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DEVELOPMENT OF TECHNOLOGY OF COMPLEX ALUMINUM-SILICON-CHROME ALLOY WITH UTILIZATION OF OFF GRADE RAW MATERIALS

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Preliminary Note – Prethodno priopćenje

Experimental studies on obtaining a complex aluminum-silicon-chrome alloy (FASCh) from Karaganda high-ash coals and high-carbon ferrochromefines were carried out. A method for smelting low-carbon ferrochrome using aluminum-silicon-chrome alloy as a reductant is suggested.

Key words: aluminum-silicon-chrome (FASCh) alloy, high-carbon ferrochrome fines, high-ash coal, complex alloy

INTRODUCTION

The scientists of Abishev Chemical-Metallurgical Institute are developing new types of efficient ferroalloys produced by complex processing of natural or human-made resources. The result of integrated extraction of alloy components from the charge is a slag-free single-stage SAF process for the smelting of a multi-component alloys.

One of the results of these studies was implemented in the “Kazakhstanski” alloy produced on the industrial scale “KSP Steel” PC LLP (Pavlodar) and at Ekibastuz mini-plant “A&C” LLP built in 1998.

THEORETICAL ANALYSIS

The technology of complex aluminum-silicon-chrome alloy (FASCh) is based on utilization of high-ash coal sthatare not used in the industry due to the high ash content. High extraction degree of charge components is achieved by complete recovery of the basic elements from coal ash. Utilization of off-grade materials permits to obtain a FASCh alloy at a low cost.

Aluminum-silicon-chrome alloy is intended for metal-thermal manufacturing of low- and medium-carbon ferrochrome, as well as for stainless steel production.

At present, the smelting of refined grades of ferrochrome is based on a multi stage pyro-metallurgical process and has a number of disadvantages. The main problem is the silicate decomposition of dumpslags that raises serious environmental issues.

The suggested solution of this problem is to replace the conventional reductant (ferrosilicon-chrome) with a new Fe – Al – Si – Cr complex alloy (FASCh) in which aluminum content is not less than 10 %. Such aluminum content in the alloy results in formation of high-alumina (Al_2O_3) slag during the metal-thermal process. As a result, the phase composition of the final slag is shifted from two-calcium silicate ($2\,CaO\cdot SiO_2$) area to the helenite ($2\,CaO\cdot Al_2O_3\cdot SiO_2$) and merwinite ($3\,CaO\cdot Al_2O_3\cdot 2SiO_2$) in the $CaO – MgO – Al_2O_3 – SiO_2$ system. Such slags are not subject to decomposition and after crystallization have sufficient strength to be used as building materials.

It should be noted that earlier studies on optimization of refined ferrochrome manufacturing showed the expediency of using aluminum-based reductants or introduction of aluminum into the charge [1,2]. The aluminum presence in the charge not only favorably effects the slag fluidity but also promotes the dissociation of high-melting refractory spinels of $Cr_2O_3\cdot MgO$ type by reaction (1) and formation of chemically stable alumina-containing spinels.

$$(MgO\cdot Cr_2O_3)+2\,Al \rightarrow (MgO\cdot Al_2O_3)+2\,Cr \quad (1)$$

$$Cr_2O_3 + 3/2\,Si \rightarrow 2\,Cr + 3/2\,SiO_2 \quad (2)$$

Such interaction increases speed and completeness of chrome recovery from the spinel by silicon according to reaction (2).

Thus, we may concludet hat use FASCh alloy as a reductant enriches the final slags with aluminum oxide in metallothermy of refined ferrochrome, which favorably affects slags physical-and-chemical properties and simplifies the problem of processing high-magnesium chrome ores.

Earlier pilot smelting described in [3] were aimed at making the AChS (aluminum-chrome-silicon) alloy from poor chrome ores by slag-free process without flux. Ekibastuz coal was used as a reductant.

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The charge of the complex AChS alloy consists of two components: poor chrome ores of the “Donskoy” mining enterprise and Ekibastuz coal. Utilization of poor chrome ore has a certain importance but suggested technology has a number of disadvantages. The magnesium oxide content in Kazakhstan chrome ore exceeds 20 %. The reaction of magnesium recovery is known to take place at high temperatures, approximately 2 000 °C [4]. The recovery reaction consumes large amounts of energy and reductant, but recovered magnesium does not dissolve in the metal but sublimates and leaves the reaction zone with off-gas. According to the heat balance calculations, recovery and sublimation of magnesium consume as many as 12 – 16 % of the total heat input [5]. To avoid this problem in the process of FASCh smelting we suggest to replace chrome ore with high-carbon ferrochrome fines as in the traditional technology of ferrosilicon-chrome FChS48 smelting.

To development of FASCh technology included theoretical studies using the thermodynamic-diagram analysis (TDA) of multi component systems invented by Abishev Chemical-Metallurgical Institute. Phase composition diagrams made on the basis of TDA allow to monitor the phase transformation and to predict the final composition of an individual system that simulates the studied melt.

To determine the area of desired metal composition we have carried out the thermodynamic-diagram analysis of the Cr – Fe – Al – Si system based on the following ternary subsystems: Fe – Al – Si, Fe – Cr – Si, Fe – Al – Cr, Si – Al – Cr.

According to TDA results, the Cr – Fe – Al – Si system consists of 11 congruent tetrahedrons, such as: Cr – Fe – Cr_3Si – Cr_2Al, Cr_2Al – Fe – Fe_2Si – Cr_3Si, Cr_2Al – Fe – Fe_2Si – Fe_2Al_5, Cr_3Si – Cr_5Si_3 – Cr_2Al – Fe_2Si, Cr_2Al – Fe_2Si – Cr_5Si_3 – Fe_2Al_5, Fe_2Si – FeSi – Cr_5Si_3 – Fe_2Al_5, Cr_2Al – Al – Fe_2Al_5 – Cr_5Si_3, Cr_5Si_3 – $CrSi_2$ – Al – Fe_2Al_5, Cr_5Si_3 – $CrSi_2$ – FeSi – Fe_2Al_5, $CrSi_2$ – Si – Al – Fe_2Al_5, $CrSi_2$ – Si – Fe_2Al_5 – FeSi. The partition of general system was performed considering only congruent compounds. The sum of elementary tetrahedrons relative volumes is equal to one (1,0) which proves the accuracy of tetrahedrons partitioning [6].

The chronology of Cr level variations in FASCh alloy with low and high chromium content takes place in $CrSi_2$ – Si – FeSi – Fe_2Al_5 tetrahedron. This tetrahedron has the second largest relative volume among the 11 tetrahedrons mentioned above [7]. Such a large volume fraction of the tetrahedron ensures the most favorable conditions for the smelting process due to possibility of wide-range regulation via charge composition.

EXPERIMENTAL

Based on theoretical developments by Chemical-Metallurgical Institute there were carried out large-scale laboratory experiments for smelting a FASCh alloy.

A high-ash coal, normally considered an industrial waste was used as a reductant. A side from fixed carbon, the coal contains high silica and alumina. A quartzite of the Tekturmas deposit was used as a major silica source and aneutralizer of excessive carbon. The charge also included the fines of high-carbon ferrochrome in different ratios (Figure 1). All charge materials were milled to fraction of +15 – 80 mm.

Prior to smelting, representative samples of high-carbon ferrochrome fines and carbon reductants were taken using triple cone quartering and mixing.

The chemical and technical composition of the charge components was as follows:

- high-ash coal of the Borly deposit, grain size 7 – 80 mm with technical composition: A^a – 59,27 %; V^a – 16,98 %; W – 0,55 %; C – 23,2 % and ash mineralogical components: SiO_2 – 56,43 %; Fe_{total} – 1,1 %; Al_2O_3 – 31,92 %; CaO – 6,26 %; MgO – 2,77 %;
- fines of high-carbon ferrochrome, grain size 5 – 15 mm of the following chemical composition: Fe – 27,55 %; Cr – 65,0 %; P – 0,03 %; C – 6,38 %;
- quartzite of the Tekturmas deposit of the chemical composition: SiO_2 – 92,92 %; Al_2O_3 – 0,87 %; CaO – 3,58 %; MgO – 2,22 %.

Technological studies of the FASCh alloy slag-free process were carried out in a single-phase submerged arc furnace with the transformer capacity of 200 kWA. The arc with the temperature of 2 500 – 4 500 ^{o}C was provided by a 150 mm graphite electrode. The furnace was lined with chamotte brick. The furnace bath was made in the form of ellipse with axes of 60 and 80 cm stretched towards the taphole. The distance from the electrode to the taphole block was 17 – 18 cm, to the furnace back wall 22 – 25 cm. The bath depth was 30 – 35 cm. The furnace bottom was made of anode paste

high-ash Borly coal

quartzite

fines of high-carbon ferrochrome

Figure 1 Charge components of aluminum silicon-chrome (FASCh) process coked for 8 hours under the current with periodical shut down of the furnace. The furnace transformer has four voltage taps: 18,2 V; 24,2 V; 36,6 V and 48,8 V. During the experiments we used voltage 24,4 V and 36,6 V.

The furnace heating was performed within 12 hours with the coke bed as an electric current conductor. After the heating the furnace bottom was completely cleaned of the remaining coke. The electric mode of the heating period was as follows: the secondary voltage was 24,6 V, current 150 – 200 A. The smelting was performed by continuous process with moderate charge feeding and periodical tapping every two hours into cast iron molds. The taphole opening was performed by electric arc or by an iron rod. Metal and slag from each tapping were weighed and sampled for chemical analysis.

The main task of the study was the complete extraction of all alloy components from high-ash coal in a continuous, stab lean deasily controlled slag-free process. The complex alloy smelting was performed according to the technology developed by the Abishev Chemical-Metallurgical Institute.

RESULTS AND DISCUSSION

The pilot smelting of aluminum-silicon-chrome alloy was carried out in two stages, with two different charge compositions.

Stage 1 For the first stage, the charge composition was calculated so as to obtain the alloy with total content of Si and Al about 60 %, and chrome content – within 15 – 20 %. The expected distribution of the elements among the smelting products is represented in the Table 1.

Table 1 **Coefficients of elements distribution among the smelting products**

Smelting products	Elements distribution / %						
	Si	Al	Fe	Ca	Mg	P	Ti
Metal	80	73	100	0	0	100	100
Slag	2	7	0	0	0	0	0
Dust and gas	18	20	0	100	100	0	0

The total duration of smelting period was 20 hours starting after furnace heating stage. The smelting process was stable with slight caking of charge on the top of the furnace fixed by forced poking and feeding new portions of the charge. To improve the gas permeability of the furnace top the additions of gas coal of Shubarkol deposit were used. Due to low electric conductivity of charge the electrodes sinking was deep, which ensured sufficient temperature in the reaction zone and complete reduction of all oxides. As a result, we observed an even gas emission all over the furnace top. Metal was well heated, without the signs of slag formation. The furnace power was high with stable electrode current.

Stage 2 For the second stage of pilot campaign the calculations were made to produce the metal containing total 50 % of Si and Al and 20 – 30 % of chromium.

The calculated charge composition was used till the end of the experiments. There were no signs of unstable operation aside from slight caking of charge after 4 – 5 tappings, probably caused by excessive quartz. The quartz fraction in the charge was subsequently reduced by 1 kg. The general indicators of the furnace operation showed the stability of the smelting process accompanied by deep and stable electrode immersion and timely active metal fall. The electrode current was stable and lost its stability only before the tapping. The alloy yield and composition were sufficiently close to calculated values. The top poking was performed once in hour and immediately after the tapping.

Thechemical composition of metal obtained in both stages is represented in the Table 2.

A total of 285 kg of alloy was obtained in the pilot campaign with average specific power consumption of 11 000 kW·hour per ton. Relatively low power consumption was achieved due to the activity of silicon-aluminum complex and the presence of metallic chrome introduced in the form of high-carbon ferrochrome fines, whichintensified the reduction processes taking place in the furnace bath.

The temperature of high-carbon ferrochrome melting depends on chrome content and varies with in the range of 1 510 – 1 540°C. As the smelting was carried out at the temperature over 1 600 °C, the liquid high-carbon ferrochrome, together with metallic iron, served as a dissolving agent for silicon and aluminum being

Table 2 **Chemical composition of aluminum-silicon-chrome obtained by non-slagging method**

Tap-ping No.	Components content by mass / %						Metal weight / kg
	Si	Al	Cr	Fe	C	P	
10	52,3	20,44	4,33	10,63	0,54	0,037	10,7
11	49,91	22,99	15,14	10,13	0,61	0,034	9,1
12	51,1	21,48	19,9	9,38	0,42	0,039	12
13	54,71	6,14	11,25	16,88	0,85	0,032	8,3
14	56,06	10,75	11,93	17,12	0,81	0,029	11,8
15	59,56	10,84	11,39	16,74	0,82	0,022	12,2
16	53,4	10,47	15,71	13,25	0,54	0,037	10,6
17	60,51	11,98	11,93	16,03	1,04	0,031	10,7
18	60,37	10,9	12,3	17,54	0,63	0,022	9,5
19	59,64	10,38	12,8	17,83	0,72	0,03	10,3
20	50,43	14,34	15,29	14,29	0,35	0,026	8,5
21	55,49	12,76	13,84	16,4	0,72	0,032	6,7
22	51,09	12,68	18,8	16,27	0,65	0,025	11,4
23	47,69	15,32	20,59	16,16	0,59	0,031	12,6
24	50,48	15,21	21,33	15,09	0,75	0,028	11,0
25	42,51	13,38	25,7	13,12	0,65	0,039	12,4
26	45,03	12,1	25,7	13,12	0,6	0,043	8,7
27	46,09	12,59	24,3	12,5	0,43	0,045	10,6
28	49,41	11,79	25,5	11,25	0,4	0,046	10,0
29	47,82	12,51	23,8	11,25	0,52	0,049	8,5
30	47,95	14,92	28,95	11,25	0,56	0,05	9,6
31	41,97	15,08	23,35	13,12	0,71	0,069	12,2
32	49,81	12,47	27,09	10,0	0,82	0,067	12,0
33	45,43	13,22	25,7	10,0	0,83	0,054	14,8
34	46,22	14,73	23,35	10,0	0,8	0,063	14,0
35	50,74	16,51	16,35	13,12	0,52	0,07	16,0

recovered during the process. It resulted in the formation of such chrome silicides as: Cr_3Si, Cr_5Si_3, CrSi, $CrSi_2$, which in turn dissolve the formed aluminum carbide with formation of complex multi component alloy.

This mechanism of silicon and aluminum reduction in the presence of iron-chrome-carbon metallic melt has significantly increased the furnace capacity due to higher extraction of silicon and aluminum and reduced losses withoff-gas.

The obtained FASCh alloy containing (Si + Al) 60 – 65 %, chrome 20 – 25 %, phosphorus 0,03 – 0,04 % was stored for a long time without any signs of disintegration.

Thus, the results of technology tests show the possibility of obtaining a complex aluminum-silicon-chrome alloy by a single-stage method. Decomposition of metal after cooling is completely prevented.

The process of the FASCh smelting differs from ferrochrome-silicon process by complete substitution of coke for high-ash coal.

CONCLUSIONS

- The experiments carried out in the pilot submerged arc furnace showed the possibility of obtaining a FASCh alloy by the continuous slag-free process using high-ash Borly coals and high-carbon ferrochrome fines.
- The obtained metal does not disintegrate into powder when stored. This is ensured by the low phosphorus content and the increased aluminum content within the range from 11 to 16 %.
- Utilization of off-grade high-ash coals ensureslow production cost due to complete removal of coke from the production scheme.

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