RECOVERY OF LOW-CARBON FERROCHROME WITH MULTI-COMPONENT ALUMINUM-SILICON-CHROME (AI - Si - Cr) ALLOY

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The paper describes pilot smelting of low-carbon ferrochrome (LCFC) with new type of reductant – multi-component aluminum-silicon-chrome alloy (FASCh). Provisional calculations confirmed by results of pilot smelting show that use of FASCh alloy helps to stabilize LCFC slag and prevent its decomposition. Due to high Al content in FASCh the phase area of slag shifts from dicalcium silicate (larnite- Ca_2SiO_4) area into the helenite area (2 CaO · Al_2O_3 · SiO_2).

Key words: low-carbon ferrochrome, chemical composition, aluminum-silicon-chrome, reductant, recovery.

INTRODUCTION

Multi-component FASCh alloy is used for deoxidation and doping of steel and for recovery of LCFC. An notable factor of chrome alloys smelting with FASCh is radical alteration of slag composition leading to stabilization of otherwise decomposing slag, which is of great importance for environment protection [1-3].

Production and application of FASCh alloy is a complex technical and scientific task that involves development of efficient smelting techniques and selection of rational alloy composition. Theoretical base for FASCh production is developed using regularities of state diagram of Fe-Al-Si-Cr-C system. The process is multivariate, as interaction of carbon with oxides of silicon, aluminum and chrome occurs via series of multiple competing reactions with a series of intermediate compounds.

Besides, it should be noted that FASCh contains pairs of Fe-Al and Cr-Al which are impossible to merge by conventional methods (e.g. by liquid mixing) [4-8].

However, these components can be mixed when FASCh is produced using high-ash coal instead of coke, using thermodynamic methods to determine optimal proportions of Fe, Al and Cr in the alloy to ensure complete assimilation of aluminum in the melt.

Research team headed by prof. Baisanov is working on investigation of melts components behavior using Bjerrum-Guggenheim osmotic coefficient. Results of our research allow to determine certain regularities of phase crystallization in multi-component system. A notable example is a novel method of smelting multi-component alloy Fe-Si-Al from high-ash coal [9]. The technology was developed using thermodynamic modelling of high-temperature processes in the system "Fe-Si-Al-Ca-C-O" with consideration of specific behavior of generalized Bjerrum-Guggenheim coefficients in the systems of Fe-Si-Al and FeO-CaO-Al₂O₃.

Also, for the oxide and metal systems of Fe, Si, Cr, Ti it was found for the first time that Bjerrum-Guggenheim osmotic coefficient can be an adequate criterion for the assessment of melt structure. Software was developed for solution and construction of Bjerrum-Guggenheim osmotic coefficient near the melting point of congruently melting compounds; for calculation of thermodynamic stability of said compounds at melting point via relation of dissociation/association degree to equilibrium constant; for calculation of Gibbs energy in heterogeneous and homogeneous reactions [10].

So, based on determined regularities of state diagrams of metal and oxide systems, we have developed efficient proportions of elements in FASCh alloy and selected suitable kinds of raw materials for FASCh smelting.

In the next stage of research plan we have carried out pilot smelting of FASCh in 200 kVA submerged-arc furnace and produced a pilot batch of metal with characteristics required for LCFC production.

After that, using differential-thermal analysis, we studied phase transformations related to LCFC smelting process. Thermodynamic-diagram analysis was applied to work out the diagram of Cr_2O_3 - CaO - MgO - Al₂O₃ - SiO₂ system phase structure, which describes composition of final LCFC slag produced with new type of reductant FASCh alloy.

The present paper contains results of pilot smelting of LCFC with new multi-component FASCh alloy used instead of traditional silicochrome reductant.

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THEORETICAL ANALYSIS

Taking into consideration certain disadvantages of conventional method of LCFC smelting, we initiated the research aimed at substitution of traditionally used silicochrome for new FASCh alloy. Sufficient amount of Al and Si in FASCh alloy makes it suitable for LCFC recovery. Presence of chemical compounds and solid solutions of Fe, Si and Al in FASCh alloy is supposed to reduce loss of silicon and aluminum due to interaction with oxygen. Compared to traditional method, the new technology of LCFC smelting has such benefits as:

- higher Cr extraction;
- optimal slag basicity resulting in lower lime consumption and lower slag yield;
- stabilization of final slag to prevent its decomposition after cooling.

EXPERIMENTAL

Based on theoretical research and charge composition calculations, the preparations for pilot smelting of LCFC in 300 kVA furnace were made using the following raw materials: chrome ore of Donskoi GOK as basic Cr source, roasted limestone as flux and FASCh alloy as reductant. Said materials have the following composition / wt. %: Chrome ore:

 $Cr_2O_3 - 47,03$; $SiO_2 - 6,44$; CaO - 1,5; MgO - 18,4; $Al_2O_3 - 7,85$; FeO - 10,42; $Fe_2O_3 - 2,4$; S - 0,024; P - 0,02 and loss on ignition - 3,44. FASCh alloy:

- Cr - 20,59; Si - 51,69; Al - 15,62; Ca + Mg - 0,5; C - 0,48; P - 0,037; Fe - the rest;

- Cr - 18,63; Si - 47,95; Al - 20,04; Ca + Mg - 0,6; C - 0,56; P - 0,022; Fe - the rest.

Limestone:

CaO - 83,5; SiO₂ - 0,23; MgO - 0,01; Al₂O₃ - 0,01; FeO - 0,01; Fe₂O₃ - 0,01; S - 0,02; P - 0,04 and loss on ignition - 14,76.

Smelting was carried out in 300 kVA single-phase submerged-arc furnace with two 200 mm graphite electrodes. Basic electric and technical parameters are shown in the Table 1.

The transformer is powered with 380 V line. Temperature of arc is around 2 500 - 4 500 °C. Furnace lining is made of magnesite bricks with lining thickness

Table 1 Technical parameters of 300 kVA furna
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Rated power / kVA	300
Transformer:	380
Primary voltage / V	
Secondary voltage range / V	18,0 - 50,0
Electrode diameter / mm	200
Hearth length / mm	1 250
Hearth width / mm	850
Hearth depth / mm	500
Shell length / mm	1 850
Shell width / mm	1 450
Shell depth / mm	1 000

300 mm. Electrodes are located asymmetrically in a rectangular hearth with distance to back wall 400 mm and 250 mm to taphole wall. Furnace bottom is made of hearth paste carbonized under current for 8-12 hours. Bottom thickness is 200 mm. The transformer has 6 voltage taps: 18, 24, 32, 38, 44 and 50 V.

RESULTS AND DISCUSSION

Pilot campaign consisted of two stages. Taps No. 1-18 were made with FASCh containing 18 % Al, further taps were made with 20 % Al.

Initial current load was reached using small portions of FASCh placed under the electrodes. After current stabilization followed the first batch of charge containing 30 kg of chrome ore, 9,3 kg FASCh and 19,4 kg lime. Charge consumption per tapping was 1,5-2 such portions. As the transformer power and hearth temperature increased, the charge consumption reached 2,5 batches per tapping.

The tapping process is shown in the Figure 1.

In the course of smelting the charge consumption was corrected and optimized and the power was increased by switching to higher secondary voltage. Slag from tapping No. 16 was decomposing, which indicated formation of dicalcium silicate. To stabilize the slag composition 1,5 kg of FASCh was added into the next charge batch, while lime amount was reduced by 1,3 kg. After this correction we had lump slag, without signs of decomposition.

Intertapping intervals were maintained at 2 hours. Right before tapping the transformer was switched off, metal and slag was tapped into cast iron moulds.

Tappings were mostly active with high slag fluidity. However, in a number of tappings the slag was slightly viscous, which complicated the tapping process.

Overall smelting process was stable, with deep immersion of electrodes. Presence of FASCh intensified recovery processes in the furnace. Current fluctuations occurred only in the final periods of smelting, directly before tapping, which was caused by metal accumulated in the hearth. Reaction zone had visible high temperature.

Total 29 tappings were made in this smelting campaign, four of which were not counted being intermedi-



Figure 1 300 kVA furnace directly after tapping



Figure 2 Slag and metal after tapping

ate between the two smelting stages. Thus, only 25 tappings were counted for smelting results analysis.

The resulting metal corresponds to medium-carbon ferrochrome according the State Standard GOST 4757-91 and ISO Standard 5448-81. Despite the relatively high carbon level in the FASCh alloy (0,52 %), the content of carbon in final metal did not exceed 0,21 - 0,29 %.

As follows from the Figure 2, the slag and metal were easily separated after tapping.

Unlike earlier smelting campaign, the slag from this pilot smelting had low levels of chrome oxide. Earlier smelting was made with chrome-magnesite lining, which caused transition of chrome oxides into the slag and skewed the campaign results. To eliminate the lining influence, in the present campaign we used magnesite brick for lining.

Visual analysis showed high metal density without gas pockets, typical for LCFC produced by traditional methods. Slag was lumpy, dark-grey and showed no signs of decomposition after several months of storage in the normal environment.

Pictures of metal and slag are represented in the Figure 3.

The following charge compositions were used in the pilot smelting depending on Al level in used FASCh (15 % / 20 %):

- chrome ore – 52,1 % / 51,8 %;

- lime (CaO ~ 83 %) – 32,2 % / 31,8 %.

Total 1 665 kg of chrome ore, 511 kg FASCh and 1 025 kg lime were consumed in the pilot smelting. 771,6 kg of standard medium-carbon ferrochrome and 1 842,2 kg of slag were obtained in the campaign.

Metal and slag had the following composition / wt. %: Cr 66,8 - 69,1; C 0,21 - 0,29, Si 2,1 - 2,58 (metal); Cr₂O₃ 4,13 - 7,94; SiO₂ 20,37 - 26,41; Al₂O₃ 18,24 -21,97; CaO 27,87 - 35,8; MgO 11,95 - 18,26 (slag). Average content of Cr₂O₃ in the slag was 6,3 %.

Slag/metal ratio was 1,9-2,36 with slag basicity range 1,26-1,61. Average slag basicity was 1,4, while CaO + MgO / SiO, ratio was 1,99.

CONCLUSIONS

Described pilot smelting confirmed the possibility of LCFC smelting with FASCh alloy. Optimal technological parameters were clarified in the course of pilot



Figure 3 Metal and slag after cooling: a - metal; b - slag

smelting. Application of FASCh alloy prevented the slag decomposition due to transition of slag composition from larnite area into helenite area.

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