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PROSPECTS OF BARIUM-CONTAINING FERROALLOYS PRODUCTION AND APPLICATION FOR NON-FURNACE TREATMENT OF STEEL AND CAST IRON

Ivan Ryabchikov[1], Viktor Kovalev[2]

[1]*NPPgroup, Chelyabinsk, st. Vaudreuil-40, p. 25*
Russia
E-mail: npp180@gmail.com
[2]*Energoterm-system, Istra, st. Panfilov, 51-A*
Russia

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ABSTRACT

The article describes the qualitative characteristics of alloys containing magnesium, alkaline-earth and rare earth elements, titanium and zirconium, for deoxidation and modifying of steel. Quality parameters of the alloys - multicomponent composition, low melting temperature, chemical and structural homogeneity of the compositions, a low oxidation, are discussed. The efficiency of multicomponent alloys with microcrystalline structure is associated primarily with exposure to molten steel as a universal barium deoxidizer and inoculant steel.

Keywords: deoxidizer modifier, quality, structure, steel components, solubility, ionization potential, solutions, enthalpy, interaction, iron, barium, lanthanum.

INTRODUCTION

Energy-saving and resource-saving technologies of barium-containing and calcium-containing ferroalloys are based on application of the carbon-thermal method and the cheap natural raw materials usage. The technical and economical indications of carbon-thermal process depend largely on the mode of burden preparation for melting [1].

Worldwide used carbon-thermal modes of silicon complex ferroalloys production are based on lump burden materials application and is realized only by short-term campaigns at much surplus (more than 20 %) of carbon in the burden. Alongside the application of the lump burden leads to the necessity of frequent correction of the burden composition due to its high-rate heterogeneity which means uneven distribution of ore proportion and carbon reducer. Small reagents contact surface results in decline of the elements reduction speed and production indicators deterioration. Even small deviation in the burden composition of required level causes consequences for the liquidation of which it is necessary to make laborious operations of the burden materials charging directly to the top of dome-covered furnace.

One of the prospective trend for improvement of complex ferroalloys quality, production cost decrease and solution of ecological issues is the briquetting of the burden. Virtually, the briquetting is a conformable stage of the development of mining and metallurgical industry caused by the necessity to process powder concentrate made of low-sort complex ores. In some foreign countries such as USA, Germany, Japan and others the fractions of finished articles are subjected to briquetting.

The burden briquetting allows to use fine fractions of cheaper ore and carbon materials (lime stone, quartz sand, coke siftings, coal, etc.).

Inside an ore-coal briquette there is a much increase of electrical resistance resulted by the increased number of contact resistances throughout the current way. This process, in its turn, provides the possibility to increase the furnaces working power and their capacity coefficient that lead to an increase of the depth of electrode dipping into the burden, top temperature decline, improvement of filtering capability and consequently - to the heat efficiency coefficient of ore-reduction furnace.

Distribution evenness of burden components and comparatively vaster contact surface of the reagents result in acceleration of the reduction process and increase of element extraction rate out of raw materials. Alongside, the briquetting allows redistribution of the carbon reducer which means to give the surplus into one part of the burden in order to cause reduction of one kind of elements and give the shortage into the other part of the burden with the aim of deceleration of the reduction process of the other elements. Consequently, the briquetting process allows to take control over chemical reactions, optimize the chemistry of the process, decrease the reduction temperature for the elements and power-consumption of ferroalloys production.

THE PRODUCTION AND APPLICATION OF BARIUM-CONTAINING FERROALLOYS

For obtaining barium sulphates with silicon dioxide, causing the oxide-sulphide melt formation and removal of the basic quantity of sulfur out of burden, it is advisably to briquette all the burden components. Alongside, favorable conditions for the silicon and barium carbides are created. There is a certain number of refractory carbides in the lower layers of the furnace basin, this number of refractory carbides prevents from turning of $SiC – BaC_2$ – oxide-sulphide melt system into liquid state [2], also it allows decrease the passing speed of burden and increase the temperature up to the point needed to form barium silicides.

The burden preparation for melting was carried out with consideration of physical-chemical features of silicon combined reduction out of dioxides and barium reduction out of sulphate by carbon. The briquettes intended to the silicon-barium melting process contained barite concentrate (SS 4682-84), quartz sand and gas coal. The melting process of silicon-barium was started in well-heated furnace with capacity of 1.6 MV·A and FS45 ferrosilicon melting process was carried out for 2 days.

The very beginning of the briquettes charging was carried out with an increased depth of electrode dipping into the burden. The burden did not cake its passing even with small-sized lumps falling. Silicon-barium melting process was carried out totally with slag-free process. In two hours and forty minutes the alloy was let out of the furnace into an iron pan formed with sand. Metal tap hole was opened with a steel stick without electroburning. After metal was let out, a gas torch shot up off the outlet. There no slag output was observed.

One of the main indicators characterizing economical effectiveness and ecology of silicon-barium melting while using briquettes is the technological process stability, as well as the high rate (93 - 94 %) of barium extraction into the alloy and slag-free process.

43.2 GJ or 12.0 MWh is the specific power-energy consumption when silicon-barium (30 - 35 % of Ba) is made of the briquettes in the furnace with capacity of 1.6 MV·A. For comparison, when ferrosilicon melted with barium (15 - 25 % of Ba) of lump burden in the furnace with capacity of 21 MV·A, this indicator had been recounted to 1 base ton (30 % of Ba) and it was 59.9 - 70.2 GJ or 16.6 - 19.5 MWh [2].

The chemical composition stability and increased content of barium in the alloy made of briquetted raw materials are important indicators of high-rate consumption properties of the modifier needed to ferrous-carbon alloys processing.

The most important feature of the silicon-barium and other complex ferroalloys production with the usage of briquetted burden is the possibility to produce exactly fixed components correlation in a briquette without any surplus of carbon in the burden. It allows to realize a stable self-organized technological process and to provide energy and resource saving.

The production mode of complex silicon ferroalloy has been developed on the base of obtained data [3]. The essence of the new mode is that gyps and\or celestine and/or barite and/or limestone are used as an ore proportion of the burden, the correlation of quartz sand and ore proportion in the burden is supported within 2.0 - 100.0.

Recently conducted researches allow to make conclusion about opportunity and advisability of various ferroalloys melting including highly-silicon sorts of ferrosilicon (FS75, FS90) from briquetted raw materials. All the new technologies can be qualified as an impetus in the ferroalloys manufacture area.

Ferrocarbon melt treatment with chemically active elements, its profound degassing process, modification and micro-alloying are known to be an essential part of contemporary technologies of competitive items and items of high quality production. However, decline of the effectiveness of steel non-furnace treatment is caused by the limited assortment, bad quality and consequently high production cost of silicon ferroalloys and modifiers manufactured by native and foreign industries.

The increased content of aluminum (up to 3 %) in ferrosilicon causes certain difficulties in production of high-rate exploitation properties rail steel and wheel steel because the residual content of aluminum in this steel must be less than 0.005 %. It is conditioned by the fact that high-aluminous inculcations causes shear tension inside the matrix [4]. The hardly solvable problem is to prevent formation of oxide aluminous inculcation in the steel in the conditions of aluminum high-rate deoxidizing property, poor and unstable assimilation of calcium by liquid state metal.

The high-aluminous inculcation contamination of steel can be decreased in the conditions of calcium-containing deoxidizers (SK30, Fe-Ca) replacement by the barium-containing complex alloys and complex alloys containing other elements. The situation is proved by thermodynamic calculation results [5] and certain industrial tests conducted when melted rail steel and wheel steel [6 - 9]. V.V. Pavlov and L.V. Korneva demonstrated [4] that the usage of silicon-barium in melting process of rail steel causes the suppression of emission of non-metallic inculcation (NI) dressed by Al_2O_3 as well as the «stitches» formed of them. This situation is caused due to the powerful energetic links in $BaO\text{-}Al_2O_3$ system. So, the heat of $(-\Delta H^0_{298})$ $BaO{\cdot}Al_2O_3$ formation from oxides is 100.3 kJ/mol, for $CaO{\cdot}Al_2O_3$ - totaling 15.0 kJ/mol [10] in its ordinary state.

The application of complex barium-containing and calcium-containing modifier for the wheel steel melting has resulted in sulphides form improvement and decline of NI total number in comparison with the process of metal treatment by silicon-calcium. Barium-containing modifier has also provided higher rate of the steel mechanical properties. The rate of stroke viscosity of the experimental metal was 15 % higher than the same rate of the metal treated by silicon-calcium. It is proved that the rate of calcium assimilation out of complex alloy is twice more than its assimilation out of silicon-calcium (13.3 and 5.9 %) in the conditions of the same expenditure of wire powder filler (0.5 kg/t) and similar duration of blow (8 - 12 min) [11].

With the aim of explanation of the obtained results there were an implementation of some calculations and conduction of comparison between deoxidizing and modifying properties of alkaline-earth elements (AEE). It is proved that the deoxidizing and modifying properties of widespread used silicon-calcium are considerably poorer than the same properties of strontium, and barium (almost three times more effective) [1].

The solutions of AEE in liquid iron indicate considerablly positive deviations from the ideal solutions. This statement can be formulated the other way: the atoms of the above named elements interact pushing from each other. The experimental determination of mixture enthalpy in Fe-AEE (Ca, Sr, Ba) system is impossible due to the full incapacity of the components to be mixed at liquid state. Thereat, the increase of element ordinal number (from calcium to barium) comes along with decrease of these elements solution properties in liquid iron [12]. In accordance with the same sequence there is an increase of enthalpy of Fe-AEE alloys formation. So, according to the data of A.S. Dubrovin [13], the maximum heat rate of interaction of calcium, strontium and barium between iron, calculated with the application of cell model, is 128, 185 and 212 kJ/mol. The calculation made by S.D. Gromakov provides the maximal figure of ΔH when calcium and barium are dissolved in iron at temperature of 1700 K, 130 and 300 kJ/gram-atom, 400 and 1000 kJ/gram-atom by the F. Kohler's equitation consequently. As the authors consider [14] that ΔH estimation according to F. Kohler is suitable for the discussed systems only in the conditions when $\chi_{Me} \leq 0.2$.

Thus barium, as one of the AEE, possesses unique complex of physical and physical-chemical properties such as minimal rate of solubility in liquid iron, high boiling temperature (1637^0C) which is superior to the temperature of liquid steel, maximal figure of solution enthalpy in iron.

The iron and silicon from the alloy dissolve when barium- containing complex alloy is dipped into liquid steel, but barium as insoluble in liquid steel leads the system to the extremely unbalanced state due to the fact that it has comparably high density (3.3 g/sm^3) and as a result of powerful interaction with iron influences actively the liquid steel structure stirring it up. Iron pushes the barium out of the melt actively and as a result it disperses much up to nano-particles and separate atoms. Comparably coarse atoms of barium (r_{Ba} = 0.217 nm) acted by pushing strength and they are forced to get through dense layers of heavy but smaller-sized atoms of iron (r_{Fe} = 0,124 nm) [15], making the powerful inter-atomic energetic action spreading throughout the melt mass. Therefore non-furnace treatment of ferrocarbon melt by barium-containing complex alloys can be classified as nano-technology of modifying by barium.

Barium possesses powerful active surface properties and while cast the steel, it is capable to prevent the steel surface from the interaction with air due to a multiple increase of its surface concentration [16]. Intensive interaction between barium and iron as well as its powerful dispersing make favorable conditions for coagulation of the liquid NI from one hand, and formation of finest barium-containing combinations from the other hand. Thereat, described above relatively high thermodynamic stability of barium aluminates and considerable lowering of Al_2O_3 edge angular wetting by liquid steel while being dipped barium into it, leads to cleaning up of the steel from dangerous high-aluminous inculcations.

As barium possesses the described above complex of physical and physical-chemical properties, it is capable to process the whole metal mass with more velocity. It is demonstrated experimentally that steel deoxidation velocity by barium is higher than by the unlimitedly soluble aluminum in iron [15].

It is well-known that the more carefully the melt is cleaned up from the admixtures the higher is the point of its supercooling. Therefore the liquid steel profound cleaning up from gases and NI by barium increases the point of its supercooling, turning the suspending into solid state by accelerated crystallization process accompanied by formation of unbalanced structures. Later, by means of prolonged keeping the items made of steel processed by barium, the unbalanced structures undergo relaxation causing improvement of physical-chemical properties of the metal.

Using the suggested mechanism of barium effect on the steel there is opportunity to explain the phenomenon of essential increase (by 6 - 7 %) of rails plastic properties in two months after they have been made of steel modified with barium [6].

The application of barium-containing modifiers at iron foundry manufacture is very prospective one. It is demonstrated [17] that only 0.05 - 0.10 % of silicon-barium dipped into liquid iron suppresses almost completely the carbides formation in the structure of iron, also it increases isotropy of properties, balances the chemical and structural heterogeneity of metal in various cross-sections of the casts. In a combination with micro-alloying by manganese when dipped a mixture of silicon-barium and silicon-manganese, there is a possibility to produce two or three iron sorts with plate graphite of one initial melt [1].

The solution of improvement the quality of cast and deformed steel, reducing its content of NI, can be found in the production and use of complex alloys containing AEE, rare earth elements (REE) and other reactive elements.

Many years of practice of use in a number of metallurgical and engineering enterprises in Russia and abroad of complex deoxidants and modifiers for steel series INSTEEL®, produced in the NPP group has proven their high efficiency. Compared with the mechanical blends, the alloys with microcrystalline structure obtained by the technology of the hardening liquid state, have the following advantages:

- The dissolution rate of microcrystalline alloy in the molten steel is greater than a mechanical mixture due to the lower (150 - 200°C) melting temperature of multicomponent alloys. This significantly reduces the pyroelectric effect and allows a 4 fold increase in feed rate of powder into the ladle wire [18];
- The increased reactivity of the barium in comparison with calcium that leads to outstripping its effect on the molten metal, higher and stable calcium absorption, effective micro-alloying element in the crystallized steel [19];
- The content of disperse fractions (less than 0.063 mm) in microcrystalline alloys made from thin (0.5 - 3.0 mm) of the plates is four times less than in the powder filler wire made by crushing larger pieces of standard ferroalloys [20];
- Low alloy saturation of dissolved gases (H, N) due to the high crystallization rate of the alloys in the casting.

At the present time, microcrystalline multicomponent alloys are prepared by melting silicobarium, ferrocerium and other components, mainly Chinese production, in induction furnaces. The fusion in an open oven leads to appreciable losses of reactive elements, increased oxidation of the alloy and its high cost. Therefore, of particular importance is the development of coal chemical production technologies of silicobarium with calcium ferrosilicotitanium, ferrosilicozirconium and other complex alloys with low (< 2 %) of aluminum with a significant decrease in their value [21].

When using multi-component alloys can form complex composition of refractory oxide and oxysulfide compounds and eutectics. For example, with the addition of silicon alloys to steel with barium, strontium, titanium or zirconium as deoxidation products can be compounds $BaSrSi_3O_8$, $BaSiTi_2O_7$, $BaSiTiO_5$, $BaZrSi_3O_9$ with melting points 1325, 1250, 1400, 1450^0C, respectively [22].

The system BaO-CaO-SiO_2 has a eutectic $BaSiO_3$-$CaSiO_3$, melting at 1268 ^0C. Thus, in contrast to steel deoxidation with silicocalcium, silicobarium or use of the alloy Si-Ca-Ba may result in more complete removal of the metal liquid deoxidation products. In this anticipatory effect barium having compared to calcium greater reactivity [23] can increase the uptake of calcium metal more than 3-fold (from 5.0 to 15.7 %) at a relatively high stability of its contents in the steel. Along with this replacement of the calcium complex ferroalloy Si-Ca-Ba-treated steel 20FL allows to increase the toughness KSV_{-60} with 29 %. Additional introduction of zirconium alloy Si-Ca-Ba in an amount of 6 - 10 % leads to a further increase in toughness of the steel with 18.9 to 22.9 J/cm^2 [18]. Application of multi-component alloy (Si-Ca-Ba-REE-Al) in the smelting of high-strength shipbuilding steel allows to increase by 10 % the level of reduction in the thickness of the sheet [18, 24].

Deoxidation iron with barium-containing alloys (15.2 % Ba; 0.8 % Al; 49.2 % Si; Fe - the remainder and 8.1 % Ba; 33.4 % Al; 30.8 % Si, Fe - the remainder is) performed in the open induction furnace at a temperature of 1600^0C [25].

The alloys in a steel shell were injected into the melt at the bottom of the magnesia crucible. The process of deoxidation with barium, practically insoluble in iron, is carried out faster than the aluminum deoxidation. There is also a high rate of removal from the melt of NI. X-ray analysis of the deoxidation products revealed the complex barium compounds: $BaO{\cdot}Al_2O_3$ and $BaO{\cdot}Al_2O_3{\cdot}2SiO_2$. The conclusion of the authors [25] for steel deoxidation is for possible complete replacement of the aluminum with complex barium-containing alloys.

I.S. Kulikov believes that the limited solubility ofAEE in liquid iron shows high capacity of the deoxidizing element in the gaseous state. He conducted the thermodynamic analysis carefully and reached to the conclusion about the effectiveness of steel deoxidation with barium [26]. According to I.V. Ryabchikov and collaborators [27] the deoxidizing of liquid steel with barium has certain thermodynamic and kinetic advantages over deoxidation of metal with calcium.

Some authors [28, 29] associate the high modifying ability of barium with a relatively large size of the atoms and the minimum value of the electronegativity, which characterizes the ability of atoms not to give, but to attract electrons. Dimensionless electronegativity values according to Pauling and Allred of calcium to barium are reduced, but not significantly, and the absolute barium electronegativity is greater than that of calcium (232.5 and 212.3 kJ/mol, respectively). The values of the potential or ionization energies of atoms were determined with more precision than the electronegativity in [15].

I.V. Gavrilin believes that an effective modifier, acting by the absorption mechanism must have the following conditions [30]:

- have a low solubility in the solid metal and limited liquid;
- donate free electrons to the metal, i.e., have a low ionization potential;
- locate on the boundaries of crystals and clusters, but does not enter into their composition.

Iron does not form a chemical compound with lanthanum, magnesium and AEE. All other REE formed with iron one or more (up to 4) compounds [31].

The extent of the effect of modifying, according to I.V. Gavrilin, can be estimated from the difference between the ionization energy and the matrix modifier: $E_{mat} - E_{mod}$. The second factor, which characterizes the activity of the element is a solubility in the matrix. He proposed the formula for determining the ability of a modifying factor elements in the iron:

$$\mu=(E_{Fe} - E_{мод})/C,$$

where C is the solubility in liquid iron element.

The calculated values of the coefficients modifying the ability of magnesium and AEE are shown in Table 1 [21].

From the Table 1 is seen that widely used calcium for modification of steel in modifying capacity is sig-

Table 1. Coefficient of the modifying ability of magnesium and AEE in liquid iron [21].

Element	C, at. % at 1600^{0}C [20]	E_{Fe} - E_{M}, kJ/mole	μ
Mg	2,26	131,9	58,36
Ca	$7{,}82\cdot10^{-2}$	585,6	$77{,}88\cdot10^{2}$
Sr	$1{,}78\cdot10^{-3}$	706,6	$39{,}70\cdot10^{4}$
Ba	$1{,}22\cdot10^{-4}$	852,4	$69{,}86\cdot10^{5}$

nificantly inferior to strontium and barium. So the value of μ for strontium in 51 times higher than for calcium, barium and the modifying capacity is by almost three orders of magnitude greater than the calcium. These coefficients for magnesium and AEE are significantly different from those given in [28, 30]. For example, the modifying ability of Mg, Ca, Sr and Ba is 1.33, 1.97, 2.15 and 2.44, respectively [28].

In molten metal the atoms interact: they attract ($\Delta H<0$), or repel to each other ($\Delta H > 0$). In the first case, the melts are negative, in the second - the positive deviation from the ideal state. For sufficiently large negative values ΔH, the atoms form chemical compounds with positive - repel each other, exerting vigorous physical and chemical effects on the melt.

Thus, barium has a maximum capacity of modifying as in the coefficient of modifying ability (Table 1), and in the enthalpy of dissolution of elements in liquid iron. Physico-chemical interactions of barium-iron reaction can be expressed: $Ba_{liqiud}+Fe_{liquid} = [Ba\text{-}Fe]$, flowing with the formation of an unstable pseudo solution. Gibbs energy change for this reaction $\Delta G = \Delta H - T\times\Delta S$ indicates the possibility of its occurrence in the $T\cdot\Delta S > \Delta H$, i.e. for large values of the entropy factor. On the possibility of an energetic interaction between barium and iron indicate the high rate of deoxidation of iron alloy Fe-Si-Ba [25] and the effect of barium on the total weight of the treated steel [6, 9, 18] at very low solubility in the liquid metal.

For improving the efficiency of barium application as a modifier a barium-containing alloy should be injected into the molten metal after preliminary deoxidation and desulfurization, and the absence of contact with air (for example, in the form of cored wire with stirring in a ladle by argon).

The given data testify to the universal role of barium as a deoxidizer and modifier of steel.

The prospect of the use of barium alloys in steelmaking practice is confirmed in the furnace steel processing. Using the alloy Si-Ca-Ba when processing metal transport has led to its deep cleansing of NI milled grain structure, increase the ductility and toughness of the cast and deformed steel [6, 9, 18]. The mechanism of action of barium in steel is presented in [21].

CONCLUSIONS

Multi barium-containing alloys with a microcrystalline structure are effective scavengers and modifiers of the steel. They offer not only high speed steel deoxidation, but also removal of metal inclusions, grain refinement and increased toughness. High-performance processing of steel containing barium alloys is due to the low ionization potential of barium, its low solubility in liquid iron and barium high energy interaction with iron. The universality of the role of barium as a deoxidizer and modifier steel is discussed.

REFERENCES

1. I.V. Ryabchikov, Modifiers and technologies of non-furnace treatment of ferrocarbon alloys, ECOMET, Moscow, 2008, (in Russian).
2. I.V. Ryabchikov, I.A. Kopyrin, Burden molded for ferroalloys melting is basis of technologies of future, Silicon ferroalloys. Scientific transaction of SRIM, Metallurgy, Moscow, 1988, (in Russian).

3. Patent of Russian Federation № 2414519, Mode of silicon complex ferroalloy production, 2011, bul. № 8, (in Russian).
4. V.V. Pavlov, L.V. Korneva, Interaction of «metallic matrix – non-metallic inculcation» system in rail steel, Scientific reports collection, JSC «Ural Institute of Metals», Ekaterinburg, 2010, (in Russian).
5. I.V. Ryabchikov, A.Yu. Akhmadeev, V.V. Andreev, Metallurgical modes of improvement of Russian rails exploitation properties, Steel, 2011, 1, (in Russian).
6. A.A. Deryabin, V.V. Pavlov, V.V. Mogilny and others, Effectiveness of nano-technologies of rail steel modifying with barium, Steel, 2007, 11, (in Russian).
7. N.A. Fomin, V.I. Vorozhishev, V.Ya. Monastyrsky and others, Production of high-rate cleanness rail steel, Steel, 1991, 3, (in Russian).
8. V.A. Golubtsov, K.Yu. Demin, Yu.S. Demin and others, Application of complex barium-containing modifiers for improvement of wheel steel quality, Steel, 2009, 12, (in Russian).
9. K.V. Grigorovich, K.Yu. Demin, A.M. Arcenkin and others, Prospects of barium-containing alloys application for deoxidizing and modifying of transport metal, Metals, 2011, 5, (in Russian).
10. O. Kubashevsky, K.B. Olkokk, Metallurgical thermochemistry. Translation from English, Metallurgy, Moskow, 1982, (in Russian).
11. I.V. Ryabchikov, L.G. Shub, R.G. Usmanov and others, Increase of modifiers consumption properties by means of their chemical and structural compositions improvement, Steel, 2010, 1, (in Russian).
12. Yu.A. Ageev, S.A. Artchugov, Research of alkaline-earth metals solubility in liquid iron and their base alloys, Journal of physical chemistry, 1985, T. LIX, 4, (in Russian).
13. A.S. Dubrovin, Metallothermy of special alloys, Published by South Ural State University, Chelyabinsk, 2002, (in Russian).
14. E.D. Pletneva, Yu.I. Esin, V.V. Litovsky, S.E. Demin, Enthalpy of alkaline-earth metals combining with iron and nickel, Izvestiya VUZov. Ferrous metallurgy, 1985, 8, (in Russian).
15. J. Emsli, Elements. Translation from English, World, Moskow, 1993, (in Russian).
16. I.Yu. Pashkeev, G.G. Mikhailov, Barium influence on contact interaction of X18H10T steel with oxidized materials, Reporter of South Ural State University, 2005, (in Russian).
17. N.N. Alexsandrov, Iron casts and main ways of their quality improvement, Foundry manufacture, 1977, 11, (in Russian).
18. V.A. Golubtsov, I.V. Ryabchikov, K.I. Yarovoy and others, Efficacy of barium-containing complex ferroalloys for steelmaking, Steel, 2013, 8, (in Russian).
19. L.A. Poznyak, P.L. Brodetsky, B.F. Belov and others, On the role of the shape and composition of the inclusions in the process of destruction and steel 10G2FT and 15GF, Metallurgy and heat treatment of metals, 1986, 11, (in Russian).
20. O.Yu. Sheshukov, M.V. Lapin, I.V. Nekrasov and others, Quality of steel and structure modifiers, Newsletter ferrous metallurgy, 2014, 8, (in Russian).
21. I.V. Ryabchikov, V.G. Mizin, V.V. Andreev, Siliceous ferroalloys new generation, Published by Chelyabinsk State University, Chelyabinsk, 2013, (in Russian).
22. N.A. Toropov, V.P. Barzakovskiy, V.V. Lapin, Diagrams of silicate systems: Handbook. V. 3, Science, Leningrad, 1972, (in Russian).
23. I.V. Ryabchikov, A.G. Panov, A.E. Kornienko, About the qualitative characteristics of the modifiers, Steel, 2007, 6, (in Russian).
24. V.G. Milyuts, V.V. Tsukanov, E.Yu. Levagin, V.A. Golubtsov, Effect of treatment of barium-containing modifiers microcrystalline high-quality shipbuilding steel, Problems of Materials Science. Science and technology magazine, 2014, 1, 77, (in Russian).
25. Shi Yufang, Chen Boping, Fu Jie, Ei Gammal Tarek, Experimental study on deoxidation of barium and barium alloy, J. Mater. Sci. Technol., 1999, 15, 5.
26. I.S. Kulikov, Deoxidation iron alkaline earth metals, Proceedings of the Academy of Sciences of USSR, Metalls, 1985, 6, (in Russian).
27. I.V. Ryabchikov, V.A. Golubtsov, K.I. Yarovoy, R.G. Usmanov, Can barium deoxidize the steel, Newsletter ferrous metallurgy, 2014, 9, (in Russian).
28. A.A. Deryabin, E.Yu. Berestov, On the mechanism of modification become alkaline earth metals, Proceedings of XIII International Conference «Modern problems of steel electrometallurgy», Published by South Ural State University, Chelyabinsk, 2007, P.I., (in Russian).
29. G.Ya. Goldstein, S.V. Pashenko, E.Yu. Radchenko

and others, Features of the modifying effects of barium in the furnace of steel melt, Proceedings of the VIII International Congress of Steelmakers, Polevskoy-Moscow, 2014, (in Russian).

30. I.V. Gavrilin, Melting and crystallization of metals and alloys, Published by Vladimir State University Publishing House, Vladimir, 2000, (in Russian).
31. N.P. Lyakishev, The phase diagrams of binary metallic systems, Handbook. V. II, Engineering, Moscow, 1997, (in Russian).