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Ferroalloy Quality for Electric Steelmaking with Nonmetallic Inclusion Control

Gasik M. I.[1], Panchenko A. I.[2], Sal`nikov A. S.[2]

[1]*National Metallurgical Academy of Ukraine*
4 Gagarin Ave., Dnipropetrovsk, 49600, Ukraine
[2]*JSC "Dneprospetsstal"*
81Yuzhnoe Shosse, Zaporizhzhya, 69008, Ukraine

Data about quality of ferroalloys used for electric steelmaking and alloys with special properties controlled by specified nonmetallic inclusions according to GOST 801-78 and ASTM E-45 (method A) are generalized and analyzed. Results of investigation of matrix and proeutectoid phases in the structure of industrial carbonaceous ferrochromium with application of electron microscopy and electron probe microanalysis as the main alloying ferroalloy at roller-bearing steel ШХ15СГ-В smelting are presented.

Keywords: FERROALLOYS, STANDARDS, MICROSTRUCTURE, MATRIX AND PROEUTECTOID PHASES, NONFERROUS IMPURITY METALS, CARBONACEOUS FERROCHROMIUM, ELECTRON MICROSCOPY, ELECTRON PROBE MICROANALYSIS, NONMETALLIC SILICATE AND SPINDEL INCLUSIONS

Introduction

The complex of strength, plastic, anticorrosive and other properties of alloyed electric steel and special purpose alloys is defined in many respects by proeutectoid precipitated phases of endogenetic origin (oxides, nitrides, sulfides, phosphides) and also impurity non-ferrous metals in the structure of rolled (cast) metal. During formation and development of electric furnace steelmaking mainly alloyed, high-alloyed steel and special purpose alloys were smelted in small capacity arc furnaces at small specific power values of furnace transformers with a rigid control of all properties of metal. This fact caused system investigation of all factors, including effect of ferroalloy quality on properties of metal products. Collected results of laboratory research carried out in main laboratories of electric steel shops, research institutes and high schools were regularly generalized and analyzed. Obtained results were used not only for improvement of smelting process but also for reconsidering corresponding standards and specifications accompanied by more severe restricted parameters of steel and alloy quality.

Large-scale development and further implementation of electric arc furnaces of large unit capacity with electric steel smelting of mass application with equipping shops by ladle-furnaces and vacuum vessels unedged attention of steel producers to the important issue of using high quality ferroalloys. It is necessary to mention that there are companies producing ferroalloys with the use of secondary raw materials along with ferroalloy production plants. They, as a rule, deliver ferroalloys according to developed provisional technical specifications without account of non-metallic inclusions and impurity non-ferrous metals in ferroalloys.

Results and Discussion

The standard makers under the "pressure" of mass applied large-scale steel producers "improved" the standards by not only reducing grades of certain ferroalloy kinds but also decreasing amount of impurity non-ferrous metals and elements - non-metals regulated by specification documents. So, for example, standard GOST 1415-78 provided production of 20 ferrosilicon grades. Along with the main element (silicon), 8 impurity elements, including Ca and Ti were regulated. In the international standard GOST 1415-93 number of grades is reduced to 8, Ca and Ti are expelled from impurity elements. Thus in standards GOST 1415-93 and DSTU 4127-2002 ferrosilicon grades FS75, FS60 (0.05 % Ti; 0.5 % Ca) and FS70 (0.1 % Al; 0.04 % Ti and 0.1 % Ca) “disappeared”. Therefore ferrosilicon producers do not control and do not guarantee delivery of alloy with titanium and calcium.

Lime carbonate (fluxing stone) is added in the furnace with the charge (quartzite and coke breeze) during ferrosilicon smelting according to technology on ferroalloy plants in order to remove refractory slag. Calcium content in ferrosilicon grows and changes from 0.3 to 0.8 %. At the same time, high and unstable content of calcium in ferrosilicon has a negative effect on type and amount of non-metallic inclusions in bearing electric steel, though the delivery control of rolled metal batches of all five dimensional groups is carried out by results of rolled metal impurity appraisal by points according to GOST 801-78 and ASTM E-45 (method A) [1].

No regulated non-ferrous impurity metal content in reconsidered standards unreasonably lowered the interest of researchers and electric steel and special purpose alloy producers to research of ferroalloy quality effect on complex of properties of finished metal products. Data generalized in [2, 3] confirm the effect of ferroalloy quality.

It is established in papers of Electrometallurgy Department of National Metallurgical Academy of Ukraine and "Dneprospetsstal" that using ferrochromium vacuum-treated in a liquid state at IX13 steel smelting raised its plasticity because of less amount of non-metallic inclusions. Using ferroalloys with lower content of non-ferrous metals - impurities (Pb, Sn, Sb, Zn, Bi) enabled to reduce bad quality steel from 30.8 to 4 %. Corundum particles in aluminothermal ferrochromium at ЭИ 483 steel smelting are found to be a reason of metal susceptibility to hot cracks. Tears during piercing X18H13M3T steel ingots smelted in arc furnaces of Zlatoustovskiy Iron & Steel Works are caused by high content of lead brought in by ferromolibdenium and ferrotitanium. Application of ferrosilicon FS75 teemed by conveyor machines and with high hydrogen content caused 30ХГСА steel rejection on flakes.

When ultra low carbon corrosion-resistant chromium-nickel steel smelting the application of vacuum heat ferrochromium produced under technology developed at Electrometallurgy Department instead of expensive aluminothermal chromium enabled to improve electric steel quality and provide pipe & tube industry with high-grade tubular billet without electroslag remelting [4].

It follows from industrial experience of "Dneprospetsstal" that replacement of ferrosilicon FS65 with not restricted content of calcium by ferrosilicomanganese MnC17 at ШХ15СГ-В electric steel smelting enables to raise yield on non-metallic inclusions from 63 to 90 %. Thus, mentioned-above data show that it is possible to raise quality of electric steel and lower discarded metal on non-metallic inclusions as a result of researching all the factors, including quality of ferroalloys affecting the properties of steel metal products.

Up-to-date methods and equipment for ferroalloy quality control

The current state of methods and equipment for ferroalloy quality control are generalized in [5]. Also there are results of content of basic elements and impurities (O, N, C, S) as well as types of non-metallic inclusions in the industrial ferroalloys (FeMo, FeNb, FeTi70, FeTi35).

Methods and instrumentation applied to define the content of basic elements and impurities in ferroalloys are shown in **Figure 1**.

It follows from **Figure 1** that analysis of ferroalloy quality depending on the target task can be carried out with application of one of three groups or their combination. The first group (chemical analysis) is subdivided in two subgroups of methods with dissolution and not dissolution of ferroalloy samples. Dissolution of FeMo is recommended in the mixture of acids $HCl + HNO_3$ (3:1), FeNb ($HF + HNO_3$; 1:3), FeTi70 and FeTi35 - in HCl. The ferroalloy solute is analyzed on device ICP-AES (combination of test method with atomic emission spectrometer). Results are represented in element-by-element type. Analysis of ferroalloy samples without dissolution is carried out on device SEM-EDAX. Impurity elements O and N are defined on LECO (type TC436 DR); C and S - by infared absorption method. Accuracy of carbon definition is ±4 ppm, sulfur - ±2 ppm. Microstructure is examined using Philips XL30FEG and energy-dispersive spectrometer (EDS). Results of representative specimens of industrial ferroalloys of silicothermal production method (FeMo) and aluminothermal smelting (FeNb, FeTi70, FeTi35) are resulted in **Tables 1, 2**. It follows from **Table 2** that the most of oxygen is in ferrotitanium FeTi35 and FeMo. At the same time, nitrogen content in FeTi35 is 2 ppm among observed ferroalloys. The high content of sulfur is observed in FeMo (614 ppm) that is related to its presence in oxidated molibdenium concentrates which are initial for smelting FeMo.

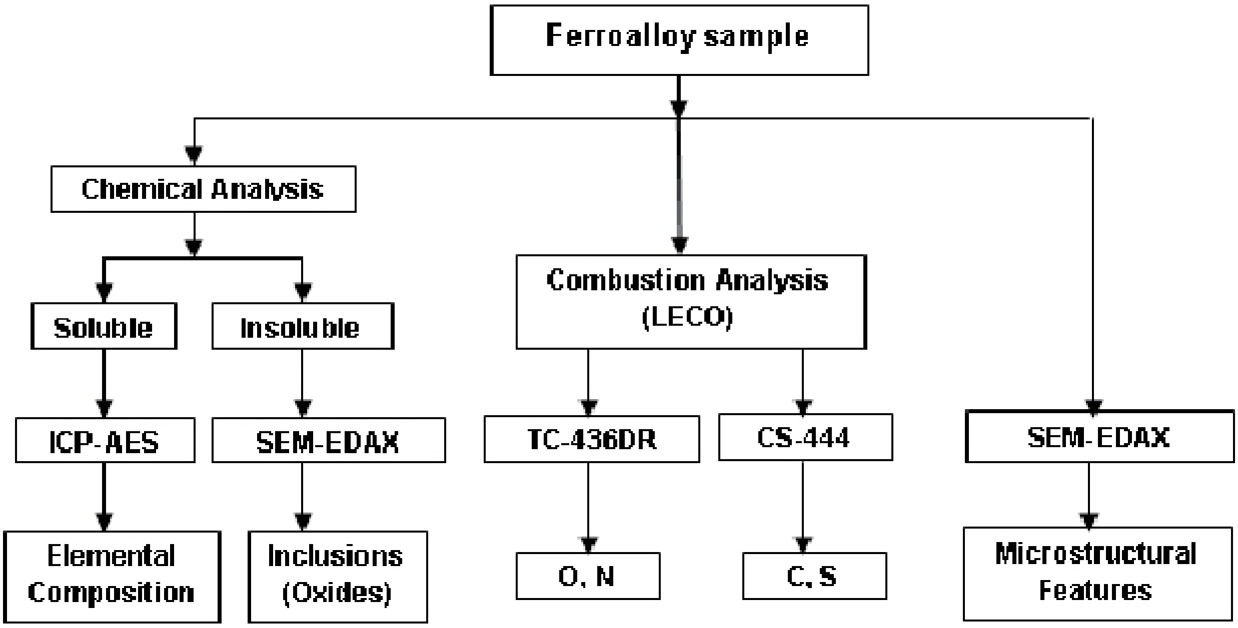


Figure 1. Methods of ferroalloy quality investigation [5]

Table 1. Chemical composition of ferroalloys defined by dissolution of samples with application of ICP device and atomically chemical spectrometre (AES) (Figure 1) [5]

Ferroalloy	Al	Ca	Fe	Mg	Mn	Mo	Nb	Ti	V
FeMo	0.85	-	27.98	-	-	70.36	-	-	-
FeNb	0.94	-	30.21	0.69	0.23	1.39	65.84	0.43	-
FeTi70	2.48	-	24.95	-	0.25	0.13	0.36	69.62	1.83
FeTi35	5.05	0.22	50.56	-	0.63	-	0.16	42.17	0.42

Table 2. Content of impurity elements in ferroalloys defined by combustion analysis (oxidation, combustion) (LECO), ppm [5]

Ferroalloy	O	N	C	S
FeMo	6047	63	681	614
FeNb	354	18	508	106
FeTi70	1859	20	1179	65
FeTi35	6476	2	845	221

It is important to note that in ferromolibdeniumproduced by silicothermal method (possibly silicoaluminothermal method) non-metallic inclusions are presented by silicates of binary system SiO_2-Al_2O_3 and ternary system CaO-SiO_2-Al_2O_3 (**Figure 2**). Two ternary compounds are known in this system: helenite $Ca_2Al_2O_7$ (t_{melt} 1539 °C) and anorthite $CaAl_2O_8$ (t_{melt} 1553 °C).

It is necessary to assume that three-componental non-metallic inclusions of system CaO-SiO_2-Al_2O_3 gravitate to concentration fields contoured by threefold system SiO2-$SaAl_2Si_2O_8$-$Al_6Si_2O_{13}$. Non-metallic inclusions in ferrotitanium FeTi70 are presented by corundum (α-Al_2O_3) and aggregated precipitations of system Fe-Ti-Al_2O_3.

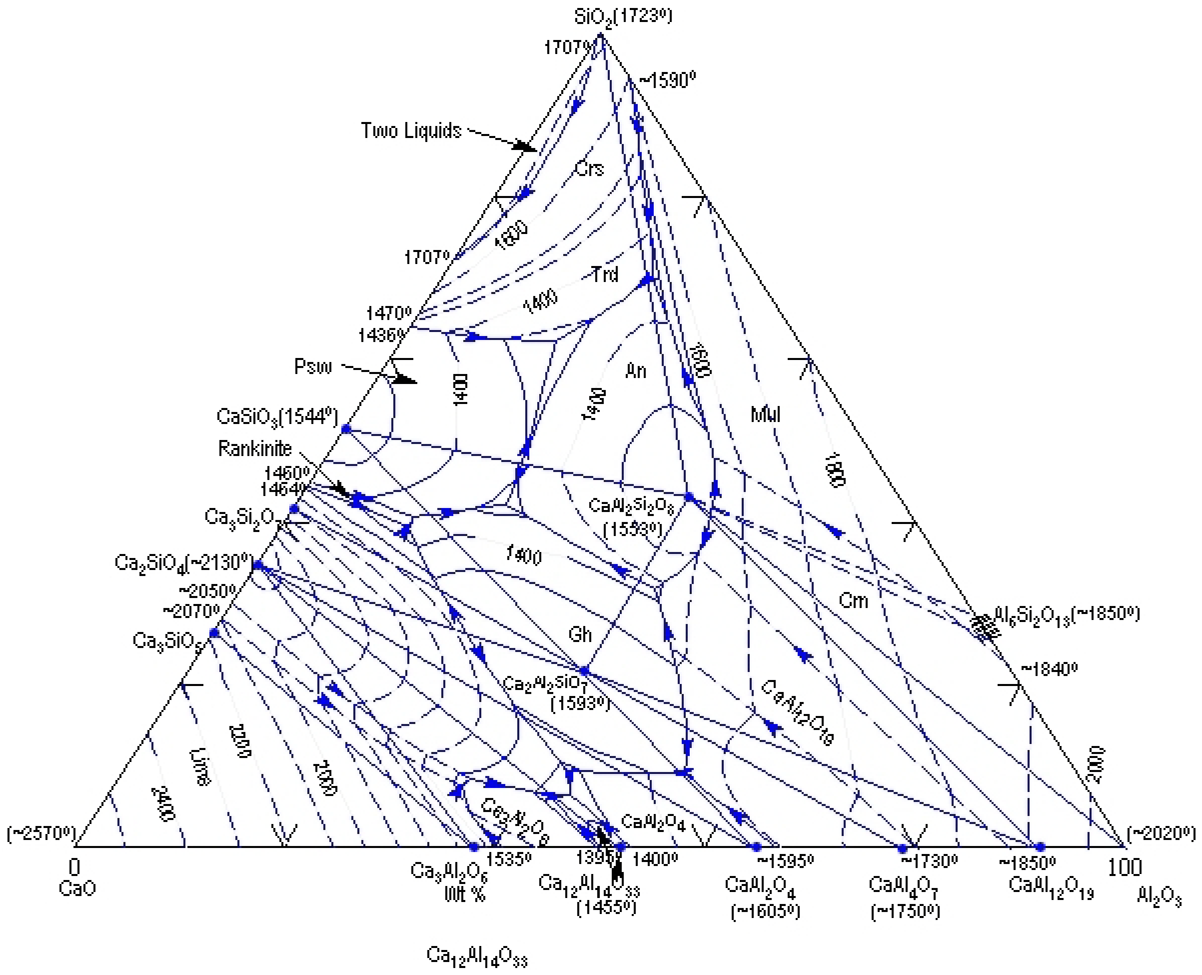


Figure 2. Structural diagram of system CaO-SiO_2-Al_2O_3

Thus, physic-chemical nature of inclusions (silicates, oxides, spinels) is defined by both properties of base metal systems of ferroalloys and silico - and aluminothermal methods of their smelting.

Experimental research of microstructure and chemical composition of base and proeutectoid phases in the industrial ferrochromium FC800

According to previous investigations the microstructure of carbonaceous ferrochromium FC800 is presented by chrome iron carbides and solid solution of carbon and silicon in the matrix phase enriched with iron (α- solid solution) (**Table 3** [6]). Proceeding from system Cr-Fe-C data, the alloy at 60-70 % Cr is melted at 1680-1700 °C. Silicon in the industrial ferrochromium FC800 reduces its fusing point.

Analysis of **Table 3** shows that there are no data on distribution of sulfur and phosphorus in the industrial ferrochromium FC800. At the same time, the level of sulfur and phosphorus content in ferrochromium FC800 ingots is one of the factors defining its quality and possibilities of using in electric steel smelting with quality control on nonmetallic and sulfidic inclusions.

In connection with urgency of studying the nature of sulfur and phosphorus as well as their distribution between the structural components in the industrial ferrochromium FC800 ingots, precision investigation of ferrochromium microstructure features is carried out in present work. Structure, chemical composition of base and proeutectoid precipitated phases of ferrochromium FC800 are investigated on electron microscope GSM-6360 with energy dispersive spectrometer - microanalyser REMMA 101A. Microanalysis is carried out on ferrochromium polished microsections. In each analyzed phase (noted by a check mark on the microstructure photo) we recorded energy dispersive spectra which are quantitatively processed using a special program on PC. Quantitative processing of spectra included definition of intensity of analytical lines of chemical elements present in the spectrum.

Chemical composition (% by weight) of researched FC800 ferrochromium samples (batch 7376) is presented in **Table 4**. Microstructure of ferrochromium FC800 obtained on the electron microscope in reflected secondary electrons is shown in **Figure 3a**. Energy spectra of elements in certain phase points (**Figure 3c**) revealed at hand inspection in the electron microscope are obtained. The results of quantitative processing of spectra are presented in table (**Figure 3b**). It is impossible to define the content of carbon and oxygen because of electronic instrumentation features. Ferrochromium microstructure (**Figure 4**, upper left) is presented by well observed structural phases: 1) light phase (white field); 2) dark phase (well contoured precipitations) and 3) black phase. The area of polished microsection with accumulation of black-colored phase is chosen for X-ray spectrum microanalysis to show a scheme of sulfide inclusions arrangement in relation to basic structures of carbide phases of carbonaceous ferrochromium FC800.

Table 3. Quantitative composition, volume content, microhardness of structural components of carbonaceous ferrochromium FC800

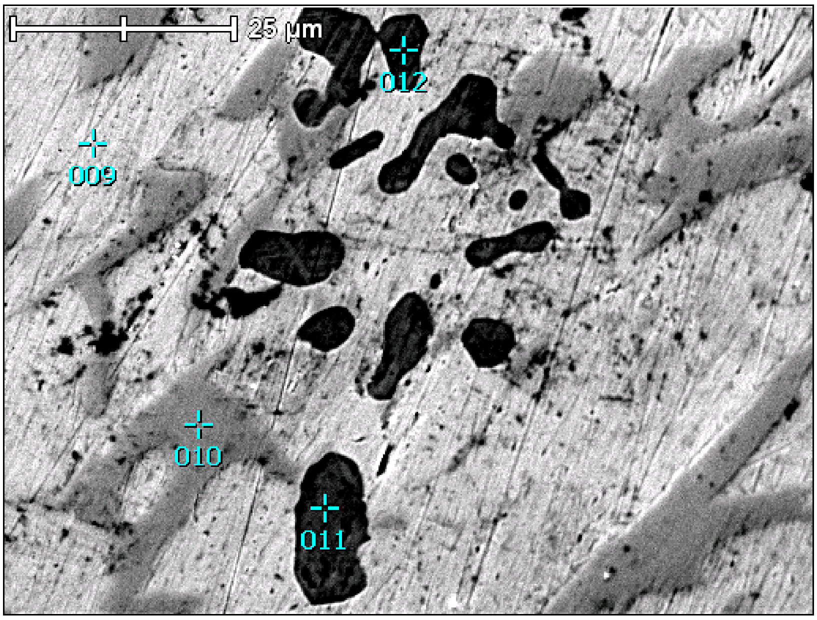
Structural components	Volume fraction of phase, % vol.	Element content, % mass.			Microhardness, H_V, kgf/mm^2
		Cr	Fe	other	
carbide $[Cr,Fe]_7C_3$	65	82.0	11.0	9.0 C	1710±50
carbide $[Cr,Fe]_{23}C_6$	11	72.5	24.5	5.6 C	1230±30
α-solid solution	24	30.0	62.0	7.0 Si	730±50
		25.0	74.0	5.6 Si	480±50

Table 4. Chemical composition (% by weight) of FC800 ferrochromium samples

	C	Cr	Si	P	S
certificate	7.61	69.63	0.87	0.025	0.031
factory inspection	8.00	70.00	0.87	0.030	0.028

It follows from data (**Figure 3b**) that the light phase (on the photo +009) is a matrix phase depleted by chromium with dissolved silicon, phosphorus and nickel. The second contoured dark phase (+010) can be identified as a complex chrome iron carbide $[Cr_{74,24}Fe_{23,77}]\ _7C_3$. The black phase (dagger +011) is presented by chromium sulfide. In system Cr-S there are six phases CrS, Cr_7S_8, etc., each of them has a narrow area of homogeneity. Sulfide CrS (59 % Cr and 41 % S) has a monoclinic lattice (a = 0.3826 nanometers, b = 0.5913 nanometers, c = 0.6089 nanometers, β = 101°36′). And CrS lattice constants depend on cooling rate that is related to homogeneity area at high temperatures. Sulfide CrS is melted at 1567 °C, heat of formation $\square H^{o}_{298}$ is 155.49 kJ/mole. Ratio %Cr: % S is 2.16 in sulfidic black phase that above than 1.43 in sulfide CrS of stoichiometric composition. Thus, the black phase represents a chromium sulfide with deficiency of sulfur atoms CrS_1 which is caused apparently by the temperature and kinetic conditions of melt crystallization at formation of carbonaceous ferrochromium ingot structure. Microprobe analysis of "black" phase (dagger +012), which is of a little different color than sulfide phase (dagger +011), represents a chromium-manganese sulfide phase in which approximately half of chromium atoms are substituted by manganese ones. Manganese sulfide MnS is thermodynamically stronger compound $\square H^{o}_{298}$ = 213.18 kJ/mole than sulfide CrS. Sulfide MnS is melted also at 1530 °C [7]. During crystallization of carbonaceous ferrochromium, carbide crystals rich in carbon $[Cr, Fe]\ _7C_3$ are originally formed. The mother metal is enriched by impurity elements, and temperature drop and reduction of sulfur solubility in the melt, sulfide inclusions CrS and [Cr, Mn]S precipitate.

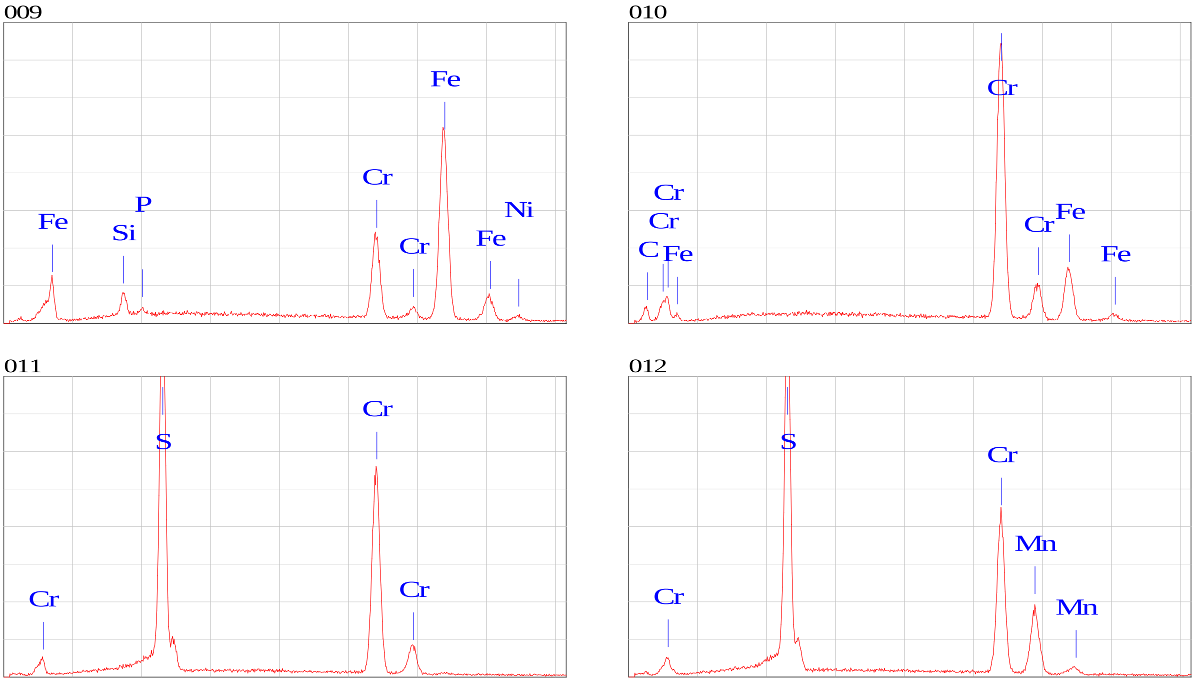
Analysis of ferrochromium microstructure obtained by means of X-ray spectrum microanalysis in mapping regime of each element (**Figure 4**) is of interest. The distribution between carbides confirms that the light-dark phase (dagger +010) is enriched in carbon which confirms the possibility of its identification as $[Cr, Fe]_7C_3$. The light phase (dagger +009) contains less carbon as compared to the dark phase.



a

Point No.	C	Si	P	S	Cr	Mn	Fe	Ni	Total,%
009		1.56	0.35		18.61		76.58	2.91	100
010	1.99				74.24		2377		100
011				31.62	68.38				100
012				29.11	50.30	20.60			100

b



c

Figure 3. Results of X-ray spectrum microanalysis of phases in FC800 alloy structure**:** *a* – daggered analysis points; *b*– approximate chemical composition according to X-ray spectrum microanalysis results, *c* – spectrograms from analyzed points

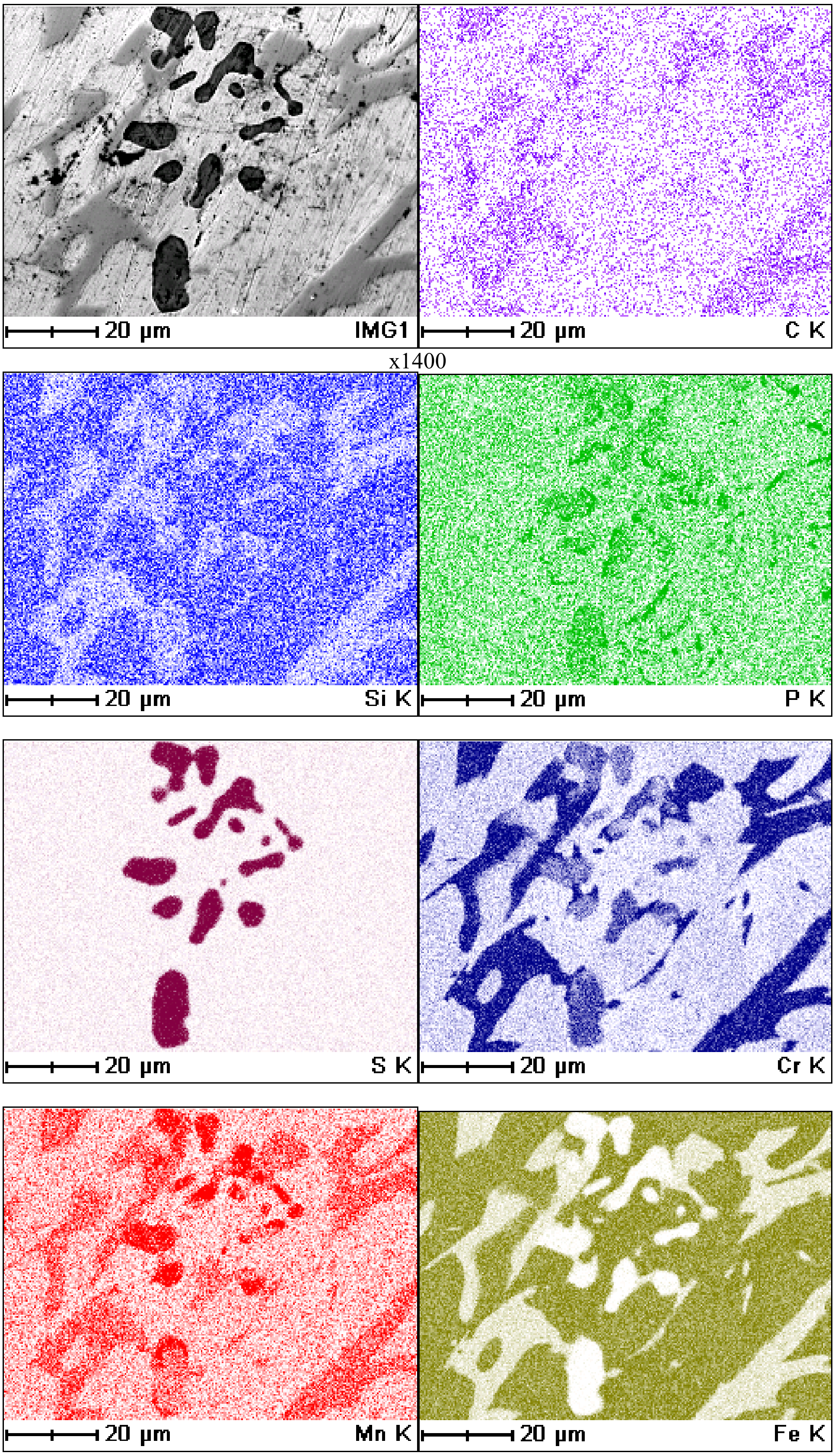


Figure 4. X-ray spectrum microanalysis results of carbonaceous ferrochromium FC800 microstructure section in mapping regime; distribution of C, Si, P, S, Cr, Mn and Fe between structural phases of ferrochromium

Silicon is concentrated in the light phase and is absent in the carbide [Cr, Fe] $_7C_3$. Phosphorus concentrates in precipitations in the area of polished microsection where sulfide phase is concentrated. Precipitations enriched in phosphorus are apparently formed during the crystallization of eutectics with complicated chemical composition. The map "sulfur" confirms that chromous sulfide CrS_1 as well as chrome-manganese sulfide [Cr, Mn] S_{1-y} have contoured phase boundary lines in ferrochromium structure.

Analysis of "chromium" map testifies that the basic amount of chromium is concentrated in the complex chrome iron carbide $[Cr, Fe]_7C_3$. Manganese is distributed among observed microstructures nonuniformly. The highest content of manganese is in chrome-manganese sulfide precipitations; the part of manganese is concentrated in the carbide phase as well which is possible to present as $[Cr, Mn, Fe]_7C_3$. The light phase is enriched in iron (76.58 %).

Spinel and silicate inclusions in ferrochromium FC800

The important quality index of ferroalloys including ferrochromium FC800 is amount, chemical composition and mineralogical nature of nonmetallic oxygen-containing inclusions. When investigating ferroalloy microstructure by using X ray spectrum microanalysis, as mentioned above, it is impossible to define oxygen concentration and study these inclusions. It is established that amount and physic-chemical nature of inclusions in ferrochromium with and without carbon depends on silicon content in it [8]. At silicon content to 0.6-0.8 % there are thermodynamically strong high-melting spinel inclusions $FeO{\cdot}Cr_2O_3$; above 1.2 to 1.8 % Si - silicate inclusions of chromium of $Cr2+O\text{-}SiO_2$ system; and in the interval 0.8-1.2 % Si - silica-spinel inclusions. Along with study of physic-chemical nature of oxygen-containing inclusions in carbon-free ferrochromium produced by silicothermal method, the effect of silicon on the nature of inclusions in carbonaceous ferrochromium FC800 is studied. Silicon concentration is 0.3 and 1.6 % in the investigated representative specimens of ferrochromium. Non-metallic inclusions are observed by chlorine-vacuum method. Investigations are carried out in the cooperation of Institute of Metallurgy and Materials Technology of National Academy of Science of Georgia and Electrometallurgy Department of National Metallurgical Academy of Ukraine. Results are shown in **Table 5**.

Data from **Table 5** confirm that there are high-melting spinels $FeO{\cdot}(Cr, Al)_2O_3$ in the structure of ferrochromium ingots at low silicon content. Thus it is important to note that the content of spinel inclusions is much more as compared to their amount in ferrochromium with 1.6 % Si. The feature of silicate inclusions in ferrochromium FC800 is that they are presented by 80.4 % low-melting silicates of chromium and only 19.6 % spinel. According to cited we can conclude that when using ferrochromium FC800 with various silicon content for alloying of bearing steel ШХ15СГ-В which quality is controlled on non-metallic inclusions according to GOST 801-78 and ASTM E-45 (method A) it is necessary to take technological measures for transformation of spinel inclusions by corresponding rational parameters of semi-finished metal product deoxidation on ladle-furnace and at vacuum treatment.

Table 5. Chemical and phase composition of oxide inclusions in carbonaceous ferrochromium FC800 with various silicon concentration

Content Si, %	Content of inclusions, %	Phase composition of inclusions,%		Chemical composition of phases					
				spinel			silicate		
		spinel	silicate	FeO	Cr_2O_3	Al_2O_3	SiO_2	Cr_2O_3	FeO
0.3	0.210	83.2	16.8	8.3	76.2	15.5	20.9	71.6	8.1
1.6	0.095	19.6	80.4	6.1	81.8	12.1	60.1	32.7	1.5

Conclusions

1. The requirements of current standards for ferroalloys concerning the content of basic elements and impurity non-ferrous metals are analyzed. It is noted that reduction of ferroalloy grades and regulated impurity elements of non-ferrous metals in the republished standards (GOST, DSTU, Specifications) is not always justified in view of electric steel smelting with quality control by point appraisal of amount and types of non-metallic inclusions.

2. Data about current methods and instrumentation for definition of basic elements, impurity non-ferrous metals and non-metallic inclusions in ferroalloys are presented. The

complex approach to estimation of ferroalloy quality and the modern instrumentation for definition of chemical composition of ferroalloys, content of impurity elements O, N, C and S, and also composition and amount of non-metallic inclusions is considered.

3. The microstructure of carbonaceous ferrochromium FC800 is investigated using electron microscopy and X-ray spectrum microanalysis; energy spectra of metals in the ferrochromium ingot structure and quantitative data on chemical composition of carbide phases, solid solutions, sulfide precipitations observed in the structure are obtained. Distribution of elements Si, P, S, Cr, Mn and Fe among structural components of carbonaceous ferrochromium FC800 is investigated by X-ray spectrum microanalysis method in mapping regime.

4. Effect of silicon concentration in the standard carbonaceous ferrochromium FC800 on amount and nature of oxygen-containing non-metallic inclusions is analyzed. There are high-melting spinels $FeO{\cdot}(Cr, Al)_2O_3$ in the structure at silicon content to 0.6-0.8 %. At silicon concentration over 1.2-1.8 % low-melting silicates of chromium of system $CrO\text{-}SiO_2$ are formed; in the interval 0.8-1.2 % Si there are multiphase inclusions consisting from spinels and silicates.

5. When bearing steel smelting with the use of carbonaceous ferrochromium FC800 it is necessary to consider the possible effect of spinels and silicates in the industrial ingots on composition and amount of non-metallic inclusions in the rolled section.

References

1. M. I. Gasik, A. I. Panchenko, A. S. Sal`nikov, S. L. Mazuruk. *Stal*, 2009, No. 6, pp. 25-28.*
2. M. I. Gasik, V. S. Ignatyev, A. F. Kablukovskiy, S. I. Khitrik. *Gasy i Primesu v Ferrosplavakh*, Moscow, Metallurgiya, 1970, 152 p. *
3. L. N. Gasik, V. S. Ignatyev, M. I. Gasik. *Structura i Kachestvo Promyshlennykh Ferrosplavov i Ligatur*, Kyiv, Tekhnika, 1975, 142 p. *
4. M. I. Gasik (Ph.D. thesis, Dnepropetrovsk Metallurgical Institute, 1968). *
5. M. M. Pande, M. Guo, Guox. *Impurities in Commtrcial*, I NFACON XII 2010, Helsinki, Finland, June 6-9, 2010, Vol. 2, pp. 935-944.
6. I. A. Bespalkova, V. S. Ignatyev, A. N. Alybina, et al. *Collection of Papers “Physico-Khimicheskiye Issledovaniya Malootkhodnykh Protsessov v Electrotermii*, Moscow, Nauka, 1985, pp. 137-143. *
7. O. Kubashevsky, S. B. Olkokk. *Metallurgicheskaya Termokhimiya*, Moscow, Metallurgiya, 1982, 392 p. *
8. M. I. Gasik, I. S. Khitrik, L. P. Shchesno. *Izvesiya Vuzov. Chernaya Metallurgiya*, 1963, No. 11, pp. 78-87. *

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Качество ферросплавов для выплавки электростали с контролем проката по неметаллическим включениям

Гасик М.И., Панченко А.И.,
Сальников А.С.

Обобщены и проанализированы данные о качестве ферросплавов, используемых для выплавки электростали и сплавов со специальными свойствами и контролируемые по регламентируемым неметаллическим включениям по ГОСТ 801-78 и ASTM E-45 (метод А). Представлены результаты исследования матричных и избыточных фаз в структуре промышленного углеродистого феррохрома с применением электронной микроскопии и РСМА, как основного легирующего ферросплава при выплавке подшипниковой стали ШХ15СГ-В.