ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational program 8D07203 – «Metallurgy»

VOROBKALO NINA RUSLANOVNA

RESEARCH AND DEVELOPMENT OF SMELTING TECHNOLOGY FOR NEW COMPLEX TITANIUM CONTAINING FERROALLOY

Relevance and novelty of the dissertation work.

This work is devoted to the research and development of smelting technology for new complex titanium-containing ferroalloy from Kazakhstan raw materials by carbothermic slag-free method.

The relevance of the topic lies in the fact that currently in the Republic of Kazakhstan, there are no industrial enterprises producing ferrotitanium. Consequently, enterprises in need of efficient deoxidizers for producing low- and medium-alloy, heat-resistant grades of steel are forced to use alternative types of ferroalloys that do not fully impart specific properties to steels. As a result, the range of high-strength steels is reduced to a minimum or is completely absent. Multi-stage, multi-component, high cost of raw materials, as well as the unsatisfactory quality of domestic titanium raw materials limit the application of existing traditional technologies for smelting ferroalloys with titanium.

All of the above necessitates the implementation of a complex of research and development work aimed at improving and implementing technological processes for the production of titanium-containing ferroalloys in ore-thermal furnaces using domestic raw materials, with the aim of increasing their production volumes and replacing imports with domestic resources.

The dissertation work was carried out within the framework of a grant project for young scientists on scientific and (or) scientific-technical projects for the years 2021-2023, funded by the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan (IRN AP09058310, №GR0121RK00348), where the applicant was the responsible executor of the project. The priority direction of scientific development is the «Rational use of natural resources, including water resources, geology, processing, new materials and technologies, and safe products and structures». The specialized scientific direction is «New multi-purpose materials based on natural raw materials and industrial waste».

The object of study is the technology of smelting a new complex titanium-containing ferroalloy using a carbothermic slag-free method.

The subject of the study is the properties of a new complex titanium-containing ferroalloy produced by a carbothermic slag-free method.

The purpose of the work is to develop a resource-saving technology for smelting a new complex titanium-containing ferroalloy from Kazakhstan raw materials using a carbothermic slag-free method.

Research objectives. To achieve this purpose, the following tasks are set in the work:

– analysis of production technologies, mineral resource base for the production of a new complex titanium-containing ferroalloy;

– prediction of the final phase composition of a new complex titanium-containing ferroalloy by thermodynamic diagram analysis based on the Ti-Fe-Al-Si system;

– carrying out a complete thermodynamic analysis of the carbothermic reduction of Ti, Fe, Al and Si to determine and clarify the temperature range of metal formation and the features of reduction processes during the smelting of a new complex titanium-containing ferroalloy;

– experimental tests on the smelting of complex titanium-containing ferroalloy using a carbothermic slag-free method in large-scale laboratory conditions;

– tudy of the physicochemical characteristics of a new complex titanium-containing ferroalloy obtained in large-scale laboratory tests.

Scientific novelty. In this work for the first time:

– the diagram of the four-component metal system Ti-Fe-Al-Si was constructed using the method of thermodynamic diagram analysis. Tetrahedration of the studied system was carried out, where 32 elementary tetrahedra were installed, which characterize a complex ferroalloy with titanium. It has been determined that the phase composition of the new complex titanium-containing ferroalloy is most fully described by the following three tetrahedra: Si-$FeAl_4Si_2$-$Fe_2Al_3Si_3$-$AlSi_2Ti$, Si-$Fe_2Al_3Si_3$-FeSi-$AlSi_2Ti$, $Fe_2Al_3Si_3$-FeSi-$AlSi_2Ti$-$TiFeSi_2$;

– the full thermodynamic modeling of the smelting process of a new complex titanium-containing ferroalloy was carried out using the HSC Chemistry software package. The nature of the carbide formation process has been studied. The optimal ratio of SiO_2/C_{solid} = 1.65-1.82 in the charge mixture was determined, which prevents the formation of titanium carbides;

– the technology for smelting a new complex titanium-containing ferroalloy using a carbothermic slag-free method using high-ash coal as a reducing agent in an ore-thermal furnace with a capacity of 0.2 MVA has been developed and tested. A pilot batch of a new complex titanium-containing ferroalloy was obtained, with the following chemical composition, %: Ti – 20-25; Si – 40-50; Al – 10-14; P no more than 0.08, the rest is iron;

– the main properties of a new complex titanium-containing ferroalloy were determined by methods of physicochemical analysis. It was determined that the phase composition of the alloy is represented by the following compounds - Al_3FeSi_2, $TiSi_2$, Ti_2FeAl, $TiFeSi_2$, and free silicon. It has been established that the resulting ferroalloy has an optimal density (4.7-5.3 g/cm^3) and melting point (T_{cr} = 1420-1450 ^oC) from the point of view of steel alloying.

The novelty is also confirmed by the patent for the invention of the Republic of Kazakhstan KZ36232 dated 05.26.2023 «Charge material for the preparation of a complex titanium-containing ferroalloy».

Practical value of the work. For the first time in metallurgical practice, a complex titanium-containing ferroalloy was produced by a carbothermic slag-free method. The data obtained make it possible to use rich titanium slag obtained from

substandard ilmenite concentrates, and high-ash coal (reducing agent), as the main charge materials for the smelting of complex titanium-containing ferroalloys. The developed alloy can replace a mechanical mixture consisting of low-percentage ferrotitanium FeTi25, ferrosilicon FeSi45 and secondary aluminum for complex alloying of steel and become a complex reducing agent for producing high-percentage grades of ferrotitanium. In addition to the technical and economic advantages, the involvement of such materials in metallurgical processing solves a serious environmental problem associated with the accumulation and lack of competent technology for recycling substandard raw materials.

Technological regulations have been developed for the smelting of a new complex titanium-containing ferroalloy (aluminosilicotitanium) in an ore-smelting furnace with 0.2 MVA transformer power.

Technical specifications (organization standard) ST RSE 120941015505-08-2023 have been developed for a new complex titanium-containing ferroalloy.

Research Methods. The present dissertation utilized research methods widely proven and demonstrating their continuity in applied physicochemical studies of complex metallurgical processes: differential thermal analysis, chemical analysis, X-ray phase analysis, specific electrical resistance determination, thermodynamic modeling using software (HSC Chemistry), thermodynamic-diagram analysis, smelting in ore-thermal furnaces, metallographic analysis, pycnometric method for density determination, and crystallization temperature determination.

Positions to be defended

– results of studying the physico-chemical properties of ilmenite concentrates from the Shokash and Obukhov deposits;

– results of thermodynamic diagram analysis of the Ti-Fe-Al-Si system;

– results of complete thermodynamic modeling of the smelting process of a new complex titanium-containing ferroalloy;

– results obtained during tests on the smelting of rich titanium slag and a new complex titanium-containing ferroalloy;

– results of studying the physicochemical properties of a new complex titanium-containing ferroalloy.

Place of research work. The work was carried out at the «Nanotechnology and Metallurgy» department of the NpJSC «Abylkas Saginov Karaganda Technical University», in the «Pyrometallurgical Processes» laboratory and at the experimental site of the Zh. Abishev Chemical-Metallurgical Institute, part of the research related to the study of the physicochemical properties of a new complex titanium-containing ferroalloy was carried out at the Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences (Ekaterinburg, Russian Federation).

Description of the main results of the study.

– An analysis of the current state, technological level and mineral resource base of titanium-containing alloys was carried out. An assessment of the physicochemical properties of domestic ilmenite concentrates from the Shokash and Obukhovskoye deposits using chemical, X-ray spectral, X-ray phase and differential

thermal analysis is given. As a result, it was found that the production of ferrotitanium directly from ilmenites of local deposits is not advisable due to the low content of titanium dioxide and the high content of impurities. The thermal properties of high-ash coals were assessed, and it was found that for the smelting of a new complex titanium-containing ferroalloy it is advisable to use coal from the Saryadyr deposit due to its relatively high electrical resistivity.

– Using the method of thermodynamic diagram analysis, the final phase composition of the developed titanium-containing complex ferroalloy was predicted. A diagram of the four-component metal system Ti-Fe-Al-Si was constructed using thermodynamic diagram analysis. Tetrahedration of the studied system was carried out, where 32 elementary tetrahedra were established, characterizing a complex ferroalloy with titanium. It has been determined that the phase composition of the new complex titanium-containing ferroalloy is most fully described by the following three tetrahedra: Si-$FeAl_4Si_2$-$Fe_2Al_3Si_3$-$AlSi_2Ti$, Si-$Fe_2Al_3Si_3$-FeSi-$AlSi_2Ti$, $Fe_2Al_3Si_3$-FeSi-$AlSi_2Ti$-$TiFeSi_2$. Here, titanium is present in a bound form with iron, aluminum, and silicon, which is favorable from the point of view of reduction processes. The excess silicon in the system serves as a solvent for titanium carbides, destroying them, which makes it easier to release the alloy from the furnace.

– According to thermodynamic modeling of the process of smelting ferroalloy with titanium using the HSC Chemistry software package, the temperature for the start of joint carbothermic reduction of the main elements of the alloy was established, corresponding to 1600 °C. With a low content of quartzite in the charge composition, a stable formation of titanium and silicon carbides is observed at temperatures above 1300 °C. At elevated quartzite contents, the formation of carbides is also observed, however, these phases are not stable and completely disappear at temperatures of 2100-2200 °C with the transition to titanium silicides $TiFeSi_2$, $TiSi_2$ and Ti_5Si_3. It has been established that by carbothermal smelting from rich titanium slag, it is possible to obtain an alloy with an optimal content of the main components, with a quartzite content in the charge of more than 15 kg (more than 10% of the composition of the charge). The optimal composition of the alloy lies in the temperature range of 1900-2100 ºC. For the first time in metallurgical practice, for the carbothermal smelting of ferroalloy with titanium, the optimal ratio of SiO_2 to solid carbon, SiO_2/C_{solid} = 1.65-1.82, was determined.

– In an ore-thermal furnace with a transformer power of 0.2 MVA, a pilot batch of rich titanium slag (RTS) was produced from ilmenite concentrate of the Obukhov deposit (TiO_2 content - 52%) with the following content of the main components, %: TiO_2 – 73-82; Al_2O_3 – 4,5-10; SiO_2 – 2-2,5; Cr_2O_3 – 1-3; Fe_2O_3 – 7,5-10. With the production of RTS, the impurity elements contained in the concentrate were converted into associated alloyed metal. Over the entire test period, 2890 kg of ilmenite concentrate were smelted, 1608 kg of RTS and 261 kg of associated alloyed metal were obtained. The amount of metal obtained is in the range of 0.15-0.25 per unit of slag. Based on the results of the work, a test report was obtained. The resulting RTS was used in the smelting of a new complex titanium-containing ferroalloy, aluminosilicotitanium, on the same furnace unit. High-ash coal from the Saryadyr deposit was used as a reducing agent. In order to obtain a

liquid alloy, at the first stages, an intermediate alloy with a rich content of silicon and ferrosilicoaluminum is smelted. For this purpose, the first composition of the charge mixture consists only of quartzite and high-ash coal. Next, rich titanium slag is gradually loaded, with a decrease in the proportion of quartzite in the charge composition. As a result of a series of experimental works, a pilot batch of a new complex titanium-containing ferroalloy was obtained, with the following average chemical composition, %: Ti – 20-25; Si – 40-50; Al – 10-14; P no more than 0.08, the rest is iron. The resulting alloy corresponds to the FeTi25 grade (GOST 4761-91) in terms of titanium content. The use of expensive coke, aluminum and iron ore is completely eliminated in the charge mixture. The process is completely slag-free and is carried out with an excess of solid carbon of 10-15%, at a ratio of oxides to solid carbon. As a result, act was obtained.

– Using X-ray phase and microstructural analysis methods, the physicochemical properties of the resulting alloy were determined, and it was found that the resulting alloy is represented by complex intermetallic compounds, such as Al_3FeSi_2, $TiSi_2$, Ti_2FeAl, $TiFeSi_2$, and free silicon. It was determined that the resulting ferroalloy has an optimal density (4.7-5.3 g/cm^3) and melting point (T_{cr}= 1420-1450 ^oC) from the point of view of steel alloying. An approximate economic assessment of the production of a new complex titanium-containing ferroalloy using the developed technology has been carried out. The cost of 1 ton of alumosilicotitanium will be $1583.4. While the cost of its analogues in the form of ferrotitanium and ferrosilicotitanium is $2250.37 and $2100.02 per ton, respectively. The developed new complex titanium-containing ferroalloy contains an optimal distribution of leading components in the form of Ti, Si and Al. The content of silicon and aluminum in the alloy will not only contribute to more complex alloying and deoxidation of steel, but will also, to some extent, help protect titanium from oxidation, and therefore will increase the degree of its absorption

Personal contribution of the doctoral student to the writing of the dissertation. The author participated in determining the purpose of the work and setting research objectives, as well as in writing articles, abstracts and filing a patent application. The author personally obtained the bulk of the scientific and practical results of this work, which determine both the scientific novelty and the practical value of the work as a whole. In addition, the entire complex of theoretical and applied research on the development of technology for smelting a new complex titanium-containing ferroalloy was carried out within the framework of a grant funding project, where the author was the responsible executor.

Approbation of work. Acts of large-scale laboratory tests simulating industrial conditions were obtained for the smelting of rich titanium slag and a new complex titanium-containing ferroalloy in an ore-thermal furnace with a transformer power of 0.2 MVA under the conditions of Zh. Abishev Chemical-Metallurgical Institute.

Technological regulations have been developed for the smelting of a new complex titanium-containing ferroalloy (aluminosilicotitanium) in an ore-smelting furnace with 0.2 MVA transformer power.

Technical specifications (organization standard) ST RSE 120941015505-08-2023 have been developed for a new complex titanium-containing ferroalloy.

A patent for the invention of the Republic of Kazakhstan KZ36232 dated 05.26.2023 «Charge material for the preparation of a complex titanium-containing ferroalloy» has been obtained.

The main theoretical and practical results were introduced into the educational process of the NpJSC «Abylkas Saginov Karaganda Technical University» for undergraduates and doctoral students of the educational program «Metallurgy» in the disciplines «Resource Saving», «Modern Resource Saving Technologies in Metallurgy», «Resource Saving and Energy Saving Technologies in Metallurgy» in the form of co-authored study guide «Modern resource-saving technologies in metallurgy» for master's and doctoral students. There is an act of implementation into the educational process.

The results of scientific research and development were introduced into the production process of NPO Manganets LLP. There is an act of implementation.

The main scientific results of the dissertation work are presented in 16 publications in domestic and foreign scientific journals, including:

– 1 article in an international peer-reviewed scientific publication with a 62nd percentile in the Scopus database – CIS Iron and Steel Review (Russian Federation);

– 1 article in an international peer-reviewed scientific publication, having the 86th percentile in the Scopus database and the 2nd quartile in the JCR Category of the Web of Science database - Heliyon (England);

– 2 articles in scientific publications included in the list of publications recommended by CQAFSHE MSHE RK – «Proceedings of the University» No. 4 (89) and «Engineering Journal of Satbayev University» No. 5 (144);

– 1 patent was received for the invention of the Republic of Kazakhstan KZ36232 dated 05.26.2023 «Charge material for the preparation of a complex titanium-containing ferroalloy»;

– 1 study guide;

– also, the research results were presented by the author in 10 reports at domestic and international scientific and practical conferences.

Structure and scope of the dissertation. The dissertation consists of an introduction, a main part consisting of 4 sections, a conclusion and appendices. The volume of the dissertation is 122 pages of typewritten text, the work contains 43 figures, 30 tables, a list of used sources, including 194 titles.