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Influence of additives on properties of high-carbon ferrochrome slag

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Abstract. Industrial slags produced by high-carbon ferrochrome are a material of complex composition consisting of an oxide part (Cr_2O_3, CaO, MgO, FeO, SiO_2, Al_2O_3) and "entangled" metal prills (Cr_{met}). In order to increase the degree of chromium utilization and reduce losses in the form of metal prills, we conducted the laboratory experiments to study changes in properties of the slag produced by high-carbon ferrochrome through the use of effective and affordable fluxing materials: expanded clay, calcium borate and refined ferrochrome slag. The effect of fluxing additives in the form of expanded clay, calcium borate and slag from the production of low-carbon ferrochrome on the properties of high-carbon ferrochrome slag was studied. Addition of up to 8 % of expanded clay and low-carbon ferrochrome slag leads to a stable decrease in the softening temperatures of the final slags. The greatest intensity of decrease in the softening temperature is observed when calcium borate is injected in an amount of 6 – 10 %. The greatest effect on reducing softening temperatures is exerted by the addition of 10 % calcium borate when introducing high-carbon ferrochrome into the slag, while the temperature of softening beginning decreases by 262 °C, and the temperature of softening end – by 135 °C. All the studied fluxing additives have a positive effect on reduction degree of the residual concentration of metallic chromium in the slag. The most intense decrease in the content of Cr_{met} in the slag is observed with the introduction of 2 % of fluxing materials. The best values for the residual content of 0.7 – 0.8 % Cr_{met} were achieved using 4 % of low-carbon ferrochrome slag and calcium borate. When using expanded clay, an additive in the amount of 10 % is required to achieve such indicators of Cr_{met}. In general, the effectiveness of using the studied fluxing materials to increase the degree of chromium extraction in the production of high-carbon ferrochrome is shown, its content in the slag is reduced by 84 %.

Keywords: metallurgy, ferrochrome, slag, metal prills, fluxing materials, expanded clay, calcium borate

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Изучение влияния флюсующих добавок на свойства шлака высокоуглеродистого феррохрома

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Аннотация. Промышленные шлаки высокоуглеродистого феррохрома имеют сложный состав. Они состоят из оксидной части (Cr_2O_3, CaO, MgO, FeO, SiO_2, Al_2O_3), а также «запутавшихся» металлических корольков ($Cr_{мет}$). С целью увеличения степени полезного использования хрома и снижения потерь в виде металлических корольков проведены эксперименты в лабораторных условиях по изучению изменения свойств шлака высокоуглеродистого феррохрома путем применения эффективных и доступных флюсующих материалов (керамзита, бората кальция и шлака рафинированного феррохрома). Изучено влияние флюсующих добавок в виде керамзита, бората кальция и шлака от производства низкоуглеродистого феррохрома на свойства шлака высокоуглеродистого феррохрома. Присадки до 8 % керамзита и шлака низкоуглеродистого феррохрома приводят к стабильному снижению температур размягчения конечных шлаков. При вводе 6 – 10 % бората кальция происходит интенсивное снижение температур начала размягчения. Наибольшее влияние на снижение температур размягчения оказывает добавка 10 % бората кальция при вводе в шлак высокоуглеродистого феррохрома, при этом наблюдается снижение температуры начала размягчения на 262 °C, конца размягчения – на 135 °C. Все исследованные флюсующие добавки оказывают положительное влияние на степень снижения остаточной концентрации металлического хрома в шлаке. При вводе 2 % флюсующих материалов наблюдается наиболее интенсивное снижение содержания $Cr_{мет}$ в шлаке. Наилучшие значения по остаточному содержанию 0,7 – 0,8 % $Cr_{мет}$ достигнуты при использовании 4 % шлака низкоуглеродистого феррохрома и бората кальция. При использовании керамзита для достижения таких показателей $Cr_{мет}$ необходима добавка в количестве 10 %. Показана эффективность использования исследованных флюсующих материалов при производстве высокоуглеродистого феррохрома для повышения степени извлечения хрома, содержание которого в шлаке снижается примерно на 84 %.

Ключевые слова: металлургия, феррохром, шлак, корольки металла, флюсующие материалы, керамзит, борат кальция

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Introduction

The operational characteristics of slag in the production of high-carbon ferrochrome depend on the nature of chrome ores, the content of main components (iron and chrome oxides), and slag-forming agents (SiO_2, MgO, and Al_2O_3). Therefore, the phase diagram of the SiO_2–MgO–Al_2O_3 system (Fig. 1) serves as the physicochemical basis for determining the optimal slag compositions [1 – 3].

The selected slag composition should ensure the overheating of high-carbon ferrochrome (HCFC) and create conditions for successful “droplet” (movement of metal droplets through the ore layer) and “bottom” (at the metal-slag interface) refining of carbon and silicon. The slag should have low viscosity and be sufficiently mobile for the precipitation of metal droplets (especially in the ladle during tapping from the furnace), easily separate from the metal ingot, and possess optimum electrical resistance to facilitate deep insertion of electrodes into the charge and obtain standard metal in terms of sulfur and phosphorus content.

The temperature regime of the metal and slag during the smelting of high-carbon ferrochrome is primarily determined by the softening temperatures of the oxide material (SiO_2 concentration and MgO/Al_2O_3 ratio) as well as the ratio between chromium and carbon content in the alloy. The melting temperatures of the selected slag composition should be higher than the melting temperature of the metal by 100 – 150 °C since the heating of the metal during the smelting of high-carbon ferrochrome occurs through the slag, and the furnace operates in resistance mode. The slag obtained from processing chrome ores of the Kempirsaiskoe deposit has a high melting temperature and viscosity, which makes it difficult to remove from the furnace and contributes to excessive overheating of the metal. To lower the melting temperature and viscosity of the slag, silicon-containing

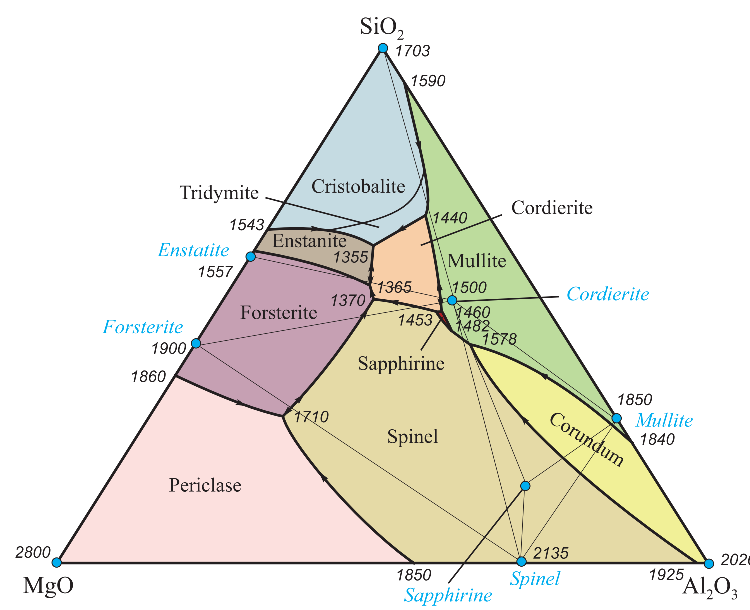

Fig. 1. State diagram of the SiO_2–MgO–Al_2O_3 ternary system [1]

Рис. 1. Диаграмма состояния тройной системы SiO_2–MgO–Al_2O_3 [1]

fluxing materials such as quartzite screenings or high-ash reducers are added to the charge.

Over the years of operation, as mining activities extended into deeper layers, ores from lower horizons began to be extracted. These ores had undergone less exposure to weathering processes, significantly impacting the composition of the host rock. There was an increase in magnesium oxide content and a decrease in aluminum oxide content. Consequently, the composition of chromite ores obtained by ferroalloy plants in recent years has undergone significant changes. The composition of the slag is determined by the composition of the chromite ores, thus their compositions have also shifted towards increased magnesium oxide content (from 28 – 32 % to 45 – 48 %) and decreased aluminum oxide content (from 28 – 29 % to 14 – 15 %), while the silicon dioxide content (SiO_2) has remained at the level of 29 – 34 %. This is evidenced by the dynamics of changes in the composition of the final slag of high-carbon ferrochrome, which indicates that the $MgO/A1_2O_3$ ratio has increased from 1.8 to 3.0 and higher over the past decades [4 – 6].

According to the chemical composition, significant changes have also occurred in the phase composition of the slag of high-carbon ferrochrome, which has shifted from the magnesioaluminate spinel field ($MgO·Al_2O_3$) to the forsterite field ($2MgO·SiO_2$). The proportion of the latter in the slag has increased from 35 to 70 % since the commissioning of the Kempirsaiskoe mine. The increase in magnesium content in the slag mainly occurred due to the supply of poorer chromite ores and the exploitation of new deposits with increased magnesium content.

Therefore, further growth in the production volume of chromium-containing ferroalloys necessitates the extensive utilization of the most common high-magnesia chromite ores with a magnesium oxide content of 18 – 22 % and an aluminum oxide concentration of 7 – 9 %.

Increasing the magnesium concentration in the slag leads to increased chromium losses. A significant amount of chromium is lost in the form of a metallic phase, which is associated with the deterioration of the physicochemical properties of the formed high-magnesia slags.

Materials and methods

In [7 – 9], it is demonstrated that the introduction of various fluxing and carbon-containing materials into the charge of high-carbon ferrochrome contributes to reducing the high melting point of the resulting oxide materials, thereby allowing for a reduction in chrome losses with the slag in the form of entangled metal droplets [10 – 12].

Laboratory experiments were conducted to reduce the softening temperatures of slags during the smelting of high-carbon ferrochrome by adding various fluxing materials for the deposition and coagulation of entangled metal droplets. Calcium borate [13 – 15], expanded clay, and stabilized low-carbon (refined) ferrochrome (RFC) slag were used as fluxing materials. Due to the different fractional compositions of the materials used, all samples were crushed and fractionated to obtain materials with a size of 1 – 3 mm. The chemical compositions of the considered fluxing materials and the initial HCFC slag are presented in the Table.

Experimental melts were carried out in a high-temperature resistance furnace according to Tamman. The technical characteristics of the furnace were as follows: power consumption – 40 kW; network voltage – 380 V; maximum voltage on the furnace buses – 15 V; maximum allowable temperature – 1800 °C; heating time to the maximum temperature – 30 min.

The weight of the initial HCFC slag for each experiment was 300 g. Fluxing additives were added in amounts of 2 – 10 % of the mass of the initial slag with a step of 2 %. At least two melts were carried out for each charging variant. The initial temperature (T_{ini}) and end temperature (T_{end}) of softening were determined in accordance with State standard GOST 26517-85. The pre-dosed mixture of slag and flux was poured into a crucible, then placed in the furnace and heated at a rate of 10 – 15 °C/min. Temperature measurements were made using a VR 5/20 tungsten-rhenium thermocouple.

Results and discussion

The introduction of fluxing additives has a multifaceted effect on the chemical composition and basicity of the processed slags [16 – 18]. According to the chemi-

Chemical compositions of the fluxing materials

Химические составы флюсующих материалов

Material	Content of elements, wt. %							
	Cr_{met}	Cr_2O_3	CaO	MgO	Al_2O_3	FeO	SiO_2	B_2O_3
Expanded clay	–	0.10	3.01	2.59	15.27	7.38	62.30	–
Calcium borate	–	–	37.20	0.50	0.05	–	–	43.80
RFC slag	1.3	8.60	46.80	12.80	5.80	1.90	22.90	0.30
HCFC slag	4.9	9.40	1.70	42.00	16.80	2.30	26.00	–

cal analysis data of the final slags, the introduction of expanded clay up to 10 % with a basicity of 0.09 leads to an increase in the concentration of SiO_2 oxide from 26.0 to 32.1 %, accompanied by a decrease in the basicity of the final slag by 0.28.

Adding high-basicity RFC slag up to 10 % leads to an increase in the basicity of the final slag by 0.12. The slag contains a minor concentration of B_2O_3 oxide at 0.01 %. It is necessary to note the additional positive impact of the addition of RFC slag, as waste from their own production is used and an additional 0.13 % of Cr metal is introduced. However, the high melting temperature of RFC slag when considering the option of introducing fluxing materials into the ladle requires a thermal balance calculation to determine the allowable amount of additives. In the case of adding fluxing materials directly into the furnace, one must consider the increase in the basicity of the final slag, which can affect both the lining of the furnace and the technological process of smelting high-carbon ferrochrome [19 – 21].

Adding calcium borate leads to an increase of up to 5 % CaO and 2.6 % B_2O_3 in the final slag. Considering that the B_2O_3 oxide belongs to "acidic" materials, it can be said that the basicity of the slag changes insignificantly (increases by 0.02).

When selecting flux materials, their cost should be considered. It is promising to utilize waste from our own production (RFC slag).

The results of temperature measurement at the beginning of softening are presented in Fig. 2, *a*, and at the end of softening in Fig. 2, *b*.

For all tested samples, an increase of up to 8 % of flux additives from the mass of HCFC slag leads to a decrease in the temperature at the beginning of softening. Increasing the flux addition to 10 % has a contradictory effect on the values of T_{ini} (Fig. 2, *a*): it increases for expanded clay and RFC slag, but decreases sharply for calcium borate.

When adding up to 8 % of RFC slag, there is a gradual decrease in the temperatures at the beginning of softening (by 35 °C). Further increasing the RFC addition leads to a sharp increase in the value of T_{ini}. When introducing 10 % of RFC slag, the temperature at the beginning of softening exceeds the value of T_{ini} for the original HCFC slag.

For comparison, the high-carbon ferrochrome slag was melted without flux additives. Up to a temperature of 1650 °C, no changes in the state of the slag were observed, starting from 1660 °C, the slag enters a pasty state. At a temperature of 1677 °C, the slag becomes a dense viscous mass, and at 1705 °C, the slag completely melts. The slag is less fluid than when processed with fluxes.

When using calcium borate in an amount of up to 10 % of the slag mass, the temperatures at the beginning and end of slag softening decrease by 265 and 135 °C. In the case of expanded clay, these indicators are 39 and 80 °C. With additions of up to 10 % of stabilized RFC slag, the slag softening temperature increases by 2 °C above the softening temperature of the original HCFC slag.

Fig. 3 presents data on the residual content of metallic chromium in the slag after processing with fluxes.

The best results for precipitating chrome spinels were achieved with a consumption of 4 % calcium borate from the slag mass. The content of metallic Cr in the slag decreased by 83.7 %. For slags treated with expanded

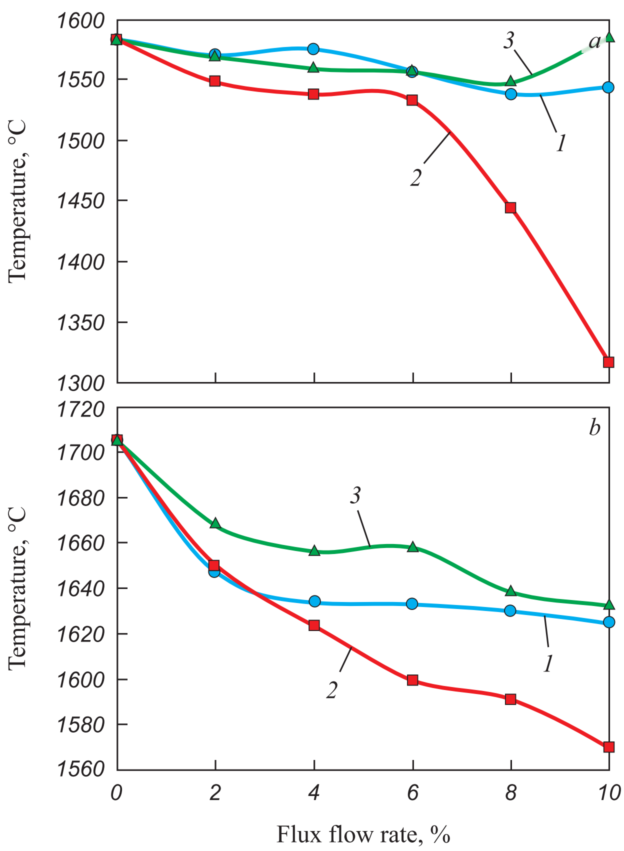

Fig. 2. Dependence of the temperature of beginning (*a*) and end (*b*) of slag softening on the flux flow rate:
1 – expanded clay; *2* – calcium borate; *3* – refined ferrochrome slag

Рис. 2. Зависимость температуры начала (*a*) и конца (*b*) размягчения шлака от расхода флюса:
1 – керамзит; *2* – борат кальция; *3* – шлак РФХ

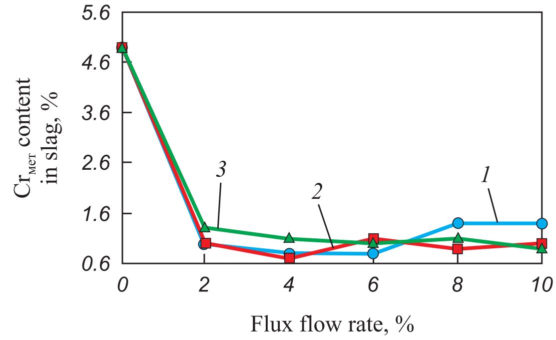

Fig. 3. Dependence of Cr_{met} content in the slag on the flux flow rate:
1 – calcium borate; *2* – refined ferrochrome slag; *3* – expanded clay

Рис. 3. Зависимость содержания $Cr_{мет}$ в шлаке от расхода флюса:
1 – борат кальция; *2* – шлак РФХ; *3* – керамзит

clay, this value is 81.7 % at a consumption rate of 10 % of the slag mass. In slags treated with stabilized RFC slag in an amount of 4 % of the slag mass, the content of Cr_{met} decreased by 85.7 %.

Significant reduction in the content of metallic chromium in the slag is observed when introducing 2 – 4 % of the tested flux materials.

Based on the reduction in the content of metallic Cr in the slag, it can be concluded that it is preferable to use expanded clay and RFC slag stabilized with boron. In industrial conditions, it is necessary to take into account the cost of each type of fluxing additives.

Conclusions

The influence of fluxing additives such as expanded clay, calcium borate, and slag from RFC production on the properties of high-carbon ferrochrome slag has been studied. It has been shown that the addition of up to 8 % expanded clay and low-carbon ferrochrome slag leads to a stable decrease in the softening temperatures of final slags. The most significant reduction in softening temperature onset is observed with the introduction of 6 – 10 % calcium borate. The greatest impact on reducing softening temperatures is achieved with the addition of calcium borate; with the addition of 10 % calcium borate to HCFC slag, the start of softening temperature is reduced by 262 °C, and the end of softening by 135 °C.

All studied fluxing additives have a positive influence on the degree of reduction in the residual concentration of metallic chromium in the slag. The most intense reduction in Cr_{met} content in the slag is observed with the addition of 2 % fluxing materials. The best values for residual content of 0.7 – 0.8 % Cr_{met} are achieved when using 4 % RFC slag and calcium borate. When using expanded clay to achieve such chromium content levels, an addition of 10 % is required.

The efficiency of using the studied fluxing materials to increase the extraction of chromium during the production of high-carbon ferrochrome is demonstrated, with the residual content in the slag reduced by approximately 84 %.

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Ye. K. Samuratov – studing the residual chromium content in slags after laboratory experiments.

D. A. Yessengaliyev – formation of research goals and objectives, writing the text.

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