

Study of Carbothermic Reduction Processes in Manufacture of High-carbon Ferrochrome

O.V. Zayakin¹, V.I. Zhuchkov¹, B.I. Afanasiev²

¹ Institute of Metallurgy of the Ural Division of the Russian Academy of Science

101 Amundsen st., Ekaterinburg, Russia, 620016., e-mail: zferro@mail.ru

² Joint Stock Company Serov Ferro-Alloy Plant, Russia, Sverdlovsk region, Serov, 1 Nakhabina st.

ABSTRACT

Complex research technique was offered and realized to study carbothermic reduction processes as applied to high-carbon ferrochrome smelting in ore-reduction electric furnace.

Carbothermic process of reduction and temperature intervals of softening for chromium-deficient ore (materials) was studied under laboratory conditions and comparison of domestic chromium-poor raw and rich ore of Kempirsaysk massif was made in an industrial situation. The process of stepwise substitution of rich ore by chromium-deficient ore materials was studied in commercial conditions. It was established that studying of reducibility is not enough for assessment of ore raw components reducibility, but softening temperatures, which make an impact on the operating cell temperature of ore-reduction furnace, should be taken into account. Though when chromium-poor raw is used, on the one hand, the manufacturing costs (consumption of raw materials, electric power) are increased and efficiency of a set is decreased, but on the other hand, normally the ferrochrome prime cost is lowered due to low price of raw ore. Hence, this paper demonstrates the means and feasibility of domestic chromium-poor ore materials usage for smelting of high-carbon ferrochrome grades.

Keywords: metallurgy, ferroalloy, high-carbon ferrochrome, carbothermic reduction

1 INTRODUCTION

The key aim of metallurgist is always to increase a transfer degree of driving elements into melting product. As for high-carbon ferrochrome production, the degree of chromium transfer into alloy varies in the wide range from 92% and down to 75% depending on different types of raw chromium ore.

A limited supply of domestic conditioned chromium raw is one of the problems of Russian ferroalloy plants. So main chromium ferroalloy plants are located far from raw material sources, the greater part of mineral resources are supplied from abroad and this leads to high transport charges and dependence on foreign suppliers. Traditionally the key raw resource for Russian metallurgical plants producing ferrochrome was chromium ores of Kempirsaysk massif (at present Republic of Kazakhstan). Such location of mineral basis presents difficulties for domestic ferroalloy plants producing ferrochrome.

The percentage of chromium-rich ores is less than 33% of worldwide chromium ore resources. Today a number of chromium ferroalloy manufacturers from different countries including Russia face scarce of ores having high qualitative characteristics (both chemical composition and granulometric structure). As for supplying of plants with domestic raw materials, some reserves of chromium-deficient ores are scattered in different regions of Russia. The key disadvantages of domestic deposits are low content of Cr₂O₃ (40 % or less) and relatively high content of iron (up to 20 % of FeO). The gap between growing manufacturers' demand in chromium ferroalloys and decreasing resources of rich chromium ores will be increased. Due to this fact both all poor chromium ores will be engaged into production cycle in Russia and worldwide.

It is generally known that use of all rich ores (chromium, iron, manganese ones, etc.) enables to reduce consumption of electric power and coke, as well as to improve efficiency of commercial sets, what makes better engineering-and-economical smelting performance in comparison with poor ore usage. Additionally, the prime cost of ferroalloy output is largely dependent on the ore material price. Share of ore raw costs vary in wide ranges according to manufactured ferroalloy, for example, for costly alloys the price of raw materials can reach up to 97 % of the total prime cost. As for high-carbon ferrochrome production, the percentage of expenses on chromium-ore raw is about 30-40 % of the alloy prime cost [1]. Thus the gain due to the low cost of metal-poor raw can exceed the production expenses when rich raw materials are used.

Poor chromium ores application feasibility was studied by comparison of Russian chromium-poor ores from Saranovsk deposit and chromium-rich ores from Kempirsaysk massif. Chemical compositions of source ore materials are listed in Table 1.

Table 1: Chemical composition of chromium-ore materials

№	Chromium-ore materials deposit	Chemical composition, mass %						
		Cr ₂ O ₃	FeO	Al ₂ O ₃	SiO ₂	MgO	CaO	P
1	Kempirsaysk massif, Republic of Kazakhstan	52.0	13.3	8.2	5.3	18.3	1.4	0.0015
2	Saranovsk deposit, Russia	38.1	19.5	14.6	5.2	14.7	2.1	0.0028

2 EXPERIMENTAL

2.1 Laboratory Tests

On the first research stage the reducibility and softening temperatures intervals which are the key characteristics of raw chromium-ore were studied. Laboratory reducibility tests were carried out to define a maximum degree (completeness) of processes progression of carbothermic reduction of chromium-poor ores components. In the result of the tests it was established that behaviour of both ore materials from Saranovsk deposit and Kempirsaysk massif are roughly identical at heating up to 1550 °C [2], and their reduction degrees exceed 94%.

In laboratory conditions the softening temperature intervals were defined for the ore materials, the top temperature in ore-reduction electric furnaces and properties of primary slag melts are governed by the initial and final softening points. The softening temperatures are the key criteria to divide ores and concentrates in two categories: easy- and hardly-reducible materials [3]. Easy-reducible ores have high values of initial softening points and narrow softening intervals. On the contrary hardly-reducible ores can be characterised by lower initial softening temperatures and wider softening intervals. In ore-reduction furnace the primary slags are formed in lower horizons when easy-reducible ores are used, the worse reducibility of the charge materials is, the higher horizons contain more slag.

When determining the initial and final softening points we were guided by GOST 26517-85. According the technique, the initial softening point is the temperature when rod is dipped into sample on 1% of the length at 0.1 MPa, and the final softening point is the temperature when rod is dipped on 40% from the initial height of sample layer. The experimental results are listed in Table 2. The ore from Saranovsk deposit is characterised by lower initial and final softening points. In comparison with Kempirsaysk massif ores the advantage of the Saranovsk ones is narrower softening interval.

Table 2: Chemical composition and softening characteristics of chromium-ore materials

№	Chromium-ore materials deposit	Temperature of onset softening, °C	Temperature of end softening, °C	Temperature range of softening, °C
1	Republic of Kazakhstan, Kempirsaysk massif	1410	1820	410
2	Russia, Saranovsk deposit	1380	1715	335

It was experimentally defined in the laboratory that ore from Saranovsk is almost good as materials from Kempirsaysk massif judging by the rate and degree of reduction. Besides Saranovsk ores have lower initial and final softening points, what may cause the temperature decrease in operating cell of ore-reduction electric furnace. On the whole the laboratory testing revealed that ores from Saranovsk deposit are technologically suitable on all studied counts for high-carbon ferrochrome production of different grades.

Commercial study of degree of chromium transfer into metal melt applying different ore materials were carried out in the workshop of Joint Stock Company Serov Ferro-Alloy Plant with electric ore-reduction furnace of RKO-22 type with the power of 22 MVA.

2.2 Commercial Tests

The performance tests of high-carbon ferrochrome smelting technology were performed in stepwise progressive way, the transition from 100% of Kempirsaysk massif rich ore to 100% of Saranovsk deposit poor raw was realized in 5 steps [4].

The performed smeltings revealed that the larger sample of Saranovsk ore in the charge, the better furnace operating performance, and the lower number of fall and releases of the charge due to more precise lump composition. The effect of poor ore materials usage is the increase of chromium-ore materials specific consumption from 3731 and up to 3920 b.kg/t of Cr (Figure 1). The decrease of Cr_2O_3/FeO ratio and Cr_2O_3 content in ore mixture is responsible for downturn of chromium content in the alloy from 68.8% to 56.8% (Figure 2). Ferrochrome conforms to FeCr60C70Si4LS grade according to ISO 5448-91 standard when 100% of Saranovsk deposit ores are used.

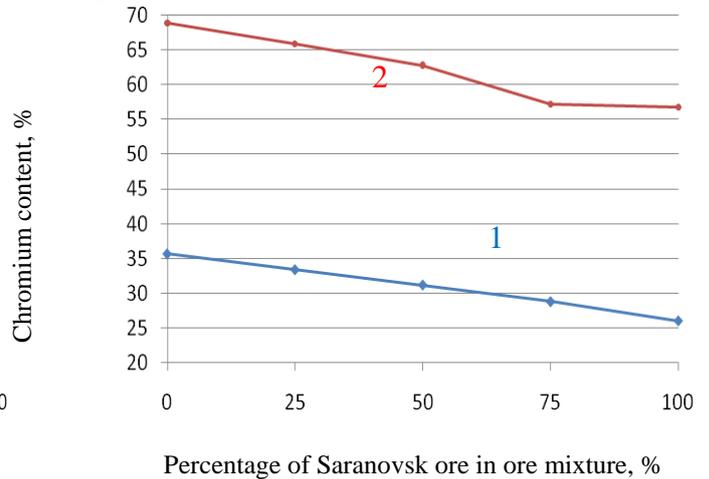
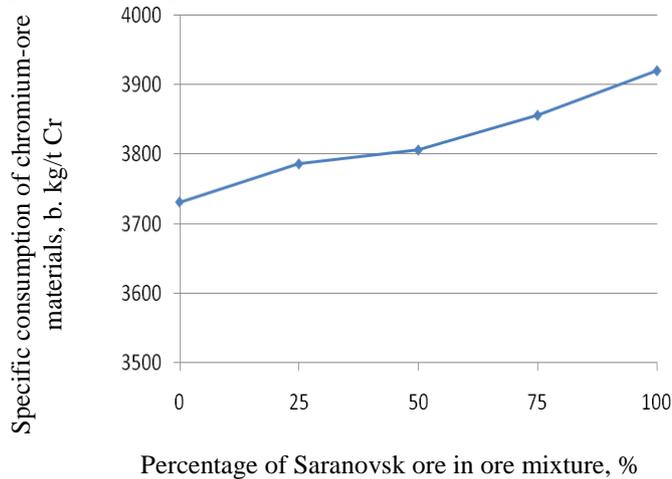


Figure 1: Relationship between variation of specific consumption of chromium-ore materials and growth of Saranovsk ore share in ore part of charge

Figure 2: Relationship between variation of chromium content and growth of Saranovsk ore in ore part of charge: 1 – initial ore mixture; 2 – high-carbon ferrochrome.

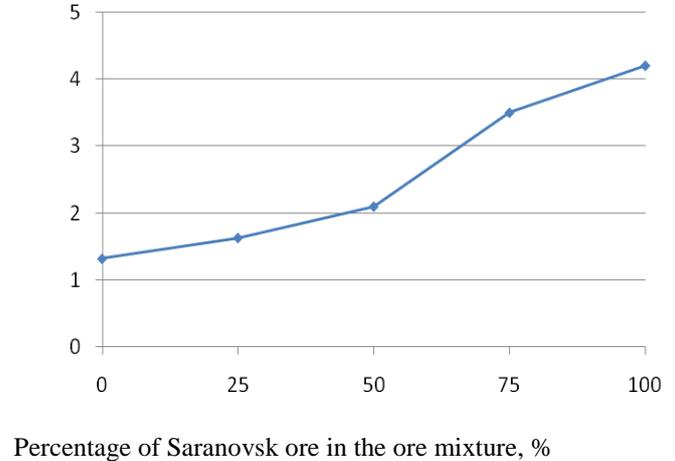
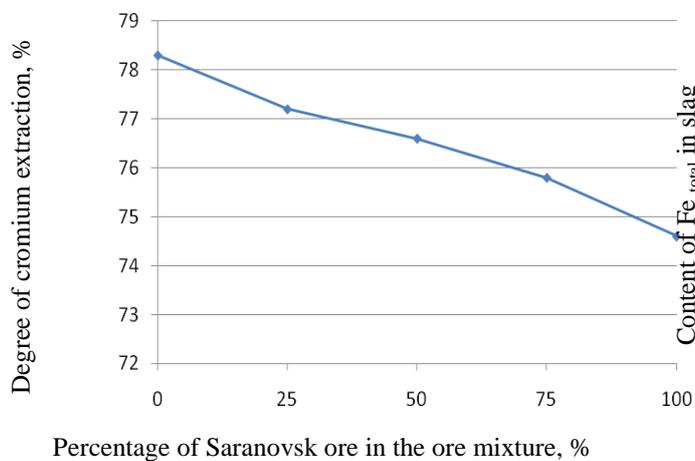


Figure 3: Change of chromium extraction into alloy caused by the increase of Saranovsk ore portion in ore part of charge

Figure 4: The change of Fe_{total} content in slag caused by the increase of Saranovsk ore portion in ore part of charge

3 RESULTS DISCUSSION

While increasing percentage of Saranovsk ore up to 100% the chromium extraction into alloy was decreased on 3.7% (Figure 3). Besides residual iron content was increased in slag (as if count on total iron) as shown in Figure 4. According to the evidence of the present research about chromium reducibility degree the poor Saranovsk ores are as good as Kempirsaysk massif ores when all factors are considered equal.

However, a decrease of degree of chromium transfer into metal is indicated by the commercial smelting tests. It is believed that this was caused by change of temperature fields in operating furnace cell.

The laboratory testing revealed that ores from Saranovsk deposit are characterized by lower final softening points in contrast to the same points of Kempirsaysk massif ores (1715⁰C versus 1820⁰C), this consideration can cause a temperature decrease of furnace reaction zone. Again the temperature measurements done during slag tapping testify the temperature decrease of furnace operating zone. The temperatures of the first slag portions were ~1760 ⁰C and ~1680 ⁰C when running on Kempirsaysk and Saranovsk ores, respectively.

Another disadvantage of Saranovsk deposit ores is high phosphorus content, the value of phosphorus content is higher than in Kempirsaysk massif ores by a factor of 1.9 (Table 1). Hence usage of chromium- poor ore raw produces a need of low-phosphorus carbonaceous reducing agents application. The compositions of applied carbonaceous reducing agents are listed in Table 3.

Table 3: Technical composition of applied reducing agents

Material	Content, %										
	W	A ^c	V ^r	S	P	C _{solid}	Ash of reducing agent				
							SiO ₂	CaO	MgO	Al ₂ O ₃	FeO
Coke NTMK	1.75	12.7	1.1	0.49	0.071	85.8	46.2	5.9	1.7	22.7	16.6
Special coke	13.6	7.0	4.1	0.32	0.020	88.6	37.6	6.6	2.8	21.3	21.3
Coal of Karaganda deposit	6.8	48.7	16.6	0.41	0.014	34.3	67.0	0.16	0.24	23.9	1.34

where W is the humidity, A^c is the ash content in carbonaceous reducing agents, V^r is the volatile substances content in carbonaceous reducing agents, NTMK - Nizhniy Tagil Iron and Steel Works, S, P, C_{solid} are elements.

The phosphorus content per carbon unit of the special coke and coal used is less than of the NTMK coke by a factor of two. By this means that an increase of phosphorus content (contributed by Saranovsk ore) in the alloy can be compensated by coke. The phosphorus content in the alloy was held at the level desired by customers which was within the ISO 5448-81 standard (0.05 % of phosphorus or less).

The key result of the present paper is in positive experience of wide application of domestic chromium-poor ores for high-carbon ferrochrome production with high engineering-and-economical performance. The increase in the technological costs, namely, consumption of raw materials and electricity (from 6530 up to 8000 kW•h/t Cr) are increased, besides smelting sets performance is decreased (from 57 t down to 40 t of Cr per 24 hours), is caused by usage of chromium-poor ore raw, nevertheless the calculated manufacturing cost of ferrochrome is decreased.

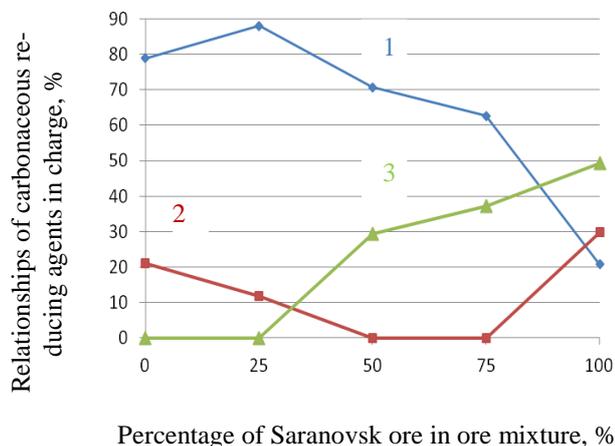


Figure 5: Relationship between variation of carbonaceous reducing agents in charge and Saranovsk ore percentage increase in ore mixture: 1 – Coke NTMK; 2 – Special coke; 3 – Coal from Karaganda

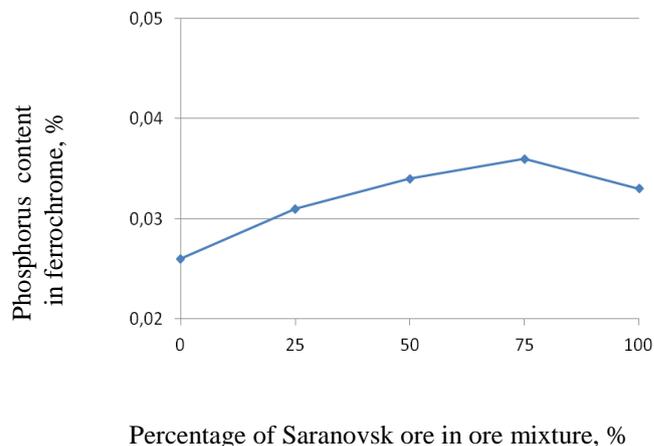


Figure 6: Relationship between variation of phosphorus content and Saranovsk ore percentage increase in ore mixture

4 CONCLUSIONS

Hence the complex laboratory-commercial research of chromium reduction of poor and rich ores samples from Saranovsk and Kempirsaysk deposits in manufacture of high-carbon ferrochrome was carried out. It was indicated that

studying reducibility is not enough for correct assessment of ore raw components reducibility; softening temperatures, which make an impact on the operating cell temperature of ore-reduction furnace should also be taken into account.

The overall performance testing of high-carbon ferrochrome smelting technology were carried out in the workshop of Joint Stock Company Serov Ferro-Alloy Plant in stepwise progressive way with increasing percentage of Russian chromium-poor ore raw. The prime cost of ferrochrome is decreased due to small price of raw poor chromium ore despite the fact that usage of such raw materials causes both increase in manufacturing costs (consumption of raw materials, electric power) and decreases the efficiency of a commercial set. Hence this paper demonstrates the means and feasibility of using domestic chromium-poor ore materials for smelting of high-carbon ferrochrome of different grades.

5 REFERENCES

- [1] Gladkikh V.A., Gasik M.I., Ovcharuk A.N., Proydak Yu.S. Engineering and equipping of steel making and ferro-alloy workshops. Dnepropetrovsk. System technology, 2004. (in Russian)
- [2] Zayakin O.V., Zhuchkov V.I. Study of reduction kinetics of chromites-poor ores components. Melts. 2 (2010). pp.3-6. (in Russian)
- [3] Cylev L.M. Reduction and slag formation in blast furnace process. Moscow, Nauka 1969. (in Russian)
- [4] Ostrovskiy Ya.I., Veselovskiy I.A., Afanasiev V.I., Zhuchkov V.I. Zayakin O.V. Development of chromium ferroalloys production technology with application of poor domestic chromium ore raw materials. Steel. 5 (2013). pp. 40-43. (in Russian)