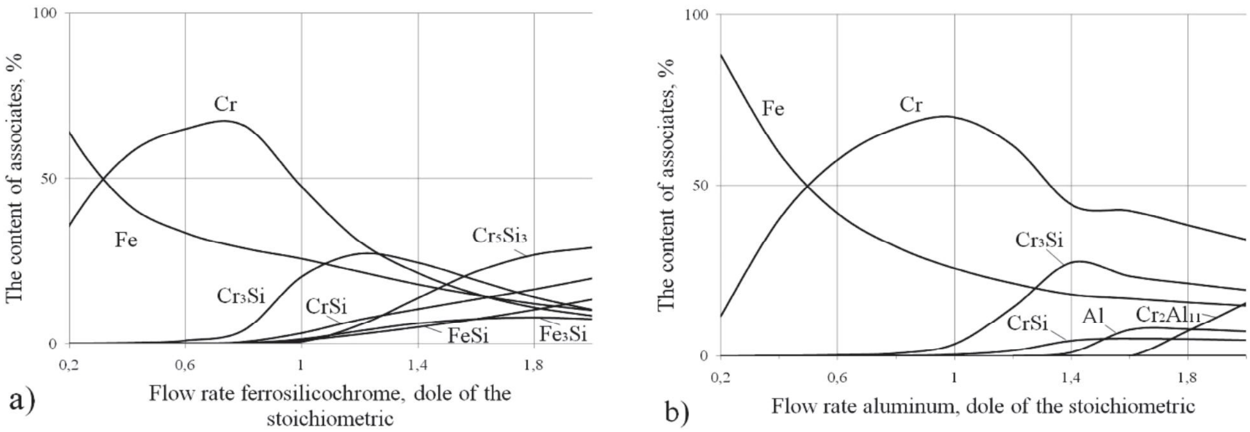
a) Ferrosilicochrome, b) Aluminum

Figure 1: Change of the content of the associates in the slag phase by reducing the charge rate

The slag phase of the ferrochrome silicon reduction of ore with the usage of a large amount of lime results in such combinations as: $CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$, which decrease SiO_2 activity being the oxide chrome reduction product. A small amount of chrome silicate Cr_2SiO_4 is formed in the slag phase, because silica is fixed in more firm calcium silicate. As a result a low chrome concentration in the divalent state is observed. A part of the lime is used for calcium aluminates formation, binding the whole aluminum oxide.

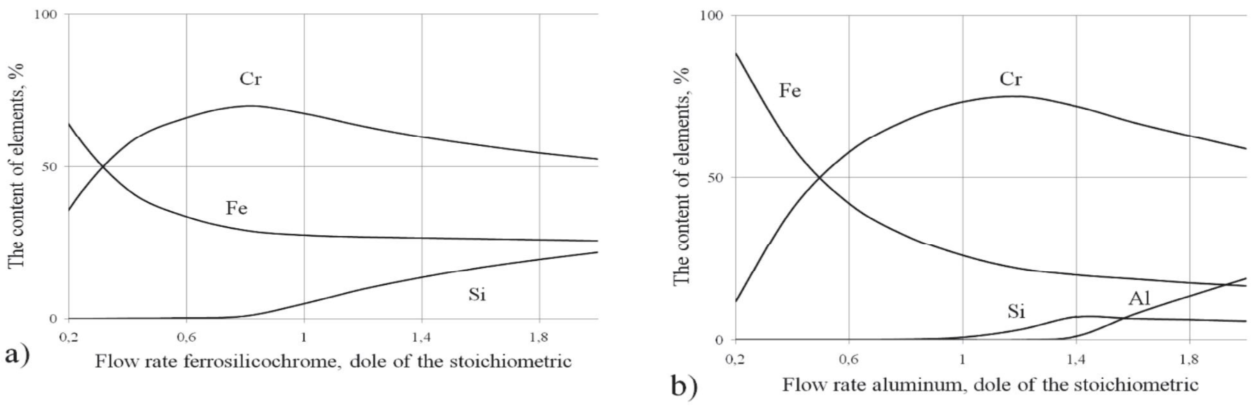
The reduction with the usage of aluminum leads to a more complex process with the formation of a large number of associates. Small lime usage in the charging material, high aluminum oxide concentration and low silicon oxide concentration, lead to the situation when in the final slag calcium oxide gets mainly fixed in calcium aluminates, but not in calcium silicates. As a result the conditions for the formation of divalent chrome silicate Cr_2SiO_4 in the slag are created, however it becomes difficult to carry out the reduction of chrome.

Figure 2 shows the calculated changes in the content of components in the metal phase with change of reducing agent charge, figure 3 - change of composition of the metal alloy on chemical elements, in figure 4 - changing of ratio of chromium extracted to metal.



a) Ferrosilicochrome, b) Aluminum

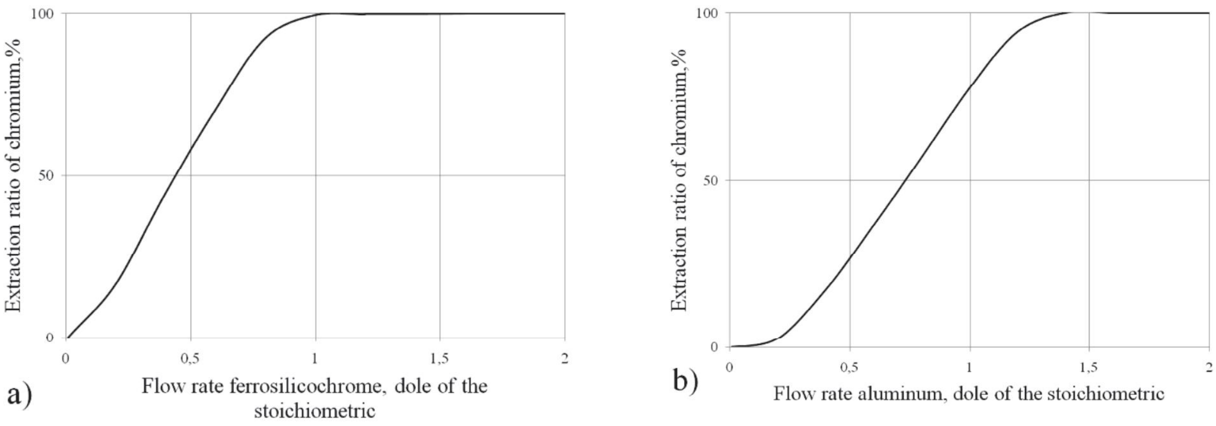
Figure 2: Changing of contents of the associates in the metal phase with increasing of reducing agent charge



a) Ferrosilicochrome, b) Aluminum

Figure 3: Changing of contents of the elements in the alloy with increasing of reducing agent charge

Chrome and iron pass into metal practically completely even with the usage of ferrochrome silicon being 0.8 from the stoichiometrically-needed. The concentration of silicon in the final alloy increases sharply due to the subsequent usage of ferrochrome silicon.



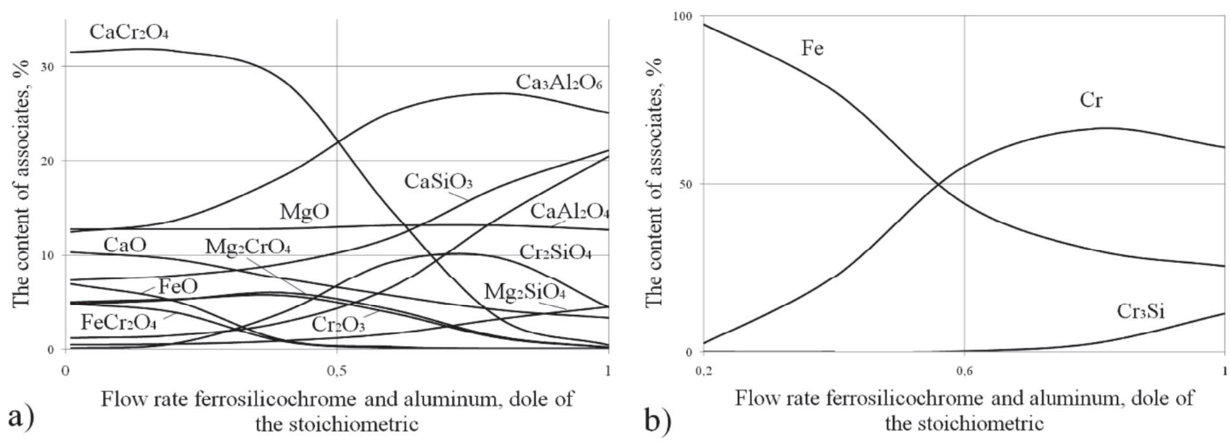
a) Ferrosilicochrome; b) Aluminum

Figure 4: The ratio of extracted chromium with increasing of reducing agent charge

The reduction of chrome by aluminum becomes difficult due to the fact that it gets fixed in chrome silicate, and the whole reduction is achieved with the consumption of aluminum that exceeds the stoichiometrically-defined by 20%. Thus, the stoichiometric aluminum consumption leads to the incomplete chrome reduction and to the reduction of silicon from ore, that has a negative effect on technical and economic indices of the smelt and also on the quality of metal.

Figure 5 shows the results of calculation of metal and slag composition using complex reducing agents - ferrosilicochrome and aluminum mixture in the ratio 1/1 by weight. Composition of the charge, kg:

Cr_2O_3	FeO	SiO_2	MgO	Al_2O_3	CaO	P	Cr	Si	Fe	Al
2601,1	626,7	361,4	1047,1	408,5	2355,1	0,28	92	178,7	82,5	294,6



a) Slag, b) Metal

Figure 5: Changes in the composition of slag and metal (associates) at the flow rate ferrosilicochrome and aluminum in the ratio 1/1

The usage of the complex reducing agents results in the process when a part of chrome fixes in the slag in the form of silicate Cr_2SiO_4 and the calculated level of chrome reduction, in the frameworks of the stoichiometric usage, comprises about 90%.

For the purpose of chrome reduction from the chrome ore it seems potentially productive to use aluminum and only then ferrochrome silicon. On the first stage it's appropriate to use only aluminum with the result of obtaining the melt with a high concentration of silicon, and only then use ferrochrome silicon that will result in the depuration of metal from silicon. Such a practice will help to obtain the metal of a higher quality. For the complete chrome reduction it is necessary to use aluminum (which is used as a reducing agent of chrome, iron and silicon from ore) in a quantity that is by 20% higher than stoichiometrically-needed, and as a result the content of silicon in the alloy will increase.

It's important to use ferrochrome silicon in a quantity that is slightly less than stoichiometrically-needed, taking into account the increased level of silicon in metal after the first stage.

The calculations that were based on the different quantity of lime were made. The increased usage of lime in slag leads to the increased level of calcium and magnesium aluminates; the level of the free aluminum oxide decreases.

However, the increased concentration of calcium oxide does not facilitate the acceleration of calcium silicate formation, and at the same time the concentration of chromium oxide is left unchanged.

Thus, a high or low amount of lime that is used as the reducing agent of aluminum has practically no influence on the change of CrO oxide and calcium silicate concentration in the slag, and thereby has no influence on the decreased amount of silicon in metal. A doubled amount of used lime, will lead to an insignificant decrease of the concentration of silicon in metal – from 0.7% to 0.5%. The increased usage of lime does not lead to the increase of chrome concentration in metal.

3. INDUSTRIAL EXPERIMENTS

The industrial smelts, with the usage of ferrochrome silicon and aluminum complex reducing agents, were carried out [3].

The process under review was the influence of different composition of charging materials that were used in different stages of the smelt. The smelts were carried out in an opened purifying electric furnace with the capacity 5 MVA.

The smelting technique was the following. A part of aluminum ingots, that were placed on a support plate of the lime-ore mixture and loaded through a furnace door, was covered with the remaining in the furnace bunker mixture of ore and lime that prevented oxidation of aluminum by the oxygen in the atmosphere.

Crushed ferrochrome silicon was loaded on the top of the charge and after that this charge was melted. After a certain amount of electric energy consumption, the furnace was turned off and the slag was tapped. Then, the second part of the charging materials was placed at the top of the liquid alloy, it all was melted and then the metal and slag were fully poured off from the furnace through the series of the steel ladles.

There were 4 types of smelting groups that varied according to the charging sequence of the reducing agents, to the proportion of the quantity of the reducing agents and to the quantity of the loaded lime. The composition of the used charge is given in table. 1.

The smelts, which were carried out according to the second type, were characterized by the unstable arc furnace operation, low chrome extraction and a high content of phosphorus in metal.

The smelts, carried out according to the fourth type, showed the best results. Chrome extraction comprised 77%, the basicity of the slag $(CaO+MgO)/(SiO_2+Al_2O_3)$ was 1.62.

The results of the metal and slag are presented in table 2.

Table 1: Raw material composition

Variant 1				
Component	**Amount of the charge, kg**		**Total for smelting, kg**	**Ratio,%**
	1 period	**2nd period**		
Chrome ore	5250	2250	7500	100
Ferrosilicochrome FHS48	770	330	1100	14,7
Aluminum	640	300	940	12,5
Lime	2520	1080	3600	48
Variant 2				
Component	**Amount of the charge, kg**		**Total for smelting, kg**	**Ratio,%**
	1 period	**2nd period**		
Chrome ore	5000	5000	10000	100
Ferrosilicochrome FHS48	730	730	1460	14,6
Aluminum	620	620	1240	12,4
Lime	2400	2400	4800	48,0
Variant 3				
Component	**Amount of the charge, kg**		**Total for smelting, kg**	**Ratio,%**
	1 period	**2nd period**		
Chrome ore	5000	5000	10000	100
Ferrosilicochrome FHS48	0	1220	1220	12,2
Aluminum	1260	0	1260	12,6
Lime	1220	2500	3720	37,2
Variant 4				
Component	**Amount of the charge, kg**		**Total for smelting, kg**	**Ratio,%**
	1 period	**2nd period**		
Chrome ore	5000	5000	10000	100
Ferrosilicochrome FHS48	0	1400	1400	14,0
Aluminum	1200	0	1200	12,0
Lime	300	3500	3800	38,0

Table 2: Metal and slag composition, weight %

Si	**P**	**C**	**N**	**Al**	**Cr**
0,83..0,96	0,0125…0,013	0,054…0,063	0,037…0,059	0,028…0,029	70,22…70,5
MgO	**Al_2O_3**	**SiO_2**	**CaO**	**Cr_2O_3**	**FeO**
13,71…14,98	11,7…19,35	15,28…19,08	37,01…41,59	9,2…15,84	1,08…2,87

4. ELECTRICAL CONDUCTIVITY OF SLAG

In the usual course of slag has a composition by weight. %: MgO – 12…15; Al_2O_3 – 3…7; SiO_2 – 20…29; CaO – 45…50; Cr_2O_3 – 3…8; FeO – 0,5…1,5.

The characteristic feature of the experimental smelts is the high amount of Al_2O_3 and Cr_2O_3 in the slag. The high amount of aluminum oxide in the slags of the experimental smelts is determined by the usage of aluminum as a reducing agent. According to the results of the thermodynamic analysis, the high amount of chrome in the slag is, apparently, the result of the process, which is characterized by the usage of aluminum, when on the first stage of the smelt a part of chrome is fixed in the slag in the divalent state. But on the second stage of the smelt this chrome is characterized by worse reduction.

The increased amount of aluminum and chrome oxides in the slag can lead to the change of the electric mode of the smelt. In the process of low-carbon ferrochrome production the slag acts as a section of the electric circuit. The amount of heat, generated in the slag bath, the length of the electric arc and the specific electric energy consumption depend on the slag's electrical conductivity [4].

The research, concerning the electric conductivity of the slags with the increased amount of aluminum and chrome oxides, was carried out. In order to define the melted slag's electric conductivity a method, which is based on the measurement of the electrical resistance of the liquid between two electrodes according to the scheme voltmeter – ammeter was applied [5]. The composition of the studied slags are presented in table 3.

Table 3: Composition slags to determine the electrical conductivity, wt.%

№ slags	MgO	Al_2O_3	SiO_2	CaO	Cr_2O_3	FeO
1	14,51	4,58	26,50	45,4	7,60	1,45
2	13,19	13,25	24,05	41,3	6,91	1,32
3	12,09	20,48	22,05	37,8	6,33	1,21
4	15,9	14,7	18,9	50,5	-	-
5	17,7	14,9	17,4	47,0	3,0	-
6	17,18	14,47	16,89	45,63	5,83	-
7	16,54	13,93	16,26	43,93	9,35	-

The basicity of the analyzed slags, which is defined as $(CaO + MgO)/(SiO_2 + Al_2O_3)$, was changed from 1.17… 2.0; the ratio of MgO/ Al_2O_3 was changed from 0.59…3.17.

The experimental dependence of the conductivity on the content of Al_2O_3 and Cr_2O_3 in the slag at 1700 ° C is shown in figure 6.

The dependence of electrical conductivity (æ) from the content of Al_2O_3 is described by the following equation:

$$æ = -0{,}08 \cdot (\%Al_2O_3) + 6{,}069, \text{ S/cm}$$

The dependence of electrical conductivity (æ) from the content of Cr_2O_3 is described by the following equation:

$$æ = -0{,}188 \cdot (\%Cr_2O_3) + 4{,}992, \text{ S/cm}$$

The increased content of Al_2O_3 and Cr_2O_3 leads to the decrease of the slags' electric conductivity. The influence of chrome oxide on the slag's electric conductivity is stronger, than the influence of aluminum oxide. It seems that it happens due to the formation of large low-energy ions in the complex multicomponent system.

The increased Al_2O_3 content (from 4.58% to 20.48%) in the slag of the thermal silicon smelting technology, that was carried out with the usage of the complex reducing agent, at the temperature 1700°C will lead to the decrease of the electric conductivity by 1.29 S/cm or by 22.8%. At the temperature 1700°C and with the increase of the content of Cr_2O_3 (from 0 to 9.83%) the slag's electric conductivity will decrease by 1.66 S/cm or by 33.4%.

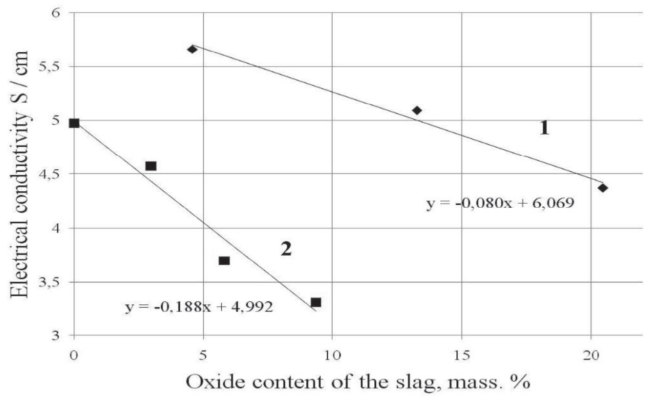


Figure 6: The dependence of the electrical conductivity of the slags content of Al_2O_3 (line 1) and Cr_2O_3 (line 2) in the slag at 1700°C

5. CONCLUSIONS

1. On the first stage of a low-carbon ferrochrome smelt that is carried out with the usage of the two reducing agents it is convenient to use only aluminum in order to get a metal smelt with a high content of silicon, and after that use ferrochrome silicon to depurate metal from silicon.

2. A low-carbon ferrochrome, containing 70% of chrome and less than 0.015% of phosphorous, was obtained in industrial conditions. In order to obtain a low-phosphorous ferrochrome it is convenient to use in the charge the chrome ore with the content of phosphorous 0.002%, ferrochrome silicon of the type FKhS–48 with the content of phosphorus 0.019…0.021%, primary aluminum with the content of phosphorus 0.0004…0.0010%, and lime with the content of phosphorus 0.002…0.003%.

3. According to the results of the industrial smelts and thermodynamic analysis the implementation of the scheme of the successive usage of the two reducing agents leads to the increased chrome content in the final slag. It is connected with the formation of a thermodynamically-stable silicate of divalent chrome in the slag.

4. With increasing content of Cr_2O_3 and Al_2O_3 in the slag of the conductivity is decreases. Effect of chromium oxide on the electrical conductivity of slag is stronger than the influence of alumina.

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