DEVELOPMENT OF AN ALTERNATIVE TECHNOLOGY FOR THE PRODUCTION OF REFINED FERROCHROME

In the article presented the refined ferrochrome smelting technologies by furnace, converter and out-of-furnace methods. The main attention is paid to the new aluminum-silicothermal process for obtaining refined ferrochrome by the furnace method using a multicomponent alloy - aluminosilicochrome. The results of laboratory experiments on the smelting of ferrochrome using the multicomponent alloy are presented. As a result, melting products were obtained: ferrochrome with 63 – 68 % chromium and 1 – 3 % carbon and slag with 2 – 6 % chromium oxide.

Key words: ferrochrome, aluminum-silicothermal process, multicomponent alloy, chrome oxide, laboratory experiments

INTRODUCTION

The main purpose of refined grades of ferrochrome is to use them as an alloying additive in the production of chromium-nickel and chromium (superferritic) steels. With its unique and richest reserves of chromium ore, Kazakhstan is one of the main producers of refined ferrochrome, while occupying a leading position. These grades of ferrochrome are smelted metallothermical method and are almost completely exported. The technological scheme is similar to the technologies of foreign countries and has equally unsolved technological problems: a relatively low degree of extraction of the leading element, inefficient use of reducing agents, an increase in the specific consumption of raw materials and electrical energy. Based on the aforementioned unresolved problems, the technology requires improvement.

RESEARCH METHODOLOGY

As known, at this time there are several methods of smelting refined grades of ferrochrome, differing both in the type of reducing agents and charge materials used, and in the equipment and technological design, namely:

- refining of high-carbon ferrochrome from carbon by oxidation of the latter with chromite ore by reaction [1]:

$$Cr_7C_3 + (FeO \cdot Cr_2O_3) = Fe \cdot 9Cr + 3CO \qquad (1)$$
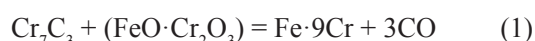
This method has been widely used in Germany. Taking into account the type of reducing agent used (carbon high-carbon ferrochrome), it should be expected that the process of refining from carbon must be carried out in a separate unit, because chromium and iron are carbide forming elements. This can predict the difficulty of obtaining low-carbon grades of refined ferrochrome;

- refining of high-carbon ferrochrome from carbon by oxidation with gaseous oxygen in the air or with pure oxygen in a converter by chemistry (2) [2]:

$$Cr_7C_3 + 3/2O_2 = 7Cr + 3 \qquad (2)$$
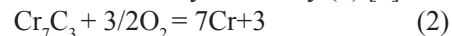
This method was developed by the Central Research Institute of Ferrous Metallurgy (Moscow) and has long been used at the Aktobe Ferroalloy Plant in the production of medium-carbon ferrochrome;

- reduction of chromium and incidentally iron from chromite ore with ferrosilicon silicon (Beckert method) according to the reaction [3]:

$$(FeO \cdot Cr_2O_3) + 2Fe \cdot Si = 3Fe \cdot 2Cr + 2SiO_2 \qquad (3)$$
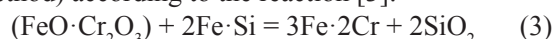
This method has not been fully used due to the production of ferro-chromium with a low chromium content. However, this process can be used in the smelting of ferrochrome using ferrosilicon for additional reduction of chromium from slag before being discharged from the furnace, and, depending on the requirements of consumers, it can be used for smelting low-carbon ferrochrome with reduced chromium content;

- aluminothermic reduction of chromium oxide. There are flux and flux-free options for smelting [4]. This method is widely used in the production of especially low carbon grades of ferrochrome and metallic chromium by reaction:

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3 \qquad (4)$$
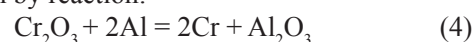
- refining of ferrosilicochrome from silicon by oxidation of silicon with oxygen (Gene method) contained in chromite ore oxides by reaction [2, 5, 6]:

$$2Fe \cdot Cr \cdot Si + (FeO \cdot Cr_2O_3) = 3Fe \cdot 4Cr + 2SiO_2 \qquad (5)$$
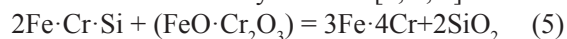
This method is currently practiced at ChEMK, Aktobe and Serov ferroalloy plants and has long been used

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at the Zaporozhye ferroalloy plant. According to the developed technology, the relative cheapness (compared to aluminothermy) of the reducing agent, the hardware design (in ore-thermal furnaces with a transformer power of 3,5 - 7 MVA) and the adjusted chromium content in the metal (i.e., ferrochrome is not diluted with silicon, as in the case of application ferrosilicon), this method has found the most widespread use in industry;
- chromite ore reduction with ferrosilicoaluminium (FSA). The chemistry of reduction is as follows from the reaction:

$$3Cr_2O_3 + Fe \cdot 3Si \cdot 2Al = Fe \cdot 6Cr + 3SiO_2 + Al_2O_3 \quad (6)$$

This technology for the production of refined grades of ferrochrome is a development of the Chemical and Metallurgical Institute Zh. Abishev (Karaganda city) [7-11].

As noted, refined ferrochrome is smelted in refining furnaces with transformers with a power of 3,5 - 7 MVA [5] with a tilting bath, which are identical in design to arc steel furnaces. There is also another variation of this process, carried out by mixing in a high-temperature reactor (ladle) previously melted in separate aggregates of ore-lime melt and liquid or solid (lumpy) ferrosilicochrome. This method allows to obtain ferrochrome with a carbon content of less than 0,06 %, since the contact of the melt with electrodes that are sources of carbon in the amount of 60 - 70 % is excluded.

An analysis of the practice of the production of refined ferrochrome shows that furnace and out-of-furnace metallothermy are widespread and successfully used in industry. Each of the above methods has both advantages and disadvantages. But, despite the successful practicability and prevalence of these technologies, it should be noted that the technical and economic indicators of the processes still remain low. Perhaps this is due to inefficient use of the reducing agent or poor quality composition of the consumed charge material.

The urgency of the task lies in the need to improve the technology for the production of refined ferrochrome with the involvement of magnesia chromium ores and to prevent silicate decomposition of final slags.

Currently, in the production of refined ferrochrome, there is a decrease in the quality of the chromium ore used, which is characterized by an increased content of gangue, in which the content of magnesium oxide is ~ 17 - 20 %, which in case of ore electrothermia adversely affects the thermophysical properties of slag, leading to the loss of metal with slag in the form of metallic inclusions. There is a deterioration in the technical and economic indicators of the process, this is due to an increase in the specific consumption of charge materials

and electricity, a decrease in the degree of extraction of the leading element and an increase in the multiplicity of slag. In addition, in the silicothermy of refined ferrochromium, there is an acute question of the susceptibility of the final waste slag to self-scattering. Fine disintegrated slag causes serious damage to the environment, occupying large areas [5, 8].

RESULTS RESEARCH

This article discusses the technology of smelting refined ferrochrome using an alloy of aluminum, silicon and chromium as a reducing agent under laboratory conditions. Based on the results obtained, it is shown that it is possible in principle to increase the technical and economic indicators of the process of smelting refined ferrochrome by replacing ferrosilicochrome with an alloy of aluminum, silicon and chromium, with an increase in the degree of extraction of chromium into metal, a decrease in the slag ratio and a reduction in lime consumption.

Aluminosilicochrome is a multicomponent aluminum-chromium-silicon-containing alloy obtained in low-power electric furnaces (up to 5 MVA) by processing substandard chromium ores by the complete reduction of all ore oxides using brown high-ash coals as a reducing agent. The smelting technology for this alloy was developed by employees of the Chemical and Metallurgical Institute. The alloy contains, on average, 38 % chromium, 25 % silicon, 13 % aluminum, 0,01 % sulfur, 0,02 % phosphorus, 0,5 - 2,5 % carbon, the rest is iron. The density of the alloy ranges from 3,3 - 3,5 g/cm³. The phase composition is described by intermetallic compounds Cr_3Si, $CrSi$, and $AlCr_2$. During crystallization, the alloy goes into a powder state.

To determine the fundamental possibility of smelting refined ferrochrome using new technology, experiments were conducted in laboratory conditions.

During the experiments, chromium ore and reducing agent aluminosilicochrome (AChS) were used as charge materials, the chemical composition of which is given in the Table 1.

The purpose of briquetting was the rational use of chrome ore and the efficient use of elements involved in the recovery processes in the metallothermy of refined ferrochrome. Given the powdery state of the AChS, it is proposed to briquette it in a certain ratio with the commercial chrome ore used in a fraction of 0 - 5 mm. It is necessary to proceed from considerations of intensification of the recovery process by increasing the contact surface of the reacting phases.

Table 1 **The chemical composition of the feed materials / wt. %**

Chrome ore								AChS				
Cr_2O_3	SiO_2	CaO	MgO	Al_2O_3	$Fe_{total.}$	S	i.l	Cr	Si	Al	C	Fe
51,73	7,76	0,53	17,75	8,32	9,42	0,012	2,10	36,92	25,11	14,41	1,48	rest.

The above materials had a fraction of 0-0,5 mm and were briquetted in a laboratory press unit with a pressing pressure of 980,7 – 1078,7 N/cm² [12].

The composition of the briquetted mixture is as follows: chrome ore (0 – 0,5 mm) – 69,1 %; AChS (0 – 0,5 mm) – 30,9 %.

As a binder, liquid glass was used in an amount of 6 – 7 % of the dry weight of the mixture. The density of water glass is 1,46 – 1,48 g/cm³, the silicate module $SiO_2 / Na_2O = 2,64 – 2,84$. Before briquetting, the materials, first in a dry state and then with a binder in the indicated ratio, were thoroughly mixed and briquettes were obtained in the form of cylinders with a diameter of 10 mm and a height of 10 - 15 mm. The briquetted mixture was dried in a laboratory muffle furnace at a temperature of 200 - 250 ° C for a duration of 3 hours. The chemical composition of the briquettes is shown in Table 2.

As fluxing material, lime with CaO content of more than 95 % was used.

After all the above operations, the charge materials were loaded into an alundum crucible, the use of which prevented the carbon from contaminating the alloy.

The crucible with the charge was installed in a laboratory high-temperature resistance Tamman furnace.

A carbon tube served as the heating element of the furnace. After loading the crucible with the charge, the furnace was turned on. Upon reaching a temperature of 930 °C, gas evolution was observed in all experimental melts with a characteristic white coating on the walls of the lid of the coal tube. At 1 330 °C, the beginning of charge melting was noted. At a temperature of about 1 640 °C, a liquid melt appeared, as evidenced by the presence of an alloy adhering to the molybdenum wire. At a temperature of 1 650 °C, gases formed in the crucible in the form of bubbles in the form of bubbles re-sembling boiling water. At this temperature, the melt was held for 60 min and cooled in an oven. When the temperature decreased to ~ 200 °C, the crucible was unloaded and after it cooled to room temperature, the melt was sorted to separate metal and slag. The metal was well separated from the slag. Metal fragment was characterized by a fine-grained structure. The slag was a stone-like mass of dark gray.

The resulting alloy in chemical composition meets the requirements of the standard. The results of the melts are shown in Table 3.

As can be seen from Table 3, the compositions of the slag were characterized by different values of basicity. The amount of reducing agent was varied to find the optimal value.

In the course of laboratory experiments, it was noted that the recovery process in the crucible was very intensive with complete melting of the entire mixture and with a clear separation of metal and slag. The achievement of this effect is provided due to the fine fraction of the components of the charge, primarily used alloy AChS. After cooling, the AChS alloy scattered and the fraction ≤ 0,5 mm is 60 – 65 % by weight, which increases the efficiency of the alloy as a reducing agent due to the more developed surface of the material itself, as well as due to its uniform distribution over the entire volume of briquettes.

As is known, a number of technological indicators depend on the chemical composition of the slag, especially on its basicity (CaO/SiO_2). As shown in Table 3, the values of basicity are in the range of 1,36 - 1,79. The choice of basicity largely determines the manufacturability of slag. In our case, the main goal was to increase the technical and economic indicators of the process, such as the degree of extraction of the lead element into the alloy, manufacturability and the multiplicity of slag.

Table 2 **The chemical composition of briquettes / wt. %**

Chemical composition													
Cr_2O_3	SiO_2	CaO	MgO	Al_2O_3	FeO	C	S	P	L.o.i.	Cr	Si	Al	Fe
35,75	5,36	0,36	12,26	5,75	6,51	0,65	0,01	0,02	1,73	11,41	7,76	4,45	7,34
34,02	6,59	0,76	11,82	5,91	8,28	0,76	0,01	0,01	1,05	10,84	7,21	4,78	7,31
33,71	5,13	0,48	14,04	6,02	7,51	0,57	0,01	0,01	1,45	11,32	7,41	4,21	7,57
33,61	5,61	0,65	12,77	6,28	8,45	0,71	0,02	0,01	0,98	10,98	7,45	4,54	7,11

Table 3 **Chemical composition of smelting products / wt. %**

№	Metal				Slag						$\frac{CaO}{SiO_2}$
	Cr	Fe	Si	C	Cr_2O_3	CaO	SiO_2	MgO	Al_2O_3	FeO	
1	66,88	29,05	1,22	1,96	5,26	31,87	23,43	13,59	30,55	0,55	1,36
2	68,08	27,82	0,66	2,33	6,31	33,69	24,23	11,43	27,29	0,62	1,38
3	63,24	33,47	0,42	0,77	5,43	33,52	23,44	13,65	18,98	0,71	1,43
4	68,72	26,79	0,39	3,24	5,67	31,88	20,50	13,22	14,90	1,08	1,55
5	67,22	28,29	1,05	1,18	5,11	37,59	24,06	13,07	18,07	1,12	1,56
6	67,28	28,31	1,02	1,31	2,17	32,62	20,46	10,07	21,07	0,82	1,59
7	66,38	30,58	1,03	1,13	4,25	39,98	24,53	13,03	17,17	0,93	1,63
8	67,48	29,81	1,06	1,25	5,07	39,75	23,66	14,11	16,09	1,04	1,68
9	67,26	28,34	0,20	3,20	5,68	34,54	21,69	14,26	15,07	1,23	1,73
10	68,87	26,01	0,78	2,94	6,26	41,43	23,18	11,16	15,32	2,05	1,79

The degree of extraction of chromium from the ore into the alloy was ≥ 85 %; manufacturability was characterized by fewer metal inclusions entangled in the slag and a clear separation of metal and slag during disassembly of the hardened melt; the slag ratio is in the range of 1,61 - 2,50. A secondary task was to obtain, at a given basicity value, slag that was not subject to decomposition with a low content of chromium oxide. Slags of laboratory experimental melts were obtained in a stone-like state without signs of decay. The above information of the optimal data corresponds to the basicity values of 1,50 – 1,65.

In terms of carbon content, the metal obtained corresponds to grades of medium-carbon ferrochrome according to GOST 4757-91.

From Table 3 it is seen that the use of a silicon-aluminum reducing agent - AChS in the metallothermy of refined ferrochrome leads to the formation of alumina-containing (Al_2O_3) slags. Alumina concentration mainly ranges from 15 – 18 %, while according to standard technology it is 5 – 7 % [9]. Therefore, there is a significant change in the chemical composition of the slag.

As is known, the process of self-scattering of slags from the traditional production of refined ferrochrome is associated with specific features of the structure of slag, which is dominated by dicalcium silicate - Ca_2SiO_4 (larnite). This compound exists in several modifications, each of which is stable only within a certain temperature range. For practice, the transition of β-Ca_2SiO_4 to γ-Ca_2SiO_4 during the cooling of slag at ≈ 670 °C is especially important. This transformation is accompanied by an increase in the volume of silicate by about 12 % [2].

Dicalcium silicate was not detected by conducted X-ray phase studies of the mineralogical composition of the experimental slags,. The phase composition of the experimental slags includes mervinite ($3CaO·MgO·2SiO_2$), gelenite ($2CaO·Al_2O_3·SiO_2$), and residual chromium oxides are part of newly formed $MgO·(Al,Cr)_2O_3$ spinel solutions.

CONCLUSIONS

- Laboratory experiments were carried out on the smelting of refined ferrochrome using a complex alloy AChS. At a temperature of 1 330 °C, the beginning of melting of the charge was noted, and at a temperature of 1 640 °C the formation of a liquid melt was noted. According to chemical analysis, metal samples fully comply with the requirements of the standard.
- Improved process performance indicators: the degree of extraction of chromium from ore 80 - 85 % (by traditional technology 71 - 76 %); the slag ratio of 2,5 – 1,6 (according to traditional – 3,1 - 2,7); slag basicity 1,50 – 1,65 (traditional – 1,9 – 2,1).
- Slags of laboratory melts were received in a stone-like state without signs of scattering.
- In the redox reactions of the process of obtaining refined ferrochrome, the participation of aluminum and a decrease in the basicity of slag prevented slag self-scattering into a powder state, which showed long-term storage of slag samples in natural conditions.

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