POTENTIAL FOR OBTAINING AND APPLYING COMPLEX NIOBIUM FERROALLOYS

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Abstract. This paper provides information regarding the application of niobium in industry and the scale of its production in the world and the Russian Federation. Most of the niobium deposits in Russia consist of pyrochlore, apatitepyrochlore and columbitepyrochlore types of ores. They contain a significant amount of phosphorus. Therefore, all enrichment schemes for these ores contain a dephosphorization stage which increases the price of the product and reduces the degree of niobium extraction. The paper explores the possibility of improving the end-to-end production scheme: niobium ore – beneficication – niobium ferroalloy. The bulk of ferriobiium is intended for steel microalloying and can be replaced by complex ferroalloys with a reduced niobium content. The paper considers the issues of obtaining complex niobium ferroalloys from a rough concentrate with a weak content of niobium. It has been established that the addition of 25 – 40 % of silicon or 12 – 30 % of aluminum to the two component metal system Fe–Nb causes the transfer of ferriobiium (15 – 20 % Nb) from the refractory category to low melting materials. The crystallization temperatures are less than 1400 ºC. The substantiation of using a complex niobium ferroalloy instead of ferriobiium is given. This alloy has reduced niobium content and increased silicon or aluminum content. Higher service characteristics of the complex ferroalloy are noted in comparison with ferriobiium (temperature of the initiation of crystallization and density). They indicate an increased assimilation of niobium when using a complex ferroalloy for steel microalloying. The paper presents data on the possibility of dephosphorization of niobium concentrates in the process of pyrometallurgical production of a complex ferroalloy. An improved scheme for the production of niobiumcontaining ferroalloys is proposed. This consists of the use of niobium concentrate for melting the intermediate ferroalloy containing a reduced concentration of niobium oxides and an increased concentration of silicon (aluminum). This ferroalloy can be used effectively for steel microalloying with niobium.

Keywords: niobium ore, beneficication, complex niobium ferroalloy, dephosphorization, pyroselection, diatillation

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ПЕРСПЕКТИВЫ ПОЛУЧЕНИЯ И ПРИМЕНЕНИЯ КОМПЛЕКСНЫХ NIОБИЕВЫХ ФЕРРОСПЛАВОВ
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Аннотация. В работе приведены сведения об областях применения ниобия и масштабах его производства в мире и РФ. Большинство ниобиевых месторождений России представлены пирохлоровыми, апатит-пирохлоровыми и колумбит-пирохлоровыми типами руд, которые содержат значительное количество фосфора. В связи с этим, все схемы обогащения данных руд содержат стадию дефосфорации, сужающую продукт и снижающую степень извлечения ниобия. В работе изучена возможность усовершенствования сквозной схемы производства: ниобиевая руда – обогащение – ниобиевый ферросплав. Основная масса феррониобия предназначена для микролегирования стали и может быть заменена на комплексные ферросплавы с пониженным содержанием ниобия. Рассмотрены вопросы получения
Due to their unique properties, rare metals (RMs) and their compounds play a key role in scientific-and-technological advancement, while being the basic components of many high-performance materials and technologies [1]. Out of 36 RMs, 19 are included in the list of main types of strategic minerals, including niobium [2 – 4].

The annual world demand for niobium reaches 100 Kt. Approximately 90 % of niobium as ferroalloy (ferroniobium, 60 – 65 % Nb) is used by the steelmaking industry for alloying and producing structural high strength steels, heat resistant, fireproof, and superconducting alloys [5 – 7].

At the present time, the main factors which determine the niobium market are increased niobium consumption in structural steel and the wide use of niobium-based alloys in the production of aircraft engines [8].

In recent decades increasing niobium application in Russia and all over the world has mainly been connected with its earlier use for improving corrosion resistance of heat resistant and stainless steels (1 – 2 % Nb). Nowadays it is used mainly for strengthening structural steels to a tenth of one percent (manufacturing of large-diameter oil and gas pipes, bridges, parts in the automobile and shipbuilding industry, etc.) [7, 9].

In Russia the consumption of ferroniobium has increased from 200 – 300 tpa at the end of the 1990s to 4.5 Ktpa nowadays. At the same time, Russia’s own production of niobium products does not exceed 550 tpa, covering the domestic demand with export.

The production of niobium and its alloys begins with crude ore [10 – 14].

Currently, the main mineral resource base for niobium in Russia is the Lovozerskoye rare-earth niobium deposit in the Murmansk Region [15]. Lovozersky GOK LLC mines the ore, which after being processed in the form of loparite concentrate is then supplied to Solikamsk Magnesium Plant OJSC for the production of niobium oxide. Loparite concentrate processing at the Solikamsk Magnesium Plant produces rare-earth and titanium products, tantalum compounds and niobium commercial products. Domestic production of niobium raw materials in Russia is diminishing and provides only 6 – 9 % of the existing consumption of niobium products [3]. At the same time, Russia possessed promising resources of mineral raw materials, suitable for the production of niobium-containing materials.

In terms of its amount of niobium balance reserves, the Russian Federation ranks second in the world after Brazil [12, 16]. There are 42 deposits on the state balance sheet, including 8 deposits with only off-balance reserves [6, 15].

Other niobium deposits known in Russia are represented by multicomponent projects. These require complex extraction of minerals and components and have different conditions and volumes of sales, increasing the risks of their development [6, 17, 18]. The Katuga deposit in alkaline rocks in the Transbaikal Territory with reserves of 0.47 Mt Nb₂O₅ with average Nb₂O₅ grade in the ores of 0.31 % include: rare-earth (ΣTR – 0.25 %); zirconium
(ZrO₂ – 1.38 %); and cryolite mineralization which complicates its comprehensive development.

The Belozeminskoye Nb–TR-phosphate deposit in the Irkutsk Region is a lithified weathering crust after carbonatites with resources of 0.75 Mt of Nb₂O₅ at an average grade of 1.5 % Nb₂O₅. The Tomtor deposit in the Republic of Sakha-Yakutia is most promising. It possesses rare-earth rare-metal mineralization in carbonatites with resources of 1.2 Mt Nb₂O₅ at an average grade of 3.99 % Nb₂O₅. The Buranny super-rich site within it accounts for 8 % of the deposit resources with an average grade of 6.7 % Nb₂O₅ and 9.3 % TR₂O₅. In addition to the above niobium projects, other niobium deposits are known in Russia, including:

- in carbonatites: Chuktukonskoye, Tatarskoye (Krasnoyarsk Territory), Arbarastakh, Gornoizerskoye (Republic of Sakha-Yakutia), Sredneziminskoye, Bolshtetagninskoye (Irkutsk Region), and Neske-Vara (Murmansk Region);
- in alkaline granites and syenites: Ulug-Tanzegskoye (Tyva Republic), Zashikhinskoye (Irkutsk Region), Taikeu, Longot-Yugan, and Ust-Mramornoye (Yamal-Nenets Region);
- in pegmatites: Vishnyakovskoye, Goltsovskoye (Irkutsk Region), Kolmozerskoye, and Rolmostundrovskoye (Murmansk Region) [10, 15, 17–22].

In order to obtain raw materials suitable for the production of niobium ferroalloys, the ore undergoes processing to produce a concentrate.

Niobium and tantalum are produced mainly from tantalite-columbite, pyrochlore, and loparite ores. The density of niobium-tantalum minerals of these ores is more than 4.5 g/cm³, and the main processing method is gravity. As a rule, ores from placer and bedrock deposits contain associate heavy minerals: magnetite; rutile; ilmenite; zircon; monazite; and cassiterite, inter alia. They also contain frequently occurring minerals of lithium and beryllium whose density is close to the density of host rock minerals (feldspars, quartz). Gravity processing of niobium-tantalum ores in screw separators and concentrates (slime) fractions making up 50 %.

When fine disseminated ores are processed, the heavy minerals are extracted only during fine crushing of the ore. This leads to losses of niobium and tantalum with fine (slime) fractions making up 50 %.

With a content of 0.2 – 0.4 % of Nb₂O₅ in the ore, pyrochlore recovery into rough concentrates exceeds 60 – 70 %. When they are processed to a salable concentrate with a content of 35 – 40 % Nb₂O₅, the pyrochlore recovery in the concentrate can decrease to 40 – 50 %.

During finishing the rough concentrate is screened into four classes. Each class is sent individually for magnetic separation. The magnetic fraction is subject to double re-cleaning. The non-magnetic ±0.2 mm fraction is sent for sulfides and apatite gravity flotation, resulting in the production of a salable pyrochlore concentrate. The non-magnetic fraction with a grain size of −0.2 mm is sent to sulfide and apatite flotation. Then the tailings are concentrated on the tables. Concentrates from the tables are sent for sphene-garnet flotation, producing a salable pyrochlore concentrate and sphene-garnet product.

The processing of niobium-containing raw materials at any deposits by any methods produces middlings which are not only purer, but also more expensive as the processing intensity increases [24–26].

Middling rough niobium concentrates have a lower Nb₂O₅ content and a higher content of detrimental impurities (P₂O₅, SiO₂, etc.). For example, rough concentrates obtained from the ores at the Belozeminskoye deposit contain 15 – 25 % Nb₂O₅, and 3 – 7 % P₂O₅. Finishing these materials to salable concentrates causes significant losses of Nb₂O₅ (up to 20 – 50 %), and an increase in their cost. The technical requirements applicable in Russia require that the pyrochlore ore concentrate for ferroniobium production shall contain (Nb, Ta)₂O₅ no less than 38 %, and impurities per 1 % (Nb, Ta)₂O₅ no more than, %: 0.003 P; 0.005 S; 0.005 C; 0.32 SiO₂; 0.35 TiO₂; moisture 1.0 [1].

According to GOST the content of the leading element in most ferroalloys shall be rather high (65 – 90 %). This requires the corresponding concentration in crude ore for melting as well.

There are a number of studies [27–29], and production data showing that standard ferroalloys often do not have all the necessary performance characteristics [30–32]. The standards for most ferroalloy grades were developed in the mid-20th century for the existing steelmaking technologies.

At the same time, increasing the content of the lead element (Cr, V, W, Mo) in many ferroalloys leads to an increase in the melting temperature of the alloy, contributing to its slower melting and dissolution in steel [33–35]. For example, the crystallization initiation temperature of high-carbon ferrochrome (tₗ) with 45 % Cr is 1570 °C; with 48 % Cr – 1580 °C; with 53.3 % Cr – 1600 °C, and with 63 % Cr – 1620 °C [36]. Ferrovanadium containing 35 % V has tₗ = 1450 °C, whereas for 50 and 75 % V the temperature is 60 and 210 °C higher, respectively [29]. For binary alloys of the Mo–Fe system an increase in the molybdenum content above 37.5 % causes a significant increase in tₗ above 1650 °C.

The melting point of ferroalloys can be reduced by introducing elements such as silicon and aluminum. Their presence in ferroalloys does not reduce the scope of its application, since these elements are present in almost all grades of steel.
The use of multicomponent (complex) ferroalloys for metal microalloying is reasonable with the following elements: Nb, V, B, etc. A small weight of trace elements introduced enables their content in the complex ferroalloy to be reduced. The presence of silicon and aluminum in the alloy does not limit the SiO₂ and Al₂O₃ oxides content in crude ore used for melting of these ferroalloys [37].

The bulk of ferroniobium is intended for steel microalloying and can be replaced with complex ferroalloys with a reduced niobium content.

Selecting the target and associate elements of the alloy enables its sound composition and can provide for the high and stable assimilation of useful elements, fast melting and their uniform distribution in the melt volume.

In order to determine the acceptable chemical composition of the ferroalloy, the physical and chemical properties of synthetic niobium-containing alloys of the Nb–Fe, Nb–Si–Fe and Nb–Al–Fe systems have been studied.

On the one hand the chemical composition of niobium ferroalloys corresponds to the product obtained during processing (concentrate) while, on the other hand, meeting the requirements of steelmakers for ferroalloys intended for steel microalloying with niobium in the ladle.

Ferroniobium (50–60 % Nb) mostly used for steel processing has a high melting point (1560–1900 °C). This creates a number of difficulties for introducing niobium in the steel bath (especially during ladle alloying). It leads to an increase in the time for niobium melting and dissolution. Its assimilation into steel is reduced, the melting time is prolonged, and ferroalloy crushing to <5 – 10 mm and melt purging are required.

The following was considered in developing the composition of new niobium-containing ferroalloys:

– the ferroalloy shall have a melting initiation temperature no higher than 1400 °C and shall melt quickly;
– the ferroalloy will be used mainly for steel microalloying (0.02–0.05 % Nb);
– the ferroalloy shall have the density below the liquid steel density (6–7 g/cm³);
– the alloy shall contain chemically active elements (Si, Ca, Al) corresponding to the processed steel grade, in order to reduce niobium losses.

For the purposes of this research, samples of two- and three-component niobium-containing alloys were melted. The chemical composition of ferroalloys is shown in Table 1.

The crystallization initiation temperature was determined by defining temperature curves during melt cooling. The density of niobium-containing alloys was determined by pycnometric method.

The results of determining the crystallization initiation temperature for alloys are shown in Figure 1.

The crystallization initiation temperatures for the Fe–Nb dual system concur with the liquidus line in the state diagram. For certain compositions the discrepancy is 20–70 °C. Of all the two-component alloys under consideration, only ferroniobium with a low Nb content (10 %) belongs to the category of readily fusible materials \((t_\text{i} = 1390 °C)\). The other alloys of the Fe–Nb system, containing >20 % Nb, are in the category of refractory materials \((t_\text{i} > 1500 °C)\).

The Fe–Si–Nb triple system (section Fe/Nb = 3) contains readily fusible eutectics and refractory silicides of the \((\text{Fe + Nb})_n \cdot \text{Si}_m\) type. The latter clearly affect at 20 % Si content. A further increase in the silicon content (up to 40 %) reduces the crystallization initiation temperature due to transition of the system to the region of readily fusible eutectics.

In the Fe–Al–Nb system (section Fe/Nb = 3), the alloy composition lacks refractory compounds throughout the considered range of aluminum content (5–30 %). As in the dual Al–Fe and Al–Nb alloys, an increase in aluminum reduces the crystallization initiation temperature.

The addition of silicon (25–40 %) or aluminum (12–30 %) to the Fe–Nb two-component metal system results in the transfer of niobium ferroalloys (15–20 % Nb) from the category of refractory materials to readily fusible materials with a crystallization initiation temperature below 1400 °C.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical composition of synthetic niobium ferroalloys(^*), % (wt)</th>
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</thead>
<tbody>
<tr>
<td>Alloy grade</td>
<td>Nb</td>
</tr>
<tr>
<td>FN10</td>
<td>10.0</td>
</tr>
<tr>
<td>FN30</td>
<td>30.0</td>
</tr>
<tr>
<td>FN45</td>
<td>45.0</td>
</tr>
<tr>
<td>FN50</td>
<td>50.0</td>
</tr>
<tr>
<td>FNS10</td>
<td>22.5</td>
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<tr>
<td>FNS20</td>
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<td>17.5</td>
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<tr>
<td>FNS40</td>
<td>15.0</td>
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<tr>
<td>FNA5</td>
<td>23.7</td>
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<tr>
<td>FNA10</td>
<td>22.5</td>
</tr>
<tr>
<td>FNA15</td>
<td>21.2</td>
</tr>
<tr>
<td>FNA20</td>
<td>20.0</td>
</tr>
<tr>
<td>FNA30</td>
<td>17.5</td>
</tr>
</tbody>
</table>

\(^*\) Remaining iron
Industrial alloys are characterized by additional impurities (Ti, Ca, etc.), while the ti values of industrial alloys and those of analogous synthetic alloys are similar. A comparison of the results obtained with the available reference data shows their qualitative correspondence.

The results of defining the density of metal alloys of the Fe–Nb, Fe–Si–Nb and Fe–Al–Nb systems are shown in Figure 2. The highest density is typical for dual iron–niobium alloys. The addition of light silicon and aluminum metals reduces the density of the alloys. Although a decrease in the niobium content to 10 % in the Fe–Nb dual alloy also reduces the alloy density from 8250 to 7650 kg/m$^3$, it does not allow these alloys to be transferred to the category of materials with optimal density values. In order to further reduce the density, light metals, such as silicon or aluminum need to be introduced into the two-component system. The Fe–Si–Nb and Fe–Al–Nb three-component systems with more than 25 % Si or more than 15 % Al under consideration have reasonable density values, both in terms of their production and application for steel melt processing.

When compared to niobium complex alloys, ferroniobium (FN) has the least favorable physical and chemical characteristics. It has the highest crystallization initiation temperature and a higher density than liquid steel (>7000 kg/m$^3$). The survey shows that a reduction in the crystallization initiation temperature of niobium complex alloys occurs with a decrease in the niobium content and increase in the silicon or aluminum concentration. Three-component Fe–Si–Nb and Fe–Al–Nb alloys with a content of 15 – 20 % Nb, 32 – 40 % Si or 12 – 30 % Al belong to the category of readily fusible ferroalloys. In order to achieve reasonable density values, light metals need to be added to the two-component system, for example, silicon (25 – 40 %) or aluminum (15 – 30 %).

Thus, the best physical and chemical characteristics which ensure high service properties are typical of the niobium complex alloys FNS and FNA. These are recommended for wide use in ladle microalloying of steels. These alloys melt quickly in liquid steel while niobium is protected against oxidation by the silicon (aluminum) of the complex alloy. This contributes to a higher assimilation of the lead element.

Complex ferroalloys have been successfully used for niobium microalloying of steel for making car posts, large diameter gas pipes (steel 9G2FB, 10G2BD) at the Nizhni Tagil and Novolipetsk Metallurgical Complexes, as well as the Likhachyov Automobile Factory. Niobium loss during melting did not exceed 4.5 % (10 – 25 % higher than when ferroniobium was used). The obtaining of finer ferrite grains as a result of the introduction of niobium carbonitrides, the more uniform distribution of niobium in the metal, and improvement of the shape of nonmetallic inclusions were also noted.

The majority of niobium deposits in Russia consist of pyrochlore, apatite-pyrochlore, and columbite-pyrochlore types of ores, with a significant amount of phosphorus content. Therefore, all processing schemes for these ores contain a dephosphorization stage. This makes the product more expensive and reduces the degree of niobium transfer to it. At the same time, during the pyrometallurgical production of complex niobium alloys, the melting of alloys with a reduced concentration of phosphorus is possible.

The Institute for Metallurgy and Material Engineering of the Ural Branch of the Russian Academy of Sciences has studied the possibility of processing rough concentrates produced from apatite pyrochlore ores of the Belozaminskoye deposit with dephosphorization by pyroselection and phosphorus sublimation methods.
Pyroselection is difficult since after melting niobium needs to remain in a practically full state of slag after deep phosphorus reduction and transfer to metal. Selective reduction, however, is a complicated physical and chemical process involving the reduction of various oxides, interaction of reduced metal beads with each other and with slag, coagulation of metal droplets, and their precipitation, inter alia.

The physical and chemical characteristics of concentrates and the effect of various factors (amount and type of reducing agent, flux and precipitating agent, melt viscosity, process temperature and duration) on the selective iron and phosphorus reduction resulting in slag with the Nb/P ratio >20 were studied in the laboratory.

The production of a complex niobium ferroalloy from a high phosphorus concentrate with phosphorus pyroselection was studied. The concentrate contained, %: 47.1 Nb₂O₅; 1.2 P₂O₅; 15.8 CaO; 8.8 SiO₂; 1.2 FeO; and 1.5 Al₂O₃. Coke was used as a reducing agent, and cast iron shavings were used as a precipitating agent.

It was found feasible to use two-step melting. In the first step at 1260 – 1450 °C, iron and phosphorus were reduced. In the second step at 1410 – 1450 °C, after completion of the reduction reaction, the viscosity of the melt was reduced and metal beads were precipitated.

The optimal amount of charge materials was determined experimentally: the coke at least stoichiometrically necessary for the reduction of iron and phosphorus; and cast iron shavings ~15 % of the concentrate weight.

This scheme was recommended for further tests.

Industrial melts for the dephosphorization by pyroselection of salable concentrates were carried out in the furnace with a 1100 kVA transformer.

A salable niobium concentrate (38.0 % Nb₂O₅; 4.5 – 6.4 % P₂O₅; 11.4 – 14.6 % Fe₂O₃), cast iron shavings and coke (68 – 73 % C) as raw materials were used.

In order to obtain a low phosphorous content in the slag (<0.5 %) with negligible reduction of niobium in the charge, the excess reducing agent in the charge should be 20 – 40 % of the amount stoichiometrically required for the reduction of iron and phosphorus. Satisfactory results were obtained. The phosphorus content in the slag was quite low (0.1 – 0.3 %) at 34 – 39 % Nb₂O₅. About 99 % of phosphorus passed to the metal and to the gas phase, and the reduction and transition of niobium to metal was less than 1 %. A total of 3 tons of slag was produced.

Industrial technology showed that in principle dephosphorization by pyroselection can be performed in an electric furnace with satisfactory results. Low-phosphorus niobium-containing slag can be used for ferroniobium production by means of the existing flow schemes after crushing.

We studied dephosphorization by sublimation for high-phosphorus niobium raw materials.

We also performed thermodynamic simulation of silicothermal production of niobium ferroalloys from high-phosphorus concentrates. The thermodynamic simulation (TDS) was carried using HSC Chemistry 6.0 software. This allows for calculations of equilibrium compositions and quantities of the formed products using the Gibbs energy minimization algorithm on the basis of the ideas about metallurgical melts as ideal solutions [38, 39].

Table 2 shows the composition of the design concentrate. Figures 3 and 4 show simulation results.

It has been demonstrated that when silicon is added to the amount stoichiometrically necessary for the reduction of iron, niobium, titanium and phosphorus from oxides, there is no complete reduction of niobium and titanium. This is due to the formation of strong niobium silicides in the alloy, while iron is reduced in full. Increasing the amount of silicon up to 130 % of the stoichiometry results in 98.5 and 97 % transition of niobium to the metal phase for compositions 1 and 2, respectively. With a further increase in the amount of the reducing agent the niobium recovery rate tends to 100 %. An excess of silicon up to 250 % increases the titanium recovery rate up to 86 – 88 %.

An increase in the amount of silicon introduced into the system decreases the phosphorus recovery to the alloy due to its sublimation into the gas phase. For composition 1 the maximum degree of phosphorus sublimation is achieved at 156 % silicon. This makes up 52, 59 and 65 % for the temperature of 1500, 1600 and 1700 °C, respectively (Figure 3, a). With a further increase in the reducing agent content the degree of sublimation increases

<p>| Table 2 |</p>
<table>
<thead>
<tr>
<th>Chemical composition of niobium concentrate</th>
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<tr>
<td><strong>No.</strong></td>
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<tr>
<td></td>
</tr>
<tr>
<td>1</td>
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<td>2</td>
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insignificantly (max. 1 %). For composition 2 the maximum degree of phosphorus sublimation is reached only at 250 % silicon, This amounts to 67, 73 and 78 % for the temperatures of 1500, 1600 and 1700 °С, respectively (Figure 3, b).

Figure 4 shows the composition of the metal phase which depends on the amount of the reducing agent. With the stoichiometric amount of silicon introduced into the system, the metal phase formed for the concentrate of composition 1 will contain, %: 79 Nb, 7.0 Si, 6.0 Fe, 1.2 P, and 0.02 Ti. With an excess of the reducing agent of 240 %, the metal phase will contain, %: 49 Nb, 45 Si, 3.0 Fe, 0.4 P, and 7.0 Ti. For the concentrate of composition 2, the metal phase with the stoichiometric amount of silicon will contain, %: 24 Nb, 7 Si, 59 Fe, 12 P, 0.01 Ti. With a silicon excess of 240 %, it will contain, %: 15 Nb, 49 Si, 31 Fe, 2.4 P, and 2.5 Ti. The best indicators in terms of the residual phosphorus content (0.4 %) in the metal were obtained by processing the concentrate with 45 % Nb_2O_5 and 2 % P_2O_5 with production of a complex alloy containing %: 49 Nb, 45 Si, 7.0 Ti, and 0.4 P.

We studied the influence of the melting process parameters on phosphorus distillation and niobium reduction. Melting was carried out in a single-electrode electric furnace with a conductive 55 – 80 kVA bed. The charge consisted of: quartzite (97.5 % SiO_2); semi-coke (53.0 % C; 27.0 % A; 7.0 % V; 8.6 % W) and niobium concentrates (12.9 % NbO; 7.7 % P; 26.2 % Fe_2O_3; 26.4 % CaO; 9.0 % SiO_2); and partially phosphorus-free niobium slag (5 – 8 % Nb_2O_5; 0.4 – 1.5 % P; 23 – 42 % SiO_2). Forty-eight melts were carried out. The content of silicon in the alloy was maintained at a level of 30 – 50 %. Melting was carried out by means of a continuous slag-free carbothermal process with a closed mouth.

The experiments showed the possibility in principle of producing siliconiobium by means of phosphorus distillation in a slag-free process with the required degree
of dephosphorization. The best raw material for melting was lumpy partially dephosphorized niobium slag.

Studies on the production of a complex ferrosilico-niobium alloy determined the dependence of the phosphorus content on the silicon concentration in the alloy (Figure 5). In addition to silicon, the [P] content is influenced by manganese, whose concentration increases the phosphorus content in the alloy with an equal silicon concentration.

In testing the technology under commercial conditions, an electric 1200 kVA furnace was used as a melting unit. At the first stage quartzite, coke and niobium concentrate, containing, %: 25.2 Nb₂O₅; 8.8 P; 20.7 Fe₂O₃; 23.1 CaO; 7.0 SiO₂, were used as a charge. The slag received 45 % P and 96 % Nb. The slag contained 29.6 % Nb₂O₅ and 5.1 % P, and the metal contained 1.1 % Nb; 17.4 % P. As a result of selective melting, partially dephosphorized, processed and pelletized raw materials (as slag) were produced for the next processing stage, as well as ferrophosphorus-forniobium alloy, which can be used for alloying certain cast iron and steel grades.

The second stage was performed in the same furnace lined with coal blocks, using a continuous process with production of ferrosilicon-niobium. The charge consisted of slag, coke and quartzite. The melting process was successful and a small amount of slag (<100 kg/t alloy) was produced. The niobium recovery in the alloy was high – 97 %. The averaged alloy composition was: 16.5 % Nb; 0.4 % P; 40.6 % Si; the rest was iron. In total, ~100 tons of alloy were produced. Dephosphorization by means of transferring phosphorus to the gas phase was 90 %, and in the Nb/P alloy = 38.

In the future, this technology can be used only in sealed ore-thermal furnaces of phosphorus type with phosphorus recovery and disposal.

Conclusions

The paper proposes an improved scheme of producing niobium-containing ferroalloys. This consists in using niobium concentrate middlings containing a reduced concentration of niobium oxides and an increased concentration of phosphorus for melting. This technology allows for melting with dephosphorization to obtain a complex ferroalloy with a reduced amount of niobium and increased amount of silicon (aluminum). This can be used more effectively for steel microalloying with niobium.

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