

TECHNICAL PAPER

STUDY OF THE EFFECT OF FLUXING MATERIALS ON THE DEPOSITION OF METAL BEADS FROM HIGH-CARBON FERROCHROME SLAG

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ABSTRACT

The study of the effect of the properties of high-carbon ferrochrome slags on the creation of favorable conditions for the deposition of metal beads with the introduction of the following fluxing additives in an amount of 3-10%: slag produced by refined ferrochrome (stale and stabilized), cryolite, fluorite, feldspar, colemanite, fused borate ore, aluminum slag of aluminum production. The influence of the type and quantity of fluxing materials on the viscosity and crystallization temperature of high-carbon ferrochrome slags has been studied. It is noted that using all types of fluxing materials under study decreases the crystallization temperatures of the processed slag. It can be seen from the results of metallographic and phase analyses that the best values for the degree of coagulation and deposition of metal crowns were achieved with the introduction of aluminum slag, colemanite and borate ore.

Keywords: high-carbon ferrochrome slag, refined ferrochrome slag, colemanite, cryolite, alumina slag, viscosity, crystallization temperature of slags.

INTRODUCTION

The involvement of high-magnesium refractory chromite ores in the production has led to a number of problems not only at the stage of their preparation for smelting but also at the stage of metallurgical processing [1-3]. There is a change in the composition of high-carbon ferrochrome slag towards an increase in MgO to 45-48%. The MgO/Al₂O₃ ratio increases to 3,0, which leads to an increase in melting point and viscosity and a decrease in the temperature range of slag fluidity. Thus, when smelting ores with a content of 50-52% Cr₂O₃, the ratio of MgO/Al₂O₃ in the primary slag reaches 2.4-2.7 with a melting point of more than 2000 °C.

In practice, the slag melting mode of high-carbon ferrochrome is regulated by the addition of silicon-containing fluxes, transferring the composition of the final slags to the region of triple eutectic periclase (MgO) - forsterite (2MgO·SiO₂) - spinel (MgO·Al₂O₃) with a melting point of 1710 °C. The melting point (release) of the final slag is 1590-1650 (1730-1750) °C, that is, it meets one of the basic requirements for the properties of the slag. However, such slags have high melting temperatures and a narrow range of liquid-mobile states, which is the main cause of metal losses with slag [4-6]. At the same time, a significant amount of chromium is lost in the form of beads. The available individual data on the selection and use of new fluxes in and outside the furnace have not been widely used. Therefore, the search for new effective fluxing additives to improve the technical and economic indicators of processing refractory chromite ores in modern conditions is becoming very relevant [7-10].

MATERIAL AND METHODS

The slag produced by the high-carbon ferrochrome of the Aktobe Ferroalloy Plant was taken as the starting material for research. Its chemical composition (%) is as follows: Cr₂O₃ – 7,34; Crmet—4,09; Al₂O₃ – 13,92; FeO—1,22; MgO—44,56; CaO—1,17; SiO₂ – 27,7.

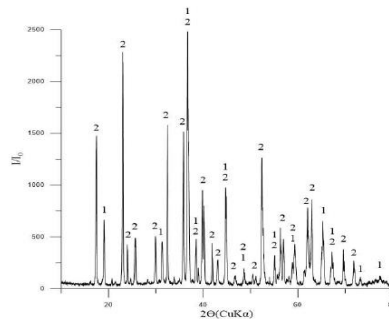


Fig. 1 Diffractogram of high carbon ferrochrome slag

X-ray diffraction analysis was used to study the phase composition of a high-carbon ferrochrome slag sample. The samples were photographed using an XRD 7000 X-ray diffractometer (SHIMADZU company) with automatic software control, using CuKα radiation and a graphite monochromator. Fig. 1 shows the result of a diffractogram of high-carbon ferrochrome slag.

The properties of the initial slag of high-carbon ferrochrome is determined by the high-temperature phases of forsterite $2\text{MgO}\cdot\text{SiO}_2$ (TCR—1900 °C) dominating in them and magnesia spinel $\text{MgO}\cdot\text{Al}_2\text{O}_3$ (TCR—2135 °C), the sum of which is more than 80%. These phases, having high melting points, have a simple anionic structure, which determines high crystallization temperatures and low viscosity values of the melts.

Laboratory experiments were conducted to study the effect of various fluxing additives on the viscosity and crystallization temperature of high-carbon ferrochrome industrial slag and to assess the effect of these physico-chemical characteristics on metal losses with slag. Experimental viscosity studies were conducted on an electrovibration viscometer in a molybdenum crucible with a molybdenum spindle. Its calibration was carried out using a «heavy liquid» specially prepared based on a solution of «Clerici» having an initial density of 4.2-4.5 g/cm³. To achieve a density of 2.7-2.8 g/cm³ (close to the density of slags),

glucose was dissolved at 3530 K. The viscosity of the resulting liquid varies with temperature changes from hundredths to 10 Pa · s or more. The stability of the installation was periodically checked using synthetic slags of known composition. All experiments were carried out in an atmosphere of purified argon, which minimized the oxidation of molybdenum.

The temperature in the furnace's working space was fixed with a tungsten-rhenium thermocouple tungsten rhenium-5/20, the end of which, reinforced with an aluminum cover, was brought to the bottom of the crucible in a special recess.

The viscosity was determined by continuously cooling the melt at 3-5 degrees per minute. The slag weight was 20 grams, the inner diameter of the crucible was 20 mm, the diameter of the spindle was 2.0 mm, and the depth of its immersion in the melt was 10 ± 0.5 mm. Readings were taken after 10-15° and near the crystallization temperature—3-5°.

The chemical composition of the materials is shown in Table 1.

Table 1 Chemical composition of the starting materials, %

Material	Cr ₂ O ₃	Cr _{met}	MgO	CaO	SiO ₂	Al ₂ O ₃	B ₂ O ₃
High carbon ferrochrome slag	7,3	4,2	45,8	-	26,8	14,3	-
Stabilized slag of refined ferro-chrome	6,9	1,5	16,7	43,0	23,6	6,3	0,4
Colemanite	-	-	2,21	25,5	6,22	1,48	35,9
Cryolite	F	Na	Fe ₂ O ₃	CaO	SiO ₂	Al	-
	53,22	29,8	0,03	0,03	0,24	14,01	-
Aluminum slag	F	Na ₂ O	Fe ₂ O ₃	-	SiO ₂	Al _{gen.}	Al _{met}
	0,17	2,59	0,58	-	0,64	57,9	17,8

The number of fluxing additives in all experiments was 3, 6, and 10%. The minimum number of fluxes was determined in advance according to their effect on the properties of the slag, and their number was proportionally increased to obtain comparative data.

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RESULTS AND DISCUSSION

Subtitle of results and discussion

The method of semi-logarithmic processing of viscosity polytheism was used to determine the crystallization temperature of slags. The crystallization temperature with one or another fracture on the $\lg\eta - 1/T$ line was identified by sequential comparison, with a similar dependence for neighbouring slags. The research results are presented in Figs. 2-5 and Table 2.

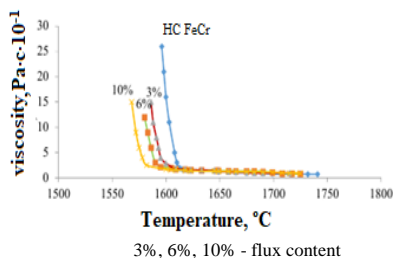


Fig. 2 Temperature dependence of the viscosity of high-carbon ferrochrome slag with the addition of slag stabilized slag refined ferrochrome

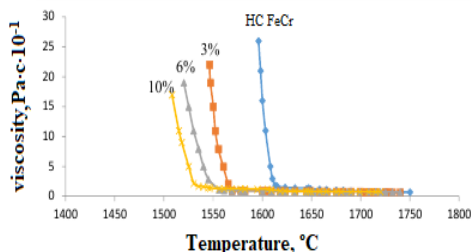


Fig. 3 Temperature dependence of the viscosity of high-carbon ferrochrome slag with the addition of colemanite

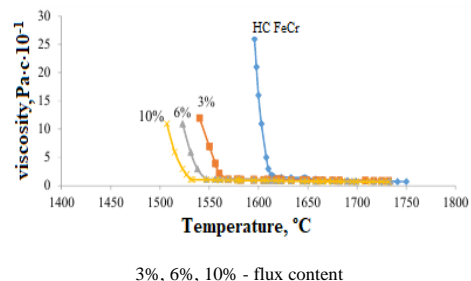


Fig. 4 Temperature dependence of the viscosity of high-carbon ferrochrome slag with the addition of cryolite

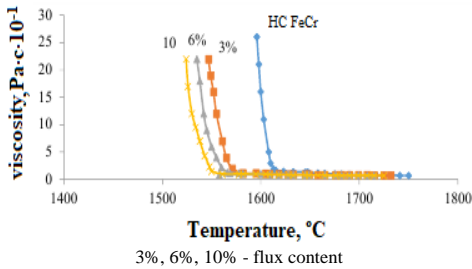


Fig. 5 Temperature dependence of the viscosity of high-carbon ferrochrome slag with the addition of aluminum slag

Table 2 Crystallization temperature and activation energy of the viscous flow of high-carbon ferrochrome slag (HC FeCr) with the addition of various fluxing materials

Slag	Equations	$t_{cr}^{\circ}, ^{\circ}C$	$E_a, kJ/mol$
<i>Flux-1. Stabilized slag of refined ferrochrome</i>			
HC FeCr	$\ln \eta_b = 538\ 230/T - 284,63$ $\ln \eta_b = 255651/T - 13,119$	1615	4474 213
3%	$\ln \eta_b = 425\ 360/T - 226,16$ $\ln \eta_b = 31533/T - 16,081$	1600	3536 262
6%	$\ln \eta_b = 481\ 720/T - 257,41$ $\ln \eta_b = 26880/T - 13,613$	1590	4005 223
10%	$\ln \eta_b = 440\ 880/T - 236,78$ $\ln \eta_b = 26880/T - 13,613$	1582	3665 223
<i>Flux-2. Colemanite</i>			
HC FeCr	$\ln \eta_b = 538\ 230/T - 284,63$ $\ln \eta_b = 255651/T - 13,119$	1615	4474 213
3%	$\ln \eta_b = 390\ 630/T - 211,63$ $\ln \eta_b = 6987/T - 3,78$	1565	3247 58
6%	$\ln \eta_b = 243\ 850/T - 132,93$ $\ln \eta_b = 6652/T - 3,65$	1545	2027 55
10%	$\ln \eta_b = 298\ 470/T - 159,55$ $\ln \eta_b = 6580/T - 3,59$	1530	2406 54
<i>Flux-3. Cryolite</i>			
HC FeCr	$\ln \eta_b = 538\ 230/T - 284,63$ $\ln \eta_b = 255651/T - 13,119$	1615	4474 213
3%	$\ln \eta_b = 271\ 360/T - 147,08$ $\ln \eta_b = 9529/T - 5,14$	1560	2256 79
6%	$\ln \eta_b = 280\ 820/T - 153,93$ $\ln \eta_b = 9987/T - 5,14$	1547	2334 83
10%	$\ln \eta_b = 294\ 990/T - 163,25$ $\ln \eta_b = 10466/T - 5,624$	1527	2452 87
<i>Flux-4. Aluminum slag</i>			
HC FeCr	$\ln \eta_b = 538\ 230/T - 284,63$ $\ln \eta_b = 25651/T - 13,119$	1615	4474 213
3%	$\ln \eta_b = 302670/T - 165,74$ $\ln \eta_b = 8693/T - 4,5894$	1571	2516 72
6%	$\ln \eta_b = 305340/T - 165,74$ $\ln \eta_b = 11230/T - 5,968$	1560	2538 93
10%	$\ln \eta_b = 31407/T - 171,64$ $\ln \eta_b = 15357/T - 8,17$	1548	2611 127

CONCLUSION

Using all types of fluxing materials under study decreases the crystallization temperatures of the processed slag. The least effect is observed when using stabilized refined ferrochrome slags. Aluminum slag, which contains aluminum oxide, has a noticeable effect on reducing its viscosity and crystallization temperature. The increased content of Al₂O₃ reduces the MgO/Al₂O₃

ratio and forms fusible compounds. Together, this has a positive effect on reducing the viscosity and crystallization temperature of the base slag.

The greatest effect on the properties of the base slag is provided by the addition of cryolite. When the viscosity of slags in a homogeneous liquid state is 0.075 – 0.12 Pa·s, the crystallization temperatures of high-carbon ferrochrome slag decrease by 90 °C. However, it is necessary to consider the high activity of

fluorine and sodium, which, with almost all slag components, give dangerous volatile compounds. Therefore, their use in practice in modern conditions is very limited.

From the point of view of reducing crystallization temperatures and slag viscosity, boron-containing flux is of interest: colemanite. When colemanite is added to the base slag, low-melting boron compounds in the form of magnesium borate have a diluting effect and a decrease in viscosity. In this case, an insignificant amount of okermanite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) is also formed, which has a more complex anionic structure, contributing to a certain increase in viscosity. These slags are slightly inferior to fluorine and sodium-containing slags in terms of melting point and viscosity. However, from the literature data, it is known about the positive effect of boron on the interfacial interaction between metal and slag helps to reduce metal losses. These slags can be considered promising for solving the problem of reducing metal losses with high-carbon ferrochrome smelting slags.

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