PHYSICOCHEMICAL FEATURES OF CHROMITE ELEMENTS REDUCTION KINETICS IN FERRO-ALLOY ELECTRIC FURNACES

[1]O.V. Zayakin, [1]V.I. Zhuchkov, [2]V.I. Afanasiev, [1]A.V. Dolmatov

[1]Institute of Metallurgy, The Ural branch of the Russian Academy of Science, 101 Amundsen st., Ekaterinburg, Russian Federation, e-mail: zferro@mail.ru
[2] Joint Stock Company Serov Ferro-alloy Plant, Serov, 1 Nakhabina st., Russian Federation

ABSTRACT

The guideline of the work is the chromium reduction kinetic features investigation in circumstances of ore-reduction electric furnace on high-carbon ferrochromium production. The complex of laboratory and commercial investigation of carbothermy reduction of chromium from chromium-ore materials was made. Empirical evidence indicated that descent and heating rates of ore lamps locating in different points of horizontal section in furnace working zone may vary several-fold. The data were obtained by slag probe technique on commercial ore-reduction electric furnace in operation. The commercial study of slag probes, which were taken during output, testifies that content of incompletely reduced chromium oxides varies in probes. When we make the traditional slag probe during output, we are able only to suggest some average chromium reduction degree of exact smelting, since dissimilar slag is outputted from furnace. The outputted slag has the high chromium reduction degree (from the lower bath horizons with high temperatures and long delay time) and low reduction degree alike (the upper bath layers) simultaneously.

The new data obtained in this study offer deeper insight into the process of chromium reduction of oxides. The data give the opportunity to direct the way to the new process solutions concerning improvement of technical-economical indexes of high-carbon ferrochromium production affecting on the reduction degree of chromium-ore raw components through the change of the charge material descent rate, of the charge softening temperatures, of the slag viscosity, of the melting electric mode, of the time difference between outputs, of the selective descent of charge material in throat horizontal section, and of the selective load in relationship with melting period.

KEYWORDS: *Metallurgy, ferro-alloy production, ferrochromium, ore reduction electric furnace, reduction degree.*

INTRODUCTION

The key task of metallurgists consists in an increase of main components transfer degree into melting product. At present the degree of chromium extraction into melt varies in the range of 75-92% in dependence of different types of chromium-ore raw and aggregates on production of high-carbon ferrochromium. Further increase of chromium extraction may be met through temperature increase of the furnace working zone and dwell time prolongation of the charge materials in the furnace. The number of research works is devoted the study of the structure and temperature areas of ore-smelting furnaces which define technical-economical indexes of melting.

The first publications concerning the study of processes taking place during high-carbon ferrochromium smelting in aggregate and of commercial ore-reduction electric furnace bath structure were made by Kh.N. Kadarmetov [1] in 1950-1960-s. The excavation method was used for structure study of furnace bath. The method consists in layer-by-layer material extraction from the bath space after furnace shut down with incomplete melting. It was defined the slag and metal melts vary in composition and structure at different horizontal sections of furnace working area, and so-called ore layer was found on the boundary between metal and slag. It was supposed the ore layer provides ferrochromium refining of carbon which formed in crucibles near the electrodes. The bath has the state of melt on the depth of 500-600 mm. Later the similar investigation was conducted by other researchers. The data of Kh.N. Kadarmetov about the bath structure in furnace centre lack support both the practical work and the electric mode investigation of furnace in operation made by I.T. Zherdev [2]. The procedure of ore-reduction electric furnace bath freeze was upgraded in Japan; the procedure offered by Japanese authors [3] was to blow nitrogen through the furnace for sharp freeze and to clamp the material composition in bath at the moment of shutdown. As a result of this work it was concluded the presence of ore layer depends on the charge materials in use and on the melt technology mode. The irregularity of charge descent in the section of throat was also defined. The results of complex investigation of bath and temperature fields of closed furnace during melting (power 14 MVA) by probe technique are listed in publications of V.P. Vorobyev et al. [4-6]. The authors opinion is the major part of reduction processes take place on the depth of 1200-2000 mm. The results of bath structure investigation in the ore-reduction electric furnace of 54 MVA rated power by probe and materials excavation technique were published by Rindalen [7]. It was defined the slag located above metal and had the form of separate lenses, and the clearly defined ore layer was not revealed.

The results of latest studies concerning the bath structure of working ore-reduction electric furnace for high-carbon ferrochromium smelting are published in the period of 2003-2008 years by A.I. Pashkeev, G.G. Mikhailov et al. [8-10]. The bath of the RKO-16.5 furnace in operation was studied by probe technique, high-carbon ferrochromium is melted from the ore of Rai-is massif in this furnace.

EXPERIMENTS

From the publications review it was concluded there is no agreement among researchers and metallurgical technologists regarding furnace bath structure, presence of ore layer, and coke pillow in ore-reduction electric furnace for high-carbon ferrochromium smelting.

Different data about bath structure might be related with the following reasons.

1. The bath of furnace during operation is not static, the working area temperature varies with each output, with charge state, its geometry and volume, besides the freeze of the furnace is made in different smelting periods between outputs.

2. The furnace shutdown cannot provide an instant bath freeze and smelting processes continue for some time. The higher the furnace power, the longer freeze time and process slowdown time are. Few researchers blew nitrogen through the furnace.

3. The use of different charge materials (different chemical and granulometric compositions) implies the different results. For example, the availability of ore layer is in strong dependence of fineness and portion of lumpy part of the charge, and type of ore materials.

The investigation was provided in the first workshop of Joint Stock Company Serov Ferro-alloy Plant, to study the heating rates of charge materials in ore-reduction furnace for high-carbon ferrochromium smelting in operation. Complex interrelated processes take place in ore-reduction electric furnaces for ferro-alloy production during smelting by carbothermic continuous method. The calculation and laboratory simulation of these processes is the most challenge task. Hence the manufacture measurements made in ore-reduction furnaces in operation is of great practical significance, since they reflect real process taking place in aggregate. The information about several simultaneously measured values and their study in interrelation between each other and other indexes of the furnace have the great significance especially during the investigation work.

The bath of the furnace in operation was studied by special probes loaded with charge. These probes measures the downtake rate and charge material heat rate. The investigation results are given in figure 1.

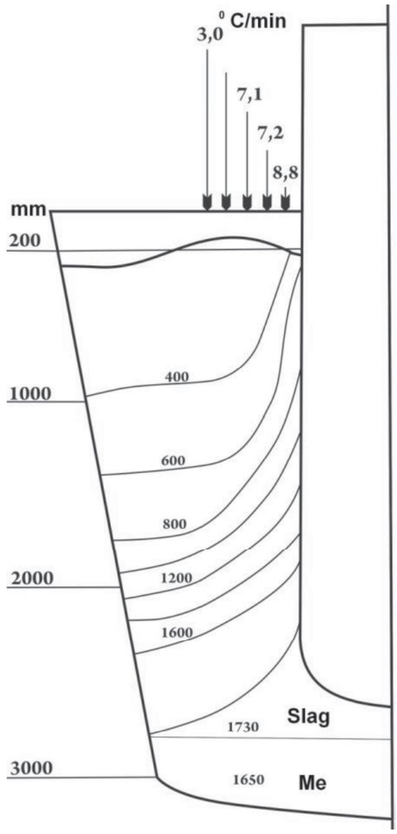

Figure 1: The temperatures in working zone of ore-reduction electric furnace and the heat rates of charge material during high-carbon ferrochromium smelting

The structure of bath temperature field of ore-reduction electric furnace depends on number of factors, namely, the interrelation between ore material and reducing agents, the heat exchange in the layer of constantly taking down charge material and up flow warm gas steam, the source charge material, and their physicochemical and heat engineering characteristics. To study the bath structure we chose electric furnace with transformer of 22 MVA rated power with the following geometric parameters: the bath diameter in bottom level is 5200 mm; the bath depth is 3000 mm; the electrode diameter is 1200 mm.

Reasoning from obtained results it is possible to assume the average value of charge descent rate is at least 2.1mm/min. The descent rate has high values in marginal zone of crucible (at 400 mm distance from electrode surface). The descent runs up to 8.1 mm/min in the nearest zone to electrodes (at 100 mm distance from electrode surface).

These values correlate well with other researchers data obtained by measurements of different alloys: calcium carbide smelting – 0.8÷1.2 mm/min, silicon – 1.5÷3.4 mm/min, silicochromium – 7.5÷27 mm/min. The average heating rate changes in the range of 3.0÷8.8^{0}C/min and it has proportional relationship with the charge descent rate. At mentioned conditions the completeness of chromium reduction is limited by the softening temperature of charge material influencing on reaction zone temperature. During high-carbon ferrochromium smelting 80-90 % of the reduction processes occur in solid state [5].

In furnace the charge descent rate is changed the throat section, and it depends on the smelting period. The furnace throat is pulled down on 200-400 mm after metal and slag output, besides the furnace throat sinking occurs in uneven way in horizontal section of the furnace bath. The maximum sinking of charge material is observed in near electrode zone. As a result of that fact the maximum load of cold charge is made in this zone later. The charge loaded in furnace has the environment temperature and an increased humidity. Some time is required to dry and warm up the charge materials that result in significant decrease of charge average temperature in the furnace throat. At the same time the temperature of up stream flow came from the lower furnace horizons to the furnace throat is about 400 – 600^{0}C, and temperature in lower part of the furnace bath is 1400 – 1600^{0}C.

During charge sinking the upper incompletely reduced ore materials get into the liquid slag, and that increases content of Cr_2O_3 in slag and decreases total degree of chromium reduction. Our experiments of slag analysis testify that. Slag samples for analysis were taken from electric ore-reduction furnace with power of 22 MVA in high-carbon ferrochromium smelting at output stage. The study of chromium residual in outputted slag revealed that chromium content is increased in slag during output (figure 2).

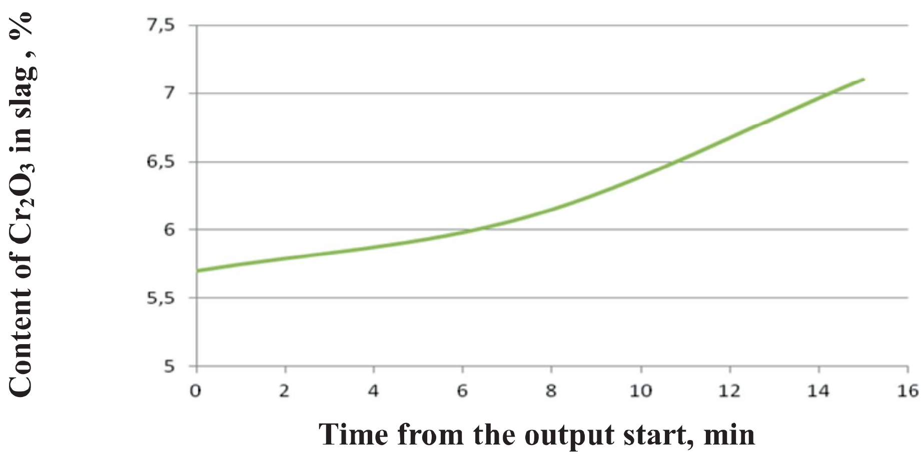

Figure 2: The change of Cr_2O_3 content in slag of high-carbon ferrochromium during the metal and slag output from the furnace

At the beginning of output the slag with smaller chromium content is released (the lower bath horizons with high temperatures and long delay time are activated); at the end of output the slag with low reduction degree is released (upper bath layers). It is therefore concluded that single slag probe cannot gain a complete picture about chromium reduction degree in different horizontal sections zones of electric furnace and at different melting periods. Since the slag mixture with different chromium reduction degree is released from furnace it is only reasonably safe to suggest about some average chromium reduction degree of exact smelting.

The chromium reduction degree in ore-reduction electric furnace has a relationship with the kinetic features of the process. In this connection we made reduction ability experiments of chromium ore elements, which are applied in modern production of ferrochromium in Joint Stock Company Serov Ferro-alloy Plant. We investigated the reduction kinetics of chromium obtained of chromium base ore mixture (50/50) from Saranovsk deposit (Russia) and Kempirsaisk massif (Kazakhstan). The chemical composition of original chromium-ore material is given in table 1. That kinetic investigation of chromium-ore material samples with coke breeze was made in laboratory at different heating rates in the region of the high temperatures (900-1600 ^{0}C). In laboratory tests the heating rates of samples were correlated with descent rates and charge material heating rates which were measured at the production stage of our study.

Table 1: Chemical composition of ore material

№	Name of chromium-ore material	Chemical composition, mass %						
		Cr_2O_3	$Fe_{Общ}$	Al_2O_3	SiO_2	MgO	CaO	P
1	Ore of Kempirsaisk massif	44,7	9,3	7,7	9,1	22,46	0,2	0,0015
2	Concentrate of Saranovsk deposit	33,0	14,3	16,8	10,5	15,5	2,5	0,0028

Carbon containing material is used as reducing agent in production of high-carbon ferrochromium. In this connection, the carbothermic reduction process is attended with CO formation and gassing, and with proper weight change of the sample. That is the reason that thermogravimetry technique has a wide application in study of ore materials reduction kinetics. This method was applied in present study too. The heat rate of furnace working zone was in the range of 4 – 64 ^{o}C/min. The results of experiments are given in figure 3.

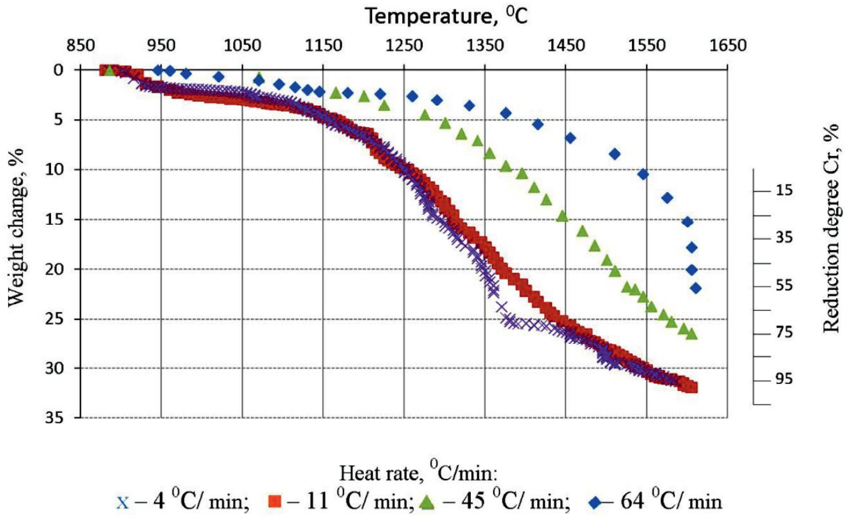

Figure 3: The relationship between the weight change with chromium reduction degree and the temperature with heat rate

The process of chromium and iron reduction from chromospinelide seems to be as follows in chemical formula [11]: $(Mg,Fe)O\cdot(Cr,Al)_2O_3 + C + SiO_2 \rightarrow [Cr\text{-}Fe\text{-}C] + (MgO\text{-}Al_2O_3\text{-}SiO_2)$.

By this means, the formation of metal phase (high-carbon ferrochromium) is caused by reduction of iron and chromium oxides. Iron is reduced in the first stage of this complex process at the lower temperatures. The equilibrium condition of this reaction is fulfilled at 912 °C. Therefore, at first the iron oxides content in chromium ore samples exerts some action on initial rate of weight change, and correspondingly, on reduction rate of ore elements in the ore samples.

The interaction reactions between chromium oxide and carbon come into play and progress in the temperature range of 1130-1160 ^{o}C with formation of carbides: Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ [11]. The temperatures, at which their formation reactions are in equilibrium, vary slightly. The reason for this is the close thermodynamic durability of the three carbides. The equilibrium temperature is 1240 ^{o}C for Cr_2O_3 reduction to metallic chromium. Hence, high-carbon ferrochromium alloy is always formed at chromium reduction by carbon. At the heating rate in the range of 4-11^{o}C/min the intense weight change starts at the temperature of 1150°C. It indicates the beginning of intense stage of chromium reduction into chromium carbides. At higher heating rate in the range of 45-64°C/min and at the same temperature chromium has no time to reduction sufficiently, and as a result the reduction degree is only 55% at 1600°C (at the heating rate 64°C/min). Whereas the chromium reduction degree is higher than 95% at the same temperature and the heating rate is in the range of 4-11°C/min.

CONCLUSIONS

The new data obtained in this study offers deeper insight into the process of chromium reduction of oxides which takes place in ore-reduction electric furnace. The data give the opportunity to direct the way to the new process solutions concerning improvement of technical-economical indexes of high-carbon ferrochromium production. The data for descent rates and for temperature distribution of charge material by zones of electric ore-reduction furnace offer explanations of working furnace features, of the change in the bath zones of electric furnace regarding different types of charge material and level of charge readiness to smelting. After analysis of obtained data it is possible to suggest that the longer time of melt release, the larger is the output of the incompletely reduced ore, the lower is the total chromium reduction index in a smelting. Even when the maximum degree of chromium reduction (up to 100%) is in the lower furnace bath horizons, which is obtained due to the release of incompletely reduced chromium ore with slag, the total chromium reduction is always decreased in direct proportion with the released incompletely reduced material.

With a knowledge of carbothermy reduction of components chromium-ore raw it is possible to operate the kinetics of chromium reduction through, for example, the change of the charge softening temperatures, of the charge material descent rate, of the slag viscosity, of the melting electric mode, of the time difference between outputs, of the selective descent of charge material in throat horizontal section, and of the selective load in relationship with melting period. These undertakings may offer the prospect of the change in temperature zones of the furnace bath, of the increase in material time delay at favourable temperature conditions of smelting and as a consequence that may lead to more complete chromium reduction in electric furnace.

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