Development of New Ferroalloys Compositions with Chromium

Zhuchkov V.I., Andreev N.A.

Institute of Metallurgy of the Ural Division of the Russian Academy of Science101 Amundsen st., Ekaterinburg, Russia, 620016. e-mail: annick1211@gmail.com

ABSTRACT

An integrated approach was applied to studying the following ferroalloy systems, namely, Fe-Cr-Si, Fe-Cr-Mn-Si, and Fe-Cr-Mn-Si-B. For these systems the melting time was calculated as well as a number of experiments were performed to determine density, melting temperature, specific oxidability and degree of chromium digestion by the iron-carbon melt.

It was established that density, melting temperature, oxidability, and melting time are improved with the increase of silicon content in the alloys. Values of these parameters are decreased, but the chromium digestion degree by steel is increased. The abovementioned properties are also improved by the increase of manganese content in the alloys, but the effect is rather small compared to silicon. Small increase in density and melting temperature, abrupt decrease in oxidizing and increase in chromium digestion of the alloys are also caused by boron addition into alloy.

Reasonable compositions of carbon and carbon-free ferrochrome, as well as complex ferroalloy systems of Fe-Cr-Mn-Si and boron admixture up to 1.5% for chromium alloys were proposed.

Keywords: *ferrochromium, density, melting temperature, oxidation degree, digestion degree*

1 INTRODUCTION

The digestion degree of principal elements by treated metal melt is one of the key ferroalloys functional characteristics which should be high and consistent. The elements digestion degree is governed by the ferroalloy physicochemical properties (density, melting temperature, oxidation degree, etc.).

Unfortunately such data are not numerous at the present time, and often they are inconsistent [1-3]. The same lack of reliable data applies to return back to widely used chromium-containing ferroalloys.

In the present paper a number of laboratory tests were carried out to determine the following physicochemical properties of chromium-containing ferroalloys: density, melting temperature, oxidability, besides melting time of alloy lumps was calculated and chromium digestion degree by steel was determined.

The samples under investigation were obtained by smelting of charge materials in crucible. Chemical composition and physicochemical properties of chromium-containing ferroalloys under investigation are listed in Table 1.

The optimal features of the lump ferroalloys for better digestion of elements added into steel are listed below. The density values should fall within the range of 5000-7000 kg/m^3, the melting temperature (liquidus) should be less on 50 K than treated steel melting temperature, the smelting time and oxidability should to be minimal [4,5].

2 RESULTS AND DISCUSSION

Provisionally the alloys (Table 1) under consideration can be divided into 4 groups: low-carbon ferrochrome with percentage of silicon within the range of 0.5-18.7% (1-4); silicochrome with silicon content within the range from 26.5 up to 53.6 % (5-8), high-carbon ferrochrome 0.3 - 8.0% of silicon (9-10), complex alloys of the Fe-Cr-Mn-Si (11-15) system.

The density was estimated by calculation procedure and picnometric technique.

In the alloys (11-15, the Fe-Cr-Si system) the effect of silicon content on alloys density was studied at rather close Cr/Fe ratios and constant carbon content. It was shown that the proportional decrease in density is governed by the percentage increase of silicon from 0.5 up to 53.6% (Figure 1). Such form of dependence is directly tied to the low density value of silicon (2320 kg/m^3) in comparison with major components density of chromium ferroalloys (Cr and Fe).

The calculated data are relatively close to experimental density evidence. The density values of the alloys (3-7) having elevated silicon content are optimal ones. The density of the 8th alloy is slightly less than optimal range, and in contrast, the 1st and the 2nd alloys have exceeding values.

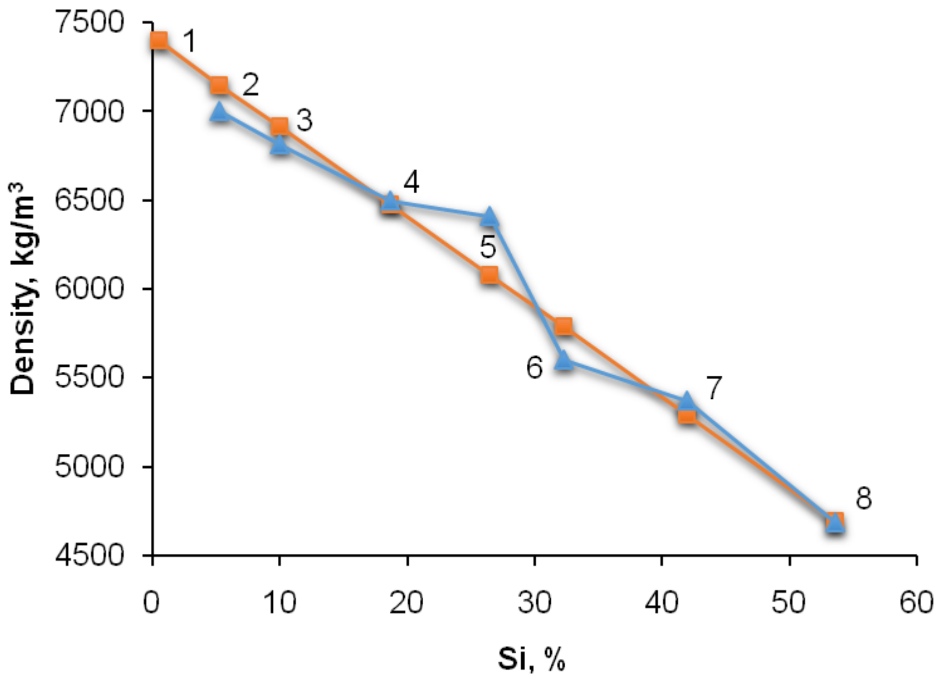

Figure 1: Relationship between percentage of Si in alloys and density ▲ –experimental evidence, ■ – calculated values. The numbers of alloys are presented in Table 1.

The density of the 9th alloy is higher than rational values despite high carbon content (7.2%). In the 10th alloy a decrease of density values down to rational values is caused by the increase of silicon content up to 8.8%.

In the complex alloys (11-15, the Fe-Cr-Mn-Si system) the effects of silicon and manganese content on density were determined at rather constant ratio of other elements. Percentage of silicon and manganese was changed within the ranges of 2.3-15.9 and 12-30%, respectively. It is shown that effect of increase in silicon content by 1% is the density decrease by about 1.3%. Besides, an increase of manganese content does not influence the alloy density values. The alloys (11-13 and 15) have optimal density values; the low-silicon alloy (14) has elevated density value.

Hence, according to the obtained data it may be concluded that an efficient way to decrease the density of chromium ferroalloys down to optimal values is the increasing of silicon content in alloy. The effect of an increase in carbon content in the alloy at the relatively constant content of other elements is a decrease of density to a lesser degree. The variation of manganese content in the alloys under consideration is slightly reflected in the density.

The melting temperatures were defined by registration of temperature curves during cooling of the alloys.

The results of melting temperatures determination tests are listed in Table 1.

Table 1: Calculated and experimental values of the alloys under investigation

Alloy number	**Chemical composition, %**					**Density, kg/m³**		**Temperature, °C**	
	Cr	**Fe**	**Mn**	**Si**	**C**	**calculation**	**experimental**	**liquidus**	**solidus**
1	64.6	34.8	–	0.5	0.1	7399	–	1641	1555
2	61.8	32.8	–	5.3	0.1	7150	7007	1521	1465
3	57.8	32.1	–	10.0	0.1	6916	6820	1468	1368
4	51.4	29.8	–	18.7	0.1	6478	6500	1464	1375
5	46.2	27.2	–	26.5	0.1	6081	6414	1461	1370
6	41.9	25.7	–	32.3	0.1	5789	5604	1439	1370
7	35.6	22.3	–	42.0	0.1	5294	5376	1382	1308
8	29.2	17.1	–	53.6	0.1	4695	4688	1342	1261
9	66.3	26.2	–	0.3	7.2	7001	7353	1676	1571
10	57.4	28.0	–	8.0	6.6	6667	6735	1516	1476
11	37.9	28.4	22.3	11.3	0.1	6886	6836	1341	1262
12	33.9	25.2	31.6	9.1	0.2	6985	6930	1311	1262
13	45.0	32.8	12.0	10.1	0.1	6946	6912	1359	1271
14	39.4	33.7	24.4	2.3	0.2	7354	7310	1442	1393
15	38.3	27.9	17.8	15.9	0.1	6645	6026	1330	1277

The influence of silicon content on the properties of the alloys (1-8, based on Fe-Cr-Si system) were studied. It is shown that a proportional decrease in liquidus and solidus temperatures is caused by the increase in silicon content from 0.5% up to 53.6%. The former alloys have melting intervals in the range of 40-105°C. A decrease in melting temperature with the increase in silicon content from 0.8 up to 10% appear to be caused by formation of low-melting phases such as Fe_3Si and Fe_5Si_3, having equal liquidus temperature (T_l=1261°C). The effect of the increase in silicon content from 10 up to 32.3% progressively is a minor effect on liquidus and solidus temperatures decrease, probably it is governed by growth of volume parts of Cr_5Si_3 refractory phases (T_l–1720°C). The effect of further increase in silicon content from 32.3 up to 53.6% is a linear decrease in melting temperature due to formation of low-melting (Fe_3Si and Fe_5Si_3) and additional silicides ($CrSi_2$ and $FeSi_2$) having melting temperatures 1475 °C and 1220 °C, respectively.

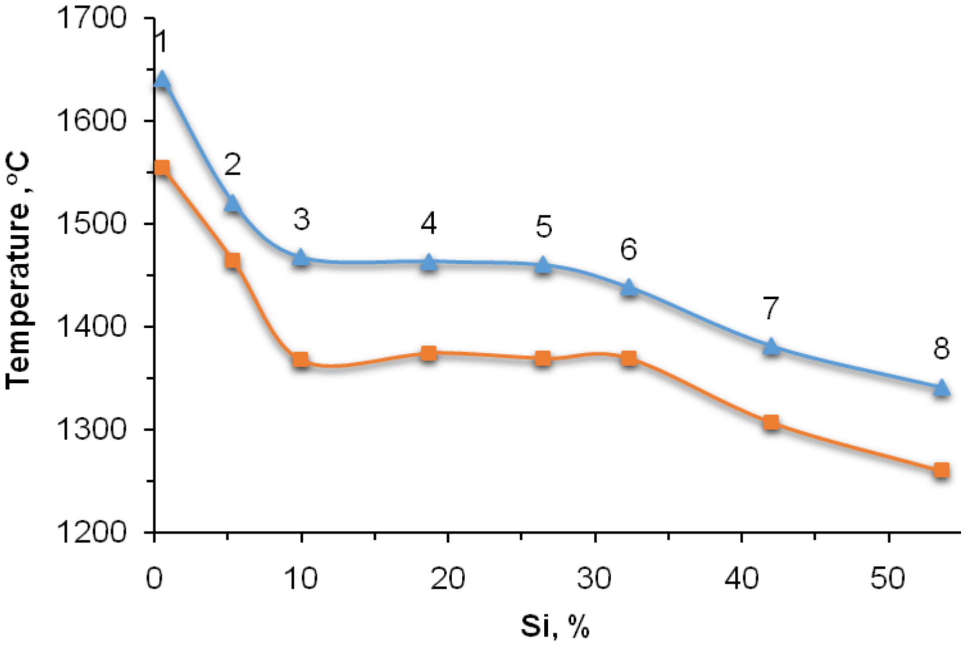

Figure 2: Relationship between alloys melting temperature and silicon content, curves ▲ – liquidus temperature, ■ – solidus temperature. Alloys numbers are listed in Table 1.

The influence of silicon percentage in the alloys (9, 10) on the melting intervals of high-carbon ferrochrome was studied. Standard high-carbon ferrochrome having high chromium content and small portion of silicon (the 9th alloy) refers to a group of extra-refractory alloys. The application of extra-refractory ferroalloys for steel treatment is undesirable due to an increase in alloying time and decreasing in chromium digestion coefficient, besides it impedes the out-of-furnace treatment process. The effect of increase of silicon up to 8% in carbonaceous ferrochrome is a significant decrease of the alloy liquidus temperature down to reasonable values, what appears to occur because of both decrease in volume concentration of the Cr_7C_3 refractory phase (T_l ~ 1780 °C) and increase in volume fraction of the Fe_3Si low-melting phase.

As for the complex alloys (11-15 of the Fe-Cr-Mn-Si system), the influence of silicon and manganese addition at the relatively constant ratio of other alloying element on the melting interval was studied. It is shown that an insignificant decreasing of liquidus and solidus temperatures is caused by the increase in manganese content from 12 up to 31.6%. The effect of the silicon content change from 2.3 up to 11.3% in the alloy is the rapid decrease in melting temperature, probably formation of low-melting phases Fe_5Si_3, FeSi, $CrSi_2$ (T_l 1290 °C, 1410°C, and 1413°C, respectively) as well as increase in volume concentration of Mn_5Si_2(T_l 1200 °C) are responsible for this decrease. All alloys have reasonable values of the liquidus temperature.

Oxidation of the ferroalloys was studied using a Netzsch Jupiter thermal analyzer providing a simultaneous technique of thermogravimetry (TGA) and thermal analyzer (DTA). Testing was carried out at the air flow (70 ml/min), at the heating rates of 40 and 20 K/min within the ranges 30-1000°C and 1000-1400°C, respectively. The time delay was 10 min at 1400°C.

Besides a relationship between specific oxidation and mass change of the sample surface area unit ($^{\Delta m}/_{S}$) was studied.

The alloys (1; 5; 8; 9; 10, and 11) were chosen to determine characteristic relationships between oxidation degree and percentage of Si, Mn, Cr, Fe, and B (Table 1).

It should be noted that oxidation degree of various chromium-containing alloys is governed by chemical and phase compositions of surface oxide film which has volatile density, continuity, and oxygen-permeability. According to rough calculations the loss of effective ferroalloy elements is less 0.1-0.2% of the ferroalloy mass at the heating of up to 1200 – 1400℃ .

It is experimentally defined that the mass growth of all alloys under consideration is increased at warming up. Besides for a number of alloys the mass growth was observed at the 10 min isothermal annealing (the 11th alloy at 1200℃ and alloys 1;5;8;9;10 at 1400℃).

The oxidability of the alloys (1, 5, 8, 9, 10) was increased during soaking at the 1400℃ , while the alloy (9) had the greater growth from $25 \cdot 10^{-3}$ up to $30 \cdot 10^{-3}$ mg/mm². The latter alloy have low silicon content and high percentage of carbon, oxide film is black, not continuous and have no adhesion with a sample surface. Probably the key reason for this is attributed to availability in the alloy of carbon which forms CO gaseous compound (in the result of oxidation) what causes a destruction of oxide film continuity. One should note that the oxidation of carbonaceous ferrochrome (10th alloy) having increased content of silicon is occurred to a lesser degree in the whole temperature interval (up to 1400℃) in comparison with other alloys. This leads to the conclusion that increased percentage of silicon (8%) in the alloy is responsible for formation of more dense and continuous film, what causes a decrease in carbonaceous ferrochrome oxidability.

Taking into account a significant increase of oxidation degree of ferroalloy elements at elevated temperatures (higher than 1000°C), it is necessary to perfect evaporation of moisture from the alloys, so it is strongly recommended to make tempering in furnace during 10-15 minutes at 700-800°C of all chromium-containing ferroalloys before adding into melt.

The time of alloys melting in iron-carbon melt was calculated in accordance with mathematical model described in previous communication [5]. The time is taken to be the interval from the melting onset and to the point of disappearance of alloy solid particle (Table 2). The following conditions were taken as the standard ones:

- for liquid steel: T_K = 1530 °C, $T_Б$ = 1600 °C (where: T_K is the temperature of steel crystallization end, $T_Б$ is the steel temperature in ladle); $L = 1{,}79 \cdot 10^9$ J/m^3 is the heat of crystallization, λ = 30 W/(m·K) is the thermal conductivity of steel in the liquid state;

- for alloy particle: 1, 5, 10, 30, and 50 mm are the sphere diameters, T_O = 20 °C is the initial temperature of an alloy particle.

Table 2: Relationship between ferroalloy smelting time and fraction size

Alloy number	**Fraction size, mm**				
	1	5	10	30	50
	Melting time, sec				
1	28.18	184.695	391.7	1233.9	2085.6
2	0.197	2.458	7.1	47.4	91.9
3	0.133	1.726	5.1	32.7	64.9
4	0.128	1.613	4.9	29.7	59.9
5	0.123	1.6	4.7	29.0	57.9
6	0.104	1.317	3.9	22.3	54.4
7	0.091	1.18	3.4	18.8	49.1
8	0.079	0.95	2.9	15.2	37.8
9	28.93	190.253	404.5	1276.1	2157.3
10	0.182	2.281	6.7	42.5	82.6
11	0.108	1.344	4.0	23.6	49.2
12	0.0998	1.374	4.1	23.2	47.9
13	0.106	1.427	4.2	24.9	51.1
14	0.141	1.717	5.2	32.7	65.8
15	0.0949	1.284	3.5	19.9	41.4

The alloys (1-8) correspond in chemical composition to low-carbon ferrochrome and ferrosilicon. For alloys melting time considerations, the alloys are divided into 3 groups: 1st – extra-refractory alloy, which have the extra-long melting time, 2nd – a refractory one, 3rd-8th are low-melting ones. The higher percentage of silicon in the range from 0.5 up to 53.4%, the shorter melting time is.

For the alloys (9 and 10) the influence of silicon content on the melting time of carbonaceous ferrochrome was estimated. The increase in silicon percentage from 0.3 up to 8% causes the carbonaceous ferrochrome to be more low-melting and melting mechanism became convective instead of diffusive one, what is reflected in melting time.

As for the complex alloys (11-15 Fe-Cr-Mn-Si system), the influence of Mn and Si addition on melting time was evaluated. An insignificant decrease of melting time is caused by the change in Mn percentage from 12 up to 31.6%. The melting time is varied linearly with the increase in silicon percentage from 2.3 up to 11.3%. This is because of silicon impact on the density and melting interval of the alloys.

The digestion degree is one of the major criteria of ferroalloy rationality. Density, melting temperature, specific oxidability are the primary factors responsible for the digestion degree. Specific consumption and consistency of elements digestion are governed by the alloy digestion degree.

According to the data review the chromium digestion by steel from ferrochrome varies from 70 to 95%, from silicochrome – from 80 to 98%, and the governing factors for digestion are the technique of ferroalloy adding into metal and its oxidation. Data on composition of chromium-containing ferroalloys are not available in the literature.

The experiments to determine the chromium digestion degree by steel were carried out in the high-temperature resistance furnace. The alundum crucible with the 100-150 g steel ingot was heated up to 1600°C, than ferroalloy lumps of 5-15 mm size was added, the time gap was 10 min. After equalizing the melt was mixed, crucible was taken out and cooled in air. The ferroalloy charge was to obtain 5% of Cr in steel. Chemical composition of steel for experiment was the following: Cr – 0.03%; Mn – 0.0023 %; Si – 0.05%; C – 0.021 %, the balance Fe.

K is the chromium digestion degree as defined in equation:

$$K = \left({[Cr]_{st}} / {[Cr]_{fer}} \right) \cdot 100\% \quad , \qquad (1)$$

where: $[Cr]_{st}$ is the chromium content in steel after experiment, $[Cr]_{fer}$ is the chromium quantity added into steel. The experimental results are listed in Table 3.

Table 3: Chromium digestion degree by steel out of ferroalloy *.

Alloy number	Component content in steel after experiment %				Ingot weight, g	Weight of Cr in charge, g	Weight of Cr in alloy, g	Cr digestion degree, %
	Cr	Mn	Si	C				
1	2.80	0.01	0.06	0.03	130.5	6.03	3.65	60.6
3	4.26	0.01	0.35	0.04	127.4	6.57	5.43	82.6
5	4.75	0.01	2.02	0.03	128.7	6.73	6.11	90.8
7	4.79	0.01	4.50	0.04	119.6	6.43	5.85	91.0
9	4.21	0.01	0.08	0.23	121.5	7.05	5.12	72.6
10	4.46	0.06	0.56	0.35	131.3	7.02	5.86	83.4
11	4.72	0.90	0.59	0.03	136.5	7.10	6.44	90.7
14	4.65	1.78	0.2	0.04	170.1	9.6	7.91	82.4

* – initial chemical compositions of the ferroalloy samples are listed in Table 1

As for the Fe-Cr-Si system (1, 3, 5, 7 alloys), the relationship between digestion degree and silicon content was investigated (Figure 3). The 1st alloy has the lowest chromium digestion degree (60.8%) owing to low percentage of silicon (0.5%). The 5th and 7th alloys have the largest values of chromium digestion degree (90.84 and 90.98 %, respectively), they contain the increased quantity of silicon 26.5 and 42.0 %, respectively. The 3rd alloy have reduced chromium digestion degree (82.62%) in comparison with the alloys (5, 7), probably it can be dedicated by relatively low silicon content (10%). Silicides of different types are formed when silicon interacts with chromium, besides Si acts as the steel deoxidizer preventing a chromium interaction with oxygen. The values of chromium digestion degree are evidence of the fact that the key factor for digestion is a silicon content (at 5-10% of Si or higher) in ferrochrome. In alloys a significant increase in silicon content can lead to loss of simplicity of ferroalloy production technology.

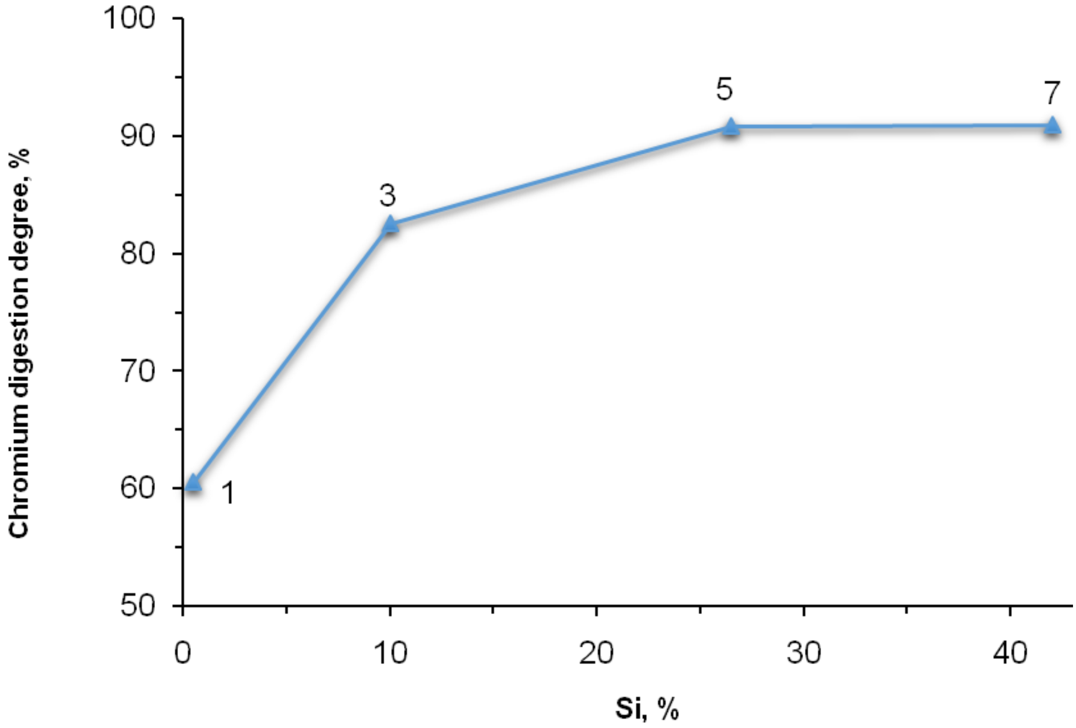

Figure 3: Relationship between chromium digestion degree and percentage of silicon in alloy. Alloys numbers are listed in Table 1.

Carbon content effect on chromium digestion degree of carbonaceous ferrochrome was evaluated. As for the alloys (1 and 9, the Fe-Cr-C system), the effect of the increase percentage of carbon up to 7.2% is the chromium digestion degree growth from 60.6 up to 72.5%.Chromium is bound in carbides in the alloys in the result of carbon content increase; carbides interact with oxygen at the stage of ferroalloy addition into steel.

The influence of silicon content in high-carbon ferrochrome on chromium digestion degree was assessed using the alloys (9 and 10) as an example. The existence of increased percentage of silicon exerts a very positive influence on the chromium digestion degree; it is increased from 72.5 to 83.4%.

In the complex alloys (11 and 14, the Fe-Cr-Mn-Si system) the effect of silicon on chromium digestion degree were estimated at rather constant ratio of other elements. The percentage of silicon 11.3 and 2.3% is in compliance with the chromium digestion degree of 90.7 and 82.4%.

The alloys having reasonable values of characteristics possess high values of chromium digestion degree starting from 82.6%. The alloys (1, 9, and 14) have unreasonable values of characteristics; their digestion degree is 60.6, 72.56 and 82%, respectively. The 14th alloy has non-optimal value, but its melting temperature is sufficiently low and melting time is short, all these reasons exert increase in chromium digestion degree.

3 CONCLUSIONS

The obtained experimental results (under laboratory conditions) about chromium digestion are in line with the literature data about chromium digestion degree attained under commercial conditions. Hence, the rational way to improve chromium digestion degree in steel is to increase silicon content in chromium ferroalloys, the effect of the increased percentage of carbon and manganese in alloy is only small growth of chromium digestion by steel at rather constant content of other elements.

Application of ferrochrome with increased content of silicon can result in improvement of technology and quality of treated steel owing to decrease in consumption of ferrosilicon used for smelting. The production of ferrochrome with ~5% of silicon will not require any significant revision of existing technology. Some increase in the alloy prime cost will be compensated by lesser chromium consumption for steel making due to increase in digestion degree.

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