OPTIMIZATION OF PHYSICOCHEMICAL CHARACTERISTICS OF CHROMIUM FERRO-ALLOYS

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ABSTRACT

The chemical compositions of 17 alloys with various chrome, silicon and carbon were researched.

The following methods were used in the research: pycnometry method, method of fixing temperature curves during alloy cooling; high-temperature gravimetric analysis.

***KEY WORDS**: Ferroalloys, measurements, density, melting temperature, oxidation rate.*

1. INTRODUCTION

During the preceding half-century steel-making technologies underwent significant changes transferring operations of alloying, deoxidation and refining from furnace to ladle.

It required the change of number of ferroalloys' physicochemical characteristics due to reduced temperature in the ladle, limited time of reactions etc.

It caused the necessity of characterization and determination of the rational composition of produced ferroalloys to fit the requirements of modern steelmaking production.

The pattern of determination of ferroalloys' rational composition was developed in the Ural branch of Institute of metallurgy of Russian Academy of Science [1]. The method based on the correlation between ferroalloys' rational composition and properties includes:

1. Preliminary selection of ferroalloy elements according to determined composition and properties of steel.
2. Determination of efficient ratio of the elements based on research of ferroalloys' physicochemical characteristics and patterns ot their reaction with iron-carbon alloy.

The method considers the main factors which effect melting of ferroalloys and properties of the treated steel. The following characteristics were studied: liquidus and solidus temperatures (t_m), density of ferroalloys (ρ), values of thermal effects of reactions, melting and recovery time of ferroalloys in steel, features of ferroallloys' structure etc.

2. EXPERIMENTAL

Chromium ferroalloys are of highest demand from steelmaking industry. They have characteristics (t_m, ρ) with boundary rational values. For example, the recommended rational density of ferroalloys used for steel treatment is 5000-7000 kg/m^3 [2], while produced ferroalloys have density of 6700-7300 kg/m^3. Low-carbon ferroalloys' density is 6700-7010 kg/m^3 [3]. The recommended liquidus temperature of ferroalloy is up to 1500^{o}C [4], for technical ferrochrome the liquidus temperature is 1490-1620^{o}C, the solidus temperature 1470-1620^{o}C, for low-carbon ferroalloys the values are 1640-1670^{o}C and 1540-1570^{o}C respectively [3]. Thus, the objective of research was to find the rational values of physicochemical characteristics of chromium containing ferroalloys affecting degree and stability of chrome recovery in steel.

Chemical composition and characteristics of chromium ferroalloys are given in the table 1.

Table 1: Chemical composition, density and melting temperature range of chromium alloys

№	Chemical composition, %						Density, kg/m³	Melting temperature, °C	
	Cr	Fe	Mn	Si	C			Liquidus	Solidus
1	64,6	34,8	–	0,5	0,1	–	–	1641	1555
2	61,8	32,8	–	5,3	0,1	–	7007	1521	1465
3	57,8	32,1	–	10,0	0,1	–	6820	1468	1368
4	51,4	29,8	–	18,7	0,1	–	6500	1464	1375
5	46,2	27,2	–	26,5	0,1	–	6414	1461	1370
6	41,9	25,7	–	32,3	0,1	–	5604	1439	1370
7	35,6	22,3	–	42,0	0,1	–	5376	1382	1308
8	29,2	17,1	–	53,6	0,1	–	4688	1342	1261
9	66,3	26,2	–	0,3	7,2	–	7353	1676	1571
10	57,4	28,0	–	8,0	6,6	–	6735	1516	1476
11	37,9	28,4	22,3	11,3	0,1	–	6836	1341	1262
12	33,9	25,2	31,6	9,1	0,2	–	6930	1311	1262
13	45,0	32,8	12,0	10,1	0,1	–	6912	1359	1271
14	39,4	33,7	24,4	2,3	0,2	–	7310	1442	1393
15	38,3	27,9	17,8	15,9	0,1	–	6026	1331	1277
16	38,4	27,3	22,3	10,4	0,1	1,5	6794	1340	1275
17	34,6	31,6	20,1	9,5	0,2	4,0	6755	1409	1369

The effect of silicon content on ferroalloy properties was studied at close Cr/Fe ratio and low carbon content (0,1 %) for alloys 1-8 of Fe-Cr-Si-C system; the affect effect of silicon in high-carbon alloys was studied for alloys 9 and 10; in complex alloys of Fe-Cr-Mn-Si-C system the effect of silicon and manganese content on alloy properties was studied for alloys 11-15, for alloys 16 and 17 – the effect of boron content.

The alloy density was determined by pycnometry method.

The correlation between silicon content and alloy density for alloys 1-8 is shown in figure 1.

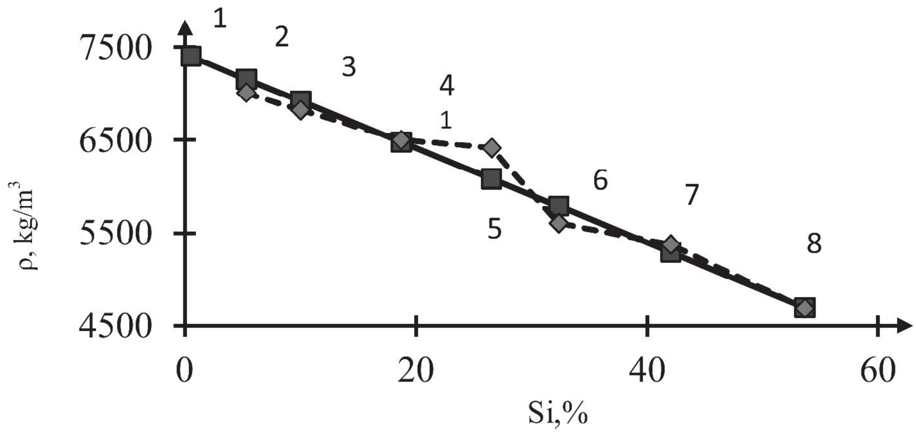

Figure 1: Correlation between alloy density and silicon content. Numbers on the figures match the numbers of alloys

3. DISCUSSION

All alloys with increased silicon content have rational density of 5000-7000 kg/m³. The deviation between actual and calculated density values for alloy 5 can be explained by presence of the following high-density phases: Fe_5Si_3 (6470 kg/m³) и Cr_5Si_3 (6430 kg/m³) [5]. The density value of alloy 8 is below rational due to high silicon content (53,6%). For alloy 9 the increase of carbon content up to 7,2% does not reduce the density to its rational values, but increase of silicon content up to 8% reduces the density to the recommended values. For complex alloys (11-15) of Fe-Cr-Mn-Si-C system the carbon and manganese content was changed from 2,3 to 15,9% and from 12 to 30%, respectively. Low-silicon alloy 14 has higher density, while the other alloys' density (11-13 and 15) is closer to rational.

For complex alloys (16 and 17) of Fe-Cr-Mn-Si-B-C system the effect of boron content on density was evaluated. It was found that increase of boron content in from 1,5 to 4,0% insignificantly reduces density in comparison to alloy 11 containing no boron.

Thus, to reduce the density of both low- and high-carbon chrome alloys, the increase of carbon content up to 9-10% is required. Liquidus and solidus temperatures were determined by means of temperature curves fixing during alloy cooling.

It was found that melting tempeartures are reduced proportionallyif silicon content increases from 0,5 to 53,6% for alloys 1-8. Alloys 3-8 with silicon content 10-53,6% have rational values of melting temperatures. Decrease of melting temperature at silicon content increase from 0,8 to 10% is apparently related to formation of low-melting phases such as Fe_3Si and Fe_5Si_3 which have the same melting temperature 1261°C [5]. All alloys except 1 and 2 have the rational melting temperatures below 1500°C.

Increase of silicon content in HC ferrochrome alloy up to 8% reduces the melting temperature. The liquidus and solidus temperatures of alloy 9 are significantly greater than rational melting temperature, and melting temperature of alloy 10 is close to the required value. In HC ferrochrome increasing of melting temperature is linked with the formation of refractory phase Cr_7C_3. X-Ray analysis shows that content of this phase reduces parallel to increase of silicon level, which affects melting temperature.

If silicon content in alloys 11-15 of Fe-Cr-Mn-Si-C system is changed from 2,3 to 11,3%, sharp drop of melting temperature is observed, and that is caused by formation of low-melt manganese silicide phases. All alloys of this system have recommended melting temperature.

The oxidation rate of alloys 1, 5, 8, 9, 10, 16 by oxygen in air at heating up to 1400°C was determined by thermogravimetric analysis and using the NETZSCH STA - 449C Jupiter thermoanalyzer.

The oxidation data of ferroalloys at charging have practical importance as the loss and recovery stability of main elements are linked with alloys oxidation as well as the pollution of steel by oxidation products.

Among the alloys 1, 5 and 8 alloy 1 has the highest oxidation rate, alloy 5 has the lowest. It means that increasing of silicon content in alloy reduces its oxidability to defined values. Further increasing of silicon content in alloy increases its oxidability.

Alloy 9 with high-carbon content showed the maximum oxidability rate, the addition of 8% Si (alloy 10) has the beneficial effect on reducing of HC ferrochrome oxidability rate (1,5 times).

Alloy 16 (1,5% of B) has the lower (5,3 times) oxidation in comparison to the same alloy 11 with no boron content, which is linked with affect of boron on formation of more solid and less oxygen-permeable oxide film.

Before charging into the melt the ferrochrome alloys will be sinking into the liquid steel with no oxidation by oxygen in air, and that is why the main oxidation of alloys will occur during their pre-charging heating. Considering significant oxidation of chromium alloys above 1000°C the heating must be done for 10-15 minutes at 700-800°C.

Standard HC ferrochrome and ferrochrome with increased silicon content show different behavior when charged into ladle due to different density and melting temperature (figure 2).

Due to high density the standard ferrochrome is not practically pulled into hydrodynamic flows being subsided at the laddle bottom. It slowly dissolves because of high melting temperature. On the contrary, ferrochrome with high silicon content is pulled into hydrodynamic flows due to its rational density. Its melting temperature is lower than steel temperature in the ladle, and melting time is significantly shorter than that of standard ferrochrome.

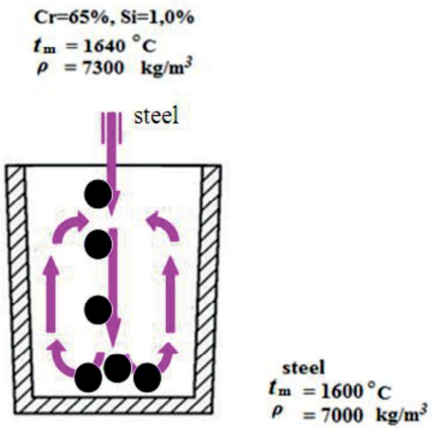

Figure 2: Comparison of melting patterns of HC ferrochrome with different silicon content

4. CONCLUSIONS

This article is a small part of a dissertation paper on working out rational compounds of chromium alloys, the target of which concerns studying of the alloys physicochemical characteristics and determining their dependence on the alloys chemical composition. Density and melting temperature are most important ferroalloys characteristics affecting chrome recovery in liquid steel and the increase of Si content decreases density and melting temperature of chromium alloys to rational values. Ferrochrome containing 10% Si is not only an alloy but also deoxidizer of metal, which increases the recovery rate of chrome in steel. High content of Si in ferrochrome improves chrome recovery in liquid steel. State Standard 4757-91 and ISO5448-81 allow silicon content up to 10% in HC ferrochrome and the production technology of such alloys is well developed [6]. All of the alloys under treatment except 1,2, 8-10 and 14 possess rational properties. The above mentioned alloys allow to simultanously deoxidate and alloy steell increasing the recovery rate of chrome.

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