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Analysis of the Effect of Fluxing Additives in the Production of Titanium Slags in Laboratory Conditions

Maxat K. Myrzakulov [1], Saltanat K. Dzhumankulova [2], Kassym K. Yelemessov [1], Madina B. Barmenshinova [2], Nikita V. Martyushev [3,*], Vadim Y. Skeeba [4], Viktor V. Kondratiev [5] and Antonina I. Karlina [6]

[1] Institute of Energy and Mechanical Engineering, Satbayev University, Almaty 050013, Kazakhstan; m.myrzakulov@satbayev.university (M.K.M.); k.yelemessov@satbayev.university (K.K.Y.)
[2] Mining and Metallurgical Institute, Satbayev University, Almaty 050013, Kazakhstan; s.jumankulova@satbayev.university (S.K.D.); m.barmenshinova@satbayev.university (M.B.B.)
[3] Department of Advanced Technologies, Tomsk Polytechnic University, Tomsk 634050, Russia
[4] Department of Industrial Machinery Design, Novosibirsk State Technical University, Novosibirsk 630073, Russia; skeeba_vadim@mail.ru
[5] Institute of Geochemistry of the Siberian Branch of the Russian Academy of Sciences, Irkutsk 664033, Russia; v.kondratiev@igc.irk.ru
[6] Stroytest Research and Testing Centre, Moscow State University of Civil Engineering, Moscow 129337, Russia; karlinat@mail.ru
* Correspondence: martjushev@tpu.ru

Abstract: The article theoretically justified and experimentally confirmed the possibility of implementing the process of the electric melting of Satbayevskiy ilmenite concentrates with new fluxing additives based on oxides and nitrides of aluminium, calcium, and boron. They also include boron carbonitride CNV that will expand the raw material base of Kazakhstan titanium production by involving local substandard material in the process, as well as the technical and economic performance of electric melting. In order to conduct experiments in the area of extremum, the ilmenite concentrate from the Satbayev deposit was taken. Furthermore, the optimum conditions of the electric melting of Satbayevski ilmenite concentrates (such as the process temperature of 1550–1600 °C, the reducing agent consumption of 8–10% of the concentrate mass, and the duration of 90 min), using new fluxing additives, were selected. As a result of the experiment (performed at a temperature of 1600 °C), it has been found that the introduction of 3 to 6% of fluxes in the charge of electric melting promotes the reduction of iron oxides from 45 to 80% and achievement of the extraction of titanium oxide in slag of up to 83.5–90.1%. The addition of 6% boron oxide and carbonitride in the charge of electric melting reduces the melting temperature of the charge to ~1400–1450 °C and the melting time to 90 min. It also creates conditions for a quieter electric melting mode.

Keywords: ilmenite concentrate; titanium slag; thermodynamic analysis; sodium carbonate; oxides; gibbs energy

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1. Introduction

Currently, more than 300 deposits of titanium minerals are registered in the world. Among them, 70 magmatic, 10 lateritic, and more than 230 alluvial deposits stand out. To date, 90 of these deposits, mostly alluvial, have been explored and classified into industrial categories.

It is estimated that about 69% of the world's titanium reserves (excluding Russia) are concentrated in magmatic deposits, 11.5% are in carbonatite weathering crusts, and 19.5% are found in alluvial deposits. Of these resources, more than 82% of titanium reserves are contained in ilmenite, less than 12% are in anatase, and about 6% are included in rutile [1].

Titanium dioxide is the most sought-after titanium compound on the market.

Commercial production of titanium dioxide began in the early 20th century, and since then it has found widespread use in a variety of industries, including paints, additives for paper and plastics, solar cells [2], cosmetics, and as a food additive [3]. In addition, titanium dioxide is used in the production of non-toxic foams [4] and in the formulation of coatings, adhesives, and sealants [5].

The main production schemes for titanium products are currently focused on the use of ilmenite concentrates. The ilmenite concentrate is a beneficiated product of ilmenite ore, containing an increased concentration of the mineral ilmenite ($FeTiO_3$). The concentrate has a significantly higher TiO_2 content, typically from 45% to 65% or more, depending on the beneficiation method and the quality of the original ore. The content of impurities, such as silica (SiO_2), iron (III) oxide (Fe_2O_3), and other metals in it, is significantly reduced compared to the original ore. However, due to the depletion of ilmenite deposits, there is a need to focus on more complex ores, such as titanomagnetites. This is an important step to ensure a sustainable supply of titanium products in the future.

With the transition to more complex ores, such as titanomagnetites, there are a number of technological challenges associated with their processing. Titanomagnetite is a mineral, representing a solid solution of magnetite (Fe_3O_4) and ilmenite ($FeTiO_3$). Its chemical formula can be approximately represented as $(Fe_2TiO_4)_x(Fe_3O_4)_{1-x}$, where x is the proportion of ilmenite in the solution, which can vary widely. Titanomagnetite is a mixture of iron and titanium oxides in various proportions. Titanomagnetites contain higher concentrations of iron and other minerals, making titanium extraction more difficult. However, the main problem of their processing remains the high resistance of titanium to dissolution by various acids. The main methods of processing these ores include magnetic separations, flotation, and pyrometallurgical technologies [6–8]. It should be taken into account that the optimal conditions for titanium leaching depend on the selected method and the specific composition of the ore. An example of choosing such parameters is given in [9] for melting cast iron and steel from the titanomagnetite concentrate. The technology includes grinding and the sulphuric acid leaching of slag, accompanied by the transfer of the metals from the slag to the suphuric acid solution in the form of sulphates. Then, the metals are precipitated from the resulting suphuric acid solution with oxide. Titanium is extracted from the sulphuric acid solution in the form of a precipitate of titanium oxyhydroxide $TiO(OH)_2$, obtained by the reaction of titanium sulphates with magnesium oxide at a pH of 0 up to 2.0 at the following stoichiometric ratio of water:sulphuric acid = 1:1.63. In this case, the maximum temperature of the solution is 125 °C.

In addition, the application of different beneficiation and extraction methods must take into account environmental aspects, such as minimising waste and environmental impact [10,11]. The development of cleaner and more efficient technologies for processing titanium ores is a priority for sustainable development. New approaches, including biotechnology and hydrometallurgy techniques, are being explored as opportunities to reduce the environmental footprint of the titanium extraction process [12].

Studying the titanium minerals also aims to optimise the properties of titanium compounds for use in high-tech applications, such as aviation and aerospace. Titanium alloys of high strength with low weight and corrosion resistance are becoming increasingly in demand. This creates additional demand for new sources of titanium minerals and increases the importance of actively exploring various deposits.

In view of the above, sustainable development of the titanium industry requires a comprehensive approach that includes not only optimisation of extraction technologies but also the development of new processing methods that can ensure competitiveness in the international market. It is important to continue scientific research aimed at improving the quality of titanium minerals and reducing their environmental impact, which will ultimately provide safer and more efficient ways of obtaining titanium products for various industries.

Therefore, ensuring a reliable supply of titanium in the future will depend on the integration of innovative technologies, optimisation of processes, and active search for new deposits that meet modern economic and environmental requirements.

Consumption of titanium dioxide (TiO_2) in various industries is expected to grow significantly in the coming years. The highest rates of consumption increase are forecasted in the production of laminated paper, when it will range from 4% to 6% per year, as well as in the production of plastic products, where the growth will be about 4% per year. At the same time, the growth of titanium dioxide consumption in the paint and varnish industry will be more moderate, ranging from 1.8% to 2% per year.

Approximately 12–13% of the total consumed TiO_2 is used as a pigment in the manufacture of paper products, with rutile for high-grade paper and anatase for low-grade paper and board, depending on the quality of the paper. On average, about 1.4 kg of titanium dioxide is needed to produce one tonne of paper.

The main method of producing titanium slag is reduction smelting in electric furnaces, during which iron oxides are reduced to a metallic state. The obtained titanium slag can be processed to obtain pure rutile, containing from 92% to 96% of titanium dioxide.

Industrial production of synthetic rutile includes two stages: reduction smelting and acid leaching. It should be noted that this stage produces a large amount of liquid waste, with a ratio of approximately 2 tonnes of waste for every tonne of produced TiO_2. This highlights the importance of developing and implementing technologies to minimise waste and improve the environmental sustainability of the production process.

There are two main industrial technologies for the production of titanium dioxide (TiO_2) pigment: sulphuric acid and chlorine.

In the sulphuric acid process, the titanium-containing product is treated with concentrated sulphuric acid, resulting in the formation of a sulphate solution. This solution undergoes hydrolysis (T = 140 °C), during which titanium dioxide is precipitated (from the solution of titanium oxy sulphate). In this process, the iron, contained in the starting material, is transferred to the solution in the form of sulphates.

The chlorine process is based on a different technology: the rutile is first exposed to chlorine gas, which converts the titanium into titanium tetrachloride ($TiCl_4$). This chloride is then converted back to titanium dioxide at high temperature in a mixture of air and oxygen to release chlorine.

Both technologies generate significant amounts of waste and toxic by-products. This creates the need to develop effective environmental protection measures [13,14]. At present, the world capacity of titanium dioxide production by chlorination exceeds that of the sulphate method and continues to increase [15].

The chlorine process has several advantages over the sulphuric acid method. It is characterised by less waste to be disposed of and higher quality of the final product. In addition, the capital investment using the chlorine process is only 60–75% of the cost of the sulphuric acid method, making it more economically viable.

The analysis of patent literature has revealed that the development of a method for obtaining titanium dioxide from substandard titanium slag with a high content of impurities requires an individual approach that takes into account the specifics of each particular slag. This underlines the need for further research to optimise the processing of various titanium materials [16–18].

In view of this, to increase the efficiency of titanium dioxide production processes and to reduce the negative impact on the environment, it becomes relevant to introduce technologies aimed at minimising waste generation and optimising processing [19].

One of the promising directions is the use of alternative sources of titanium raw materials, such as titanium slag obtained from the processing of rutile and ilmenite sands. Such sources can offer advantages, including lower cost and a lower environmental footprint. However, the use of such raw materials requires careful process design to minimise the negative effects associated with high levels of impurities.

In addition, attention should be paid to improving the catalytic systems used for titanium chlorination. Improvements in these systems can lead to increased selectivity of reactions and reduced formation of by-products, which in turn will make the process more sustainable and environmentally friendly.

It is important to note that in recent years, there has been a growing interest in reductive and exothermic processes to improve overall production performance. For example, the use of oxygen-containing agents and optimisation of temperature regimes can lead to improved yields of product titanium dioxide and significant reductions in harmful substances in the waste [20].

In addition, the need to comply with environmental regulations and standards requires the introduction of emission cleaning technologies and recycling of secondary resources [21]. Increased emphasis on closed-loop production and reuse of by-products can not only improve the sustainability of processes but also reduce their cost.

In conclusion, the study of new methods and technologies in titanium dioxide production represents an important area for future research. Continuous improvement of existing processes, as well as the introduction of innovative solutions, will ensure more efficient and environmentally friendly pigment production that meets global standards.

The purpose of this work is to develop a technology for obtaining titanium slag that is suitable for the production of titanium sponge from low-grade ilmenite concentrates of the Satbaevskoye deposit in Kazakhstan. The work uses an innovative approach, consisting in the use of new fluxing additives, which allows solving the problem of the inefficient processing of this raw material. To achieve the main purpose, the following studies and experiments were conducted:

1. The influence of fluxing additives, such as oxides and nitrides of aluminium, calcium, boron, and boron carbonitride, on the process of the electric smelting of ilmenite concentrates was studied. As a result, the optimal type and amount of the flux were determined that allowed reducing the melting temperature, decreasing the viscosity of the slag, and improving the separation of the metal (iron) and slag (titanium) phases.
2. The electric smelting process parameters were optimised. Based on experimental data, optimal process conditions were established, including temperature, holding time, and the amount of the reducing agent (anthracite) and fluxing additives. This ensures the maximum iron extraction in the form of cast iron and the production of titanium slag of the required quality.
3. The efficiency of the proposed technology was experimentally confirmed. The possibility of producing high-quality titanium slag from low-grade local raw materials using new fluxing additives was demonstrated, which discovered prospects for further production of titanium sponge.

Therefore, this work proposes an innovative solution for the efficient processing of low-grade ilmenite concentrates, which can significantly improve the efficiency of using local raw materials.

2. Materials and Methods

Titanium slag is extracted from the ilmenite concentrate, and this paper presents the results of laboratory studies that were conducted on the basis of ilmenite concentrates produced at Malyshevskoye deposit (Russia), Medvedevskoye deposit (Russia), and Irshanskoye deposit (Ukraine). A two-stage technological scheme was developed by the authors of the paper. It includes the recovery of ilmenite-coal briquettes in a ring furnace and the subsequent melting of the obtained metallised briquettes in an ore-thermal furnace. As a result of the process, titanium slag and pig iron were obtained [22].

The experimental procedure consisted of mixing ilmenite concentrates with anthracite and a binder, after which this mixture was subjected to briquetting. The briquettes were reduced in a ring furnace (Viterm, St. Petersburg, Russia). After the completion of the reduction process, hot metallised briquettes were melted in the electric furnace at a temperature of 1650 °C, and the obtained melting products were cast into ingots.

At the first stage of the study, the chemical and granulometric compositions of the used ilmenite concentrates were analysed. The chemical composition of the metallised briquettes was also determined. The study pays special attention to the technical performance of the ring furnace that was used to produce metallised briquettes. It was found that obtaining briquettes with a high degree of metallisation was possible in the ring furnace, which is subject to the heat treatment regime, ensuring the rapid heating to a temperature of 1400–1500 °C.

The heat treatment cycle of briquettes in the ring furnace varies from 15 to 30 min and includes the stages of loading, heating, firing, cooling, and unloading, which depends on the chemical composition of a particular ilmenite concentrate. These results underline the efficiency of the proposed technology and open new opportunities for further study and optimisation of processing the ilmenite concentrate.

In order to conduct experiments in the region of the extremum, the ilmenite concentrate of the Satbayevskogo deposit was selected with the following initial composition, wt %: TiO_2—49.65; FeO—16.77; Fe_2O_3—26.46; SiO_2—4.5; Al_2O_3—1.15; Cr_2O_3—0.10; MgO—0.20; MnO—0.35; CaO—0.3; others—0.52.

Laboratory experiments on the electric melting of the Satbaev ilmenite concentrate with the addition of oxides (Al_2O_3, CaO, B_2O_3) and nitrides (AlN, Ca_3N_2, BN, CNB) in the extreme region were performed in a high-temperature tube furnace Nabertherm RHTH 120/150/1600 (Nabertherm GmbH, Lilienthal, Germany) of the vertical type. It was equipped with a type B thermocouple, a power supply unit, separated from the furnace by a low-voltage transformer, a thyristor regulator, and a switchgear. The furnace body is made of structural stainless steel, which provides high strength and corrosion resistance. The heating elements, made of molybdenum disilicide, are arranged vertically to improve heat transfer efficiency. The furnace is insulated with vacuum-formed ceramic fibres, which minimise heat loss and ensure stable temperature conditions. The working tube is made of C799 gas-tight ceramic, containing 99.7% of aluminium oxide (Al_2O_3), which guarantees high temperature resistance and chemical inertness at high temperatures. The minimum temperature that was reached during the process was 1550 °C, while the maximum temperature reached 1750 °C. The duration of the experiments varied from 60 to 120 min, providing enough time to reach thermodynamic equilibrium and a complete reaction cycle.

Anthracite had the following chemical composition, wt.%: the moisture content of 7%; the ash content of 3.5%; volatile matter of 2.1%; sulphur of 0.28%. Carbon of 87.12% was used as a carbonaceous reducing agent in this study. The consumption of the reducing agent (anthracite) was calculated to achieve a complete reduction of iron (Fe). Taking into account the reducing power of the additive components, the reducing agent consumption varied. At the minimum point, it was 10% of the concentrate mass, and at the maximum point, it was 14% of the concentrate mass.

High-purity oxides and nitrides of aluminium (Al), calcium (Ca), and boron (B) were used as fluxing materials. The consumption of additives, such as Al_2O_3, CaO, B_2O_3, AlN, Ca_3N_2, BN, and CNB, was 3% of the concentrate weight at the minimum point, and it increased up to 6% of the concentrate weight at the maximum point. The initial weight of the concentrate injected into the smelting furnace was 40 g.

Taking into account the above parameters, the required number of experiments was planned. The order of each experiment was as follows: before the start of the process, a charge consisting of a mixture of a given amount of the concentrate, reducing agent, and flux was prepared. After loading the charge into the alumina crucible, the furnace was switched on at full power. The heating rate up to 1100 °C was 55–60 °C/min. At 1100 °C, the holding time was 10–15 min, after which the furnace was switched on again at full power with the temperature, increasing to the maximum temperature; the heating rate was 10–12 °C/min.

After holding at the set maximum temperature for a certain time, the crucible was removed from the furnace and cooled to room temperature. To evaluate the results, the mass loss was determined by the weighing method. Weighing was conducted using the Bel Engineering LG20001 scales (Bel Engineering, Monza, Italy). The degree of the iron oxide reduction was determined by chemical analysis of the samples as the ratio Femet/Feobsh = 100%, which is the ratio of the amount of iron in the smelting products to its total amount in the initial charge. This provided the quantitative data about the result of the reduction process (with anthracite).

In the framework of this study, laboratory experiments were conducted to analyse the influence of fluxing additives, such as oxides and nitrides of aluminium (Al), calcium (Ca), and boron (B), as well as boron carbide nitrides (CNB), on the melting temperature of the charge. The phase and chemical compositions, viscosity, and electrical conductivity of the melts obtained by melting the charge that was based on the Satbaev ilmenite concentrate, carbonate reducing agent, and fluxing materials were also studied.

The experiments were performed in the temperature range from 1150 °C to 1750 °C in a specialised laboratory setup consisting of a Tamman vacuum electric furnace (Electrotechnics, Moscow, Russia). There was the equipment for measuring electrical conductivity (the ohmmeter and the PP-63 potentiometer (ProfKiP, Mytishchi, Russia)) and viscosity (the vibration viscometer with a molybdenum spindle (the diameter was 2 mm, the length was 400 mm), and a digital millivoltmeter).

To evaluate the electrical conductivity, an alundum tube with an inner diameter of 20 mm was used, with a material heating rate of 25–30 °C/min. For viscosity determination, a molybdenum crucible with an inner diameter of 35 mm and an outer diameter of 40 mm was used, with a controlled cooling rate of 5 °C/min. The temperature during the experiment was measured using a tungsten-rhenium thermocouple (BAP-5/20) that was mounted on the bottom of the furnace.

After viscosity and conductivity measurements, the composition of the samples was analysed by X-ray diffraction and chemical analysis. X-ray diffractometric analysis was carried out on an ARL X’TRA X-ray diffractometer with a copper source (CuKa radiation) and β-filter (Thermo Fisher Scientific Inc., Basel, Switzerland). The diffractograms were recorded under the following conditions: voltage of 35 kV, current of 20 mA, θ-2θ mode, detector speed of 2 deg/min. Semi-quantitative X-ray phase analysis was based on the diffractograms of powder samples, using the method of equal weights and compound mixtures, which allowed determining the quantitative ratios of crystalline phases. The interpretation of diffractograms was carried out using the ICDD, the Powder Diffraction File (PDF2) database, and available diffractograms of minerals without impurities.

3. Results and Discussion

The traditional (flux-free) technology of titanium production is based on the following processes: the ore-thermal smelting of raw materials to produce titanium slag; the chlorination of titanium slag to produce tetrachloride; and the magnesium-thermal reduction of tetrachloride to produce titanium metal. The ore-thermal smelting of the mineral raw materials to obtain titanium slag is the most energy- and labour-consuming process step, as the quality of titanium slag determines the cheapness of the following processes and the quality of the final product (titanium sponge). Therefore, titanium slag is an important intermediate and commercial product in the production of titanium sponge.

Many overseas plants produce titanium metal from rich ilmenite concentrates, containing not less than 55–65% of TiO_2, not more than 23% of iron (II) oxide, and not more than 2% of silicon dioxide, by chlorine technology. Concentrates with the low TiO_2 content (from 30 to 45%) are not suitable for the production of titanium metal and are used only for the production of pigments. Slags that were containing at least 80% of TiO_2 are suitable for the chlorine technology and were obtained from ilmenite concentrates by heat treatment (electrical melting). To obtain such slags from ilmenite in Kazakhstan, containing 48–55% TiO_2, only flux electric melting is applicable.

Based on literature data, it was found that the proposed fluxing materials (oxides and nitrides of Al, Ca, and B) could help to reduce the melting temperature and viscosity of slag [23]. Also in the literature, there is little data on the use of oxides of Al and B as a flux and nitrides of Al, Ca, and B. Nevertheless, the review revealed that they were applicable as a flux because many of them in a reducing environment are stable, have high electrical resistance at high temperatures, and can have a catholic effect, being on the walls of the device (as a lubricant). All this serves as a basis for studying the impact of the above oxides and nitrides as fluxing materials in obtaining titanium slag from domestic low-grade ilmenite concentrates. As the initial data for the research, the ilmenite concentrates of Satbayevskoe field, which is located 40 km from Ust-Kamenogorsk, where the only titanium production in the country (JSC "Ust-Kamenogorsk Titanium-Magnesium Plant") is located, was chosen.

The separate melting of local ilmenite concentrates for titanium slag is practically impossible due to the formation of refractory and viscous melts with the high melting point (over 1700 °C) and requires additional expenses for electric power. Therefore, to date, the Satbayevskiy ilmenite concentrate is not smelted separately (100%) (because of its refractoriness).

In addition, the melting of a mixture of local and imported concentrates also requires additional costs for transportation of imported raw materials.

When adding fluxing materials to ilmenite concentrates, there is an opportunity to significantly reduce the melting temperature of the charge from the Satbayev concentrate and to use the pure domestic ilmenite concentrate in the production of titanium slag. At the same time, the known world practice methods of flux melting, where fluxing materials are mainly Ca, Mg, and Mn oxides or chlorides of alkali and alkaline earth metals, are characterised by being capital- and energy-intensive and, due to inefficiency, they have not been used at the production scale.

The lack of effective technology for obtaining titanium slag from local raw materials forces us to develop an innovative technology for obtaining titanium slag from domestic low-grade and refractory ilmenite concentrates with the use of fluxing additives.

A technology for obtaining titanium slag that is suitable for the production of titanium oxide from local raw materials has been proposed, using new fluxing additives at the existing technological units and equipment in the JSC "Ust-Kamenogorsk Titanium-Magnesium Plant".

The relevance of the study is due to the ability of new fluxing additives to increase the degree of extraction of iron in cast iron and reduce the melting temperature of slag. Thereby, this will lead to a better separation of melting products into separate phases. Such additives also reduce energy consumption and improve other technical and economic indicators of electric melting.

As a result of the experiment, 112 melts were performed. In all samples, the initial mass of the concentrate was 40 g. The consumption of anthracite (reducing agent) and flux was taken in the specified amounts—10–14 and 3–6% of the mass of the concentrate, respectively. The results of some melts are shown in Table 1.

Table 1. Results of experiments in the areas of extremum (anthracite consumption of 10% of the concentrate weight).

Experiment Number	Temperature, °C	Additive	Extraction of TiO_2 into Slag, %	Extraction of Fe in Cast Iron, %
1	2	3	4	5
8	1750	without additive	282.9	75.6
21	1550	Al_2O_3, 6%	81.6	85.3
38	1550	CaO, 6%	86.6	90.4

52	1550	B_2O_3, 6%	88.5	92.1
68	1550	AlN, 6%	85.7	89.8
77	1550	CNB, 3%	92.5	95.2
92	1550	BN, 6%	90.2	95.3
106	1550	Ca_3N_2, 6%	85.3	89.3

As a result of the melting of the local Satbayev ilmenite concentrate without additives, even in the areas of maximum (i.e., at 1750 °C and 120 min of holding time), a very hard, refractory, and homogeneous mass was obtained. This product was very magnetic and did not separate into separate phases. This explains that there was no separation of slag and pig iron into separate phases during melting, which is confirmed by previous experiments under such conditions.

When adding aluminium, calcium, and boron oxides to the product in the region of minimum, small iron coronels were found that did not connect with each other [24]. With an increase in temperature and holding time to the maximum, the iron corollas increased slightly, but they did not fully combine. In this case, the degree of reduction of iron into cast iron was from 85 to 92.3%. The addition of aluminium oxide both in the region of maximum and in the region of minimum showed the formation of a viscous melt, which strongly prevented the complete separation of iron into pig iron. Among the mentioned oxides, boron oxide was preferred because, in this case, the smelting was quiet, and the obtained results even in the region of minimum were more satisfactory. It should be noted that an increase in the reducing agent consumption up to the maximum would lead to the formation of titanium carbide already at 1550 °C. At the same time, the slight foaming of the melt was observed. Also, the addition of the above fluxes did not increase the TiO_2 content in the slag, which is explained by the fact that the fluxing oxides replace the iron oxides in the slag.

The addition of aluminium, calcium, and boron nitrides in the minimum region revealed fairly large iron corollas in the product. It is noted that increasing the duration of the process to the maximum is better to increase the size of the corollas than increasing the temperature to the maximum (i.e., no special changes at high temperatures were found). During melting with boron nitride and CNB at the bottom of the crucible, quite large ingots of metal (iron) were found, which were well separated from the slag and not connected with each other (small corollas were not found). In this connection, it is emphasised that the addition of boron nitride and CNB contribute to a better separation of the slag and metal phases than other nitrides. At the same time, the degree of reduction of iron into cast iron was up to 98%, and the FeO content in the slag was 3.2–4.2%.

As a result, it is concluded that the addition of the above materials in the form of flux differently affects the degree of reduction and separation of iron as a separate phase (in the form of cast iron). For completeness of these processes, it is possible to increase the holding time to the maximum, but not the temperature. Since the addition of the specified fluxes, the process temperature slightly decreases, compared to smelting without the addition of fluxes. It is also found that the addition of these fluxes reduces the reducing agent consumption, i.e., the addition of anthracite to the charge in the area of maximum leads to foaming, the formation of viscous slag, and an increased content of refractory titanium carbide in the slag.

When carrying out experiments to determine the optimal parameters and indicators of the melting process of low-grade and hard-to-recover ilmenite concentrates with new fluxing additives under laboratory conditions, such parameters as temperature, duration, reducing agent consumption, and consumption of fluxing additives in the form of oxides (Al_2O_3, CaO, B_2O_3) and nitrides (AlN, Ca_3N_2, BN, and CNB) were studied.

The experiment was conducted similarly to the first one. Melting was carried out in a high-temperature tubular furnace (Nabertherm RHTH 120/150/1600) of the vertical mode (Figure 1), in alundumina (96% Al_2O_3 and a small amount of slag and ferroalloy) and graphite crucibles (crucible-in-crucible) in the temperature range of 1500–1700 °C. Taking into account the results of the experiments in the area of extremum, the reducing agent (anthracite) consumption was set in the amount of 8, 10, and 12% of the concentrate weight. Fluxing additives were added in the amounts of 3, 4.5, and 6% of the weight of the concentrate. The duration of the experiments was 60, 90, and 120 min.

In all samples, the initial mass of the concentrate was 40 g. The consumption of anthracite (reducing agent) and flux was taken in specified quantities (8–10–14% and 3–4.5–6% of the mass of the concentrate, respectively). Upon completion of the process, the obtained products (titanium slag and pig iron (or metal crowns)) were firstly separated and then weighed. The complete chemical analysis of the products was carried out for each melting; some results are given in Table 2.

Table 2. Results of the analysis of some samples of the products of electric smelting (reducing agent consumption was 8% of the concentrate weight, the temperature was 1600 °C, and time was 90 min).

Number of Smelting	Additive	Content in the Slag, %	
		TiO_2	FeO
	Al_2O_3		
140	3.0	75.20	12.50
141	4.5	75.15	10.55
142	6.0	73.80	8.60
	CaO		
143	3.0	75.15	12.05
144	4.5	75.55	10.10
145	6.0	73.85	7.80
	B_2O_3		
146	3.0	78.75	7.35
147	4.5	78.15	6.85
148	6.0	77.80	5.85
	AlN		
149	3.0	79.66	6.75
150	4.5	79.65	6.75
151	6.0	78.10	5.85
	CNB		
152	3.0	81.00	3.53
153	4.5	79.10	4.15
154	6.0	78.80	5.35
	BN		
155	3.0	80.70	3.85
156	4.5	80.00	4.75
157	6.0	78.55	5.60

The addition of Al_2O_3, CaO in an amount of 3–4.5% does not influence particularly the composition of products and does not reduce the melting temperature of the charge (1680–1700 °C). Boron oxide, in comparison with aluminium and calcium oxides, influences the content of iron oxides in the slag and reduces the melting temperature by 60–80 °C. When adding from 3 to 6% of boron oxide from the weight of a concentrate, there was no full stratification of slag and metal (pig iron) phase; small corions of metal did not incorporate with each other.

Aluminium nitride and calcium nitride in these amounts reduce the iron oxide in the slag and the melting temperature to 1600–1650 °C [25]. However, a complete separation of cast iron and slag still did not occur. Compared with them, the addition of boron nitride and CNB in small amounts (3% of the weight of the concentrate) melts noticeably liquefies; there is a better separation of the slag and metallic phase. In this case, the content of iron oxides in the slag decreased to 3.5%, and the process temperature increased to 1500 °C. It is also possible to further reduce the iron oxide content in the slag. This can be achieved using various methods (increasing the smelting time, increasing the temperature, increasing the purity of the raw material, decreasing the particle size, adding catalysts, etc.). However, the use of these methods is associated with fairly significant economic costs. Therefore, the use of such additional improvements in technology is not always economically justified.

Consequently, in determining the optimal parameters of the electric smelting process, the best results were obtained when adding boron nitride and CNB to the charge of electric smelting in an amount of up to 3% of the initial mass of the concentrate. Therewith the most optimal conditions of carrying out the processes for the maximum transfer of iron into pig iron are: the process temperature of 1550–1600 °C; the reducing agent consumption of 8–10% of the concentrate mass; the duration of 90 min. These data are confirmed by the data that were obtained earlier in laboratory studies.

The addition of boron oxide to the charge also showed the prospects of their use in smelting titanium slag from the ilmenite concentrate of Satbayev deposit compared with aluminium and calcium oxides.

On the basis of previously conducted experiments, the limiting levels of fluxing additives (oxides and nitrides Al, Ca, and B, as well as CNB) and reducing agents were determined. The marginal rates of fluxing additives were taken in the amount of 3 to 6% of the weight of the concentrate. The consumption of the carbonaceous reducing agent (anthracite) was taken on average 8% of the weight of the concentrate. The duration of the experiments was from 30 to 120 min.

In the present study, the effect of fluxing additives, including aluminium (Al), calcium (Ca), boron (B) oxides and nitrides, and boron carbide nitrides (CNB), on the melting temperature of the charge was investigated. The study also covered the phase and chemical composition, viscosity, and electrical conductivity of melts produced from the Satbaev ilmenite concentrate, which was combined with the carbonate reducing agent and fluxing materials.

The experiments were carried out in the temperature range from 1150 to 1750 °C in a Tamman vacuum electric furnace, using specialised equipment for measuring electrical conductivity (ohmmeter and potentiometer PP-63) and viscosity (vibro-viscosimeter with a molybdenum spindle of 2 mm diameter and 400 mm in length, as well as a digital millivoltmeter). An alundum tube with an inner diameter of 20 mm and a controlled heating rate of 25–30 °C/min was used to study the electrical conductivity. Viscosity was determined in a molybdenum crucible with an inner diameter of 35 mm and an outer diameter of 40 mm at a temperature reduction rate of 5 °C/min. The temperature was measured using a tungsten-rhenium thermocouple (BAP-5/20), placed at the bottom of the furnace.

After completion of viscosity and conductivity measurements, X-ray phase and chemical methods were used to analyse the compositions of the samples. X-ray diffractometric analysis was carried out on an ARL X'TRA X-ray diffractometer (Thermo Scientific, Waltham, MA, USA) with CuKα-radiation and β-filter. The diffractograms were recorded under the following conditions: U = 35 kV; I = 20 mA; θ-2θ; the detector was 2 deg/min. Semi-quantitative X-ray phase analysis was conducted on the basis of diffractograms of powder samples by the method of equal weights and artificial mixtures, which allowed determining quantitative ratios of crystalline phases. The interpretation of diffractograms was performed using the ICDD database: Powder Diffraction File (PDF2) and diffractograms of minerals without impurities. Content calculations were performed for the major phases. Possible impurities, the identification of which cannot be unambiguous due to low concentrations and the presence of only 1–2 diffraction reflections or weak oxidation (Figures 1 and 2), are listed in the table below (Tables 3 and 4).

Table 3. Interplanar distances and phase composition of sample #1 slag (dated 18 November 2020).

d, Å	I %	Mineral
5.02477	31.4	Pseudobrookite
4.88354	40.8	Pseudobrookite, Mn_5O_8
3.48606	100.0	Pseudobrookite
3.28972	24.7	$NaAlSi_3O_8$
2.76027	67.6	Pyrophanite
2.55219	23.3	
2.45035	30.0	
2.41480	28.8	
2.22738	23.6	
2.19348	24.1	
1.97115	24.0	
1.88064	31.2	
1.86635	43.0	
1.67477	22.1	

Note: All the diffraction peaks shown belong only to the above phases. The characteristic diffraction reflexes are marked to allow identification of the phases present.

Table 4. Results of semi-quantitative X-ray diffraction analysis of sample #1 slag.

Mineral	Formula	Concentration, %
Pseudobrookite	Fe_2TiO_5	65.2
Pyrophanite	$MnTiO_3$	17.9
Manganese Oxide	Mn_5O_8	11.3
Albite	$NaAlSi_3O_8$	5.6

Previous laboratory studies have shown the prospects of using boron nitride and CNB as fluxing additives, which allow a more complete recovery of iron from the ilmenite concentrate. The amounts of fluxing additives (oxides and nitrides Al, Ca, B, and CNB) should not exceed 6% because their increase in the composition of slag may adversely affect the further chlorination (Tables 5 and 6).

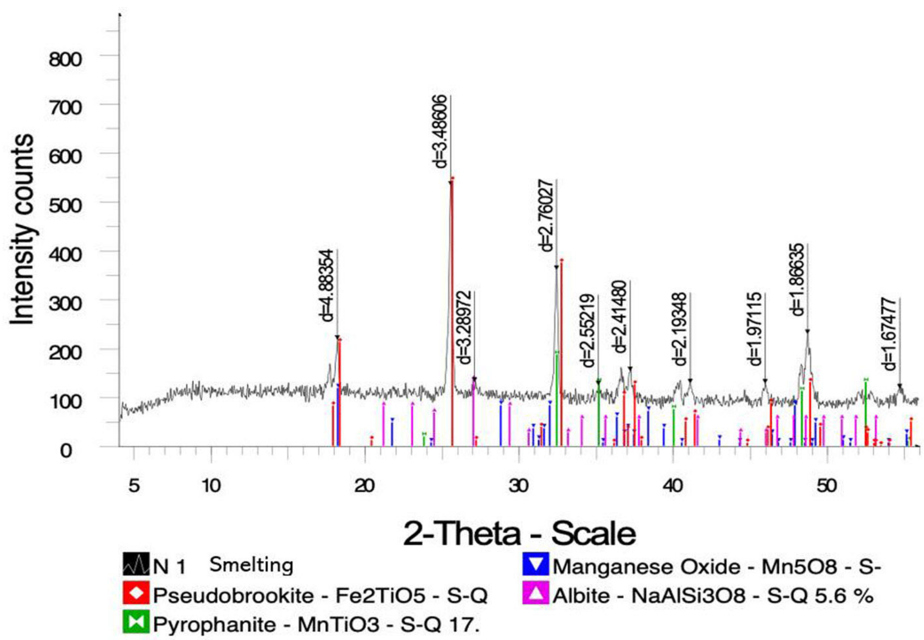

Figure 1. The diffractogram of sample #1 slag (dated 18 November 2020).

Table 5. Interplanar distances and the phase composition of sample #2 slag (dated 18 November 2020).

d, Å	I %	Mineral
4.86872	33.0	
4.17549	15.9	Pseudobrookite, Mn_5O_8
3.46358	100.0	Nepheline, Mn_2O_7
3.27118	16.2	Pseudobrookite
2.99128	16.2	
2.74032	36.7	Nepheline
2.55125	24.8	Pseudobrookite, $MnTiO_3$
2.43595	22.8	$MnTiO_3$
2.21163	17.6	
2.18077	20.6	
1.95920	16.3	
1.85307	37.9	

Note: All the shown diffraction peaks belong only to the above phases. The characteristic diffraction reflexes are marked to allow identification of the present phases.

Table 6. Results of the semi-quantitative X-ray diffraction analysis of sample #2 slag.

Mineral	Formula	Concentration, %
Pseudobrookite	Fe_2TiO_5	57.9
Pyrophanite	$MnTiO_3$	15.2
Manganese Oxide	Mn_2O_7	12.5
Manganese Oxide	Mn_5O_8	8.0
Nepheline	$NaAlSiO_4$	6.3

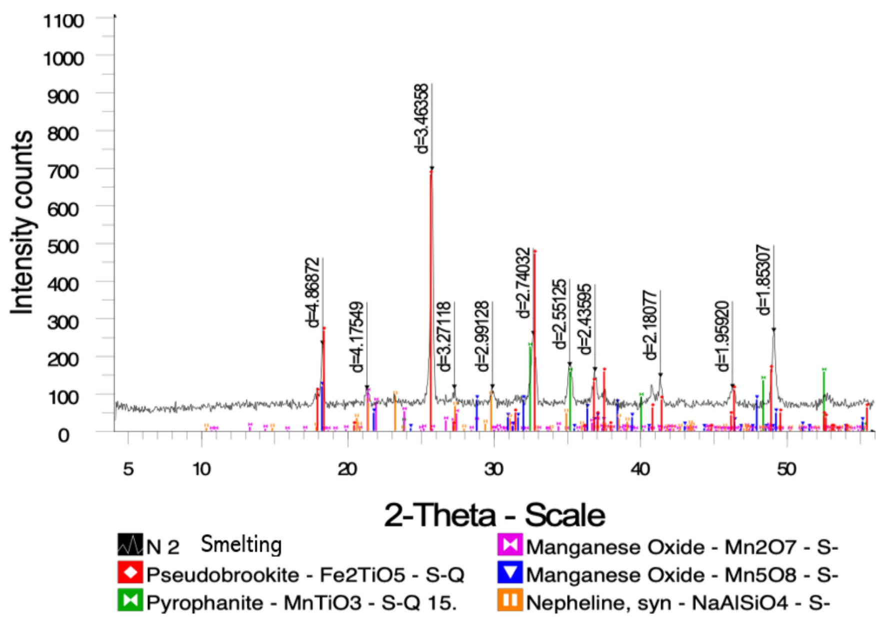

Figure 2. The diffractogram of sample #2 slag (dated 18 November 2020).

The previously conducted laboratory studies have shown the prospects of using boron nitride and CNB as fluxing additives, which allow more complete recovery of iron from the ilmenite concentrate. The amount of fluxing additives (oxides and nitrides Al, Ca, B, as well as CNB) should not exceed 6% because their increase in the composition of slag can adversely affect the further chlorination.

Following the literature review [26], it has been revealed that the refractoriness of slags obtained from the charge without fluxes is explained by the presence in them of a complex solid solution consisting of lower titanium oxides, which prevent the separation of iron into a separate phase [27].

The vibrational method was used to determine the viscosity of melts; by the design and application, it is considered the simplest and most accurate. In this case, a molybdenum spindle, fixed on a suspension, is immersed into the slags under study (Table 7), and data are recorded on its oscillations by means of a signal generator.

Table 7. The composition of the examined titanium slag, %.

Slag Number	1	2	3	4	5	6	7	8	9	10
TiO_2	73.02	81.00	79.10	76.72	73.85	74.75	74.95	74.93	79.29	77.73
FeO	10.66	3.53	4.15	4.86	9.57	8.81	8.54	7.26	3.21	6.64

According to experiments studying the properties of the melts, obtained from the electric melting of Satbayev ilmenite concentrates without the addition of fluxing materials, it was found that the softening temperature of the charge is ~1450–1480 °C (that is significantly higher than that with the addition of fluxes), and the temperature of complete melting was over 1600 °C. In this case, the viscosity and electrical conductivity of the melts are relatively higher, which may be due to the formation of an acidic and conductive phase—a solid solution consisting mainly of iron and lower titanium oxides.

The study of the charge consisting of Satbayev concentrate with the addition of oxides of Al and Ca showed a relatively low softening temperature (~1300–1380 °C) and the melting point of the charge (~1450–1500 °C) compared to the charge without the addition. Moreover, the viscosity and electrical conductivity of the slag and the conditions for the deposition of metal corollas were not reduced, especially with the addition of aluminium oxide.

The addition of nitrides of Al and Ca and boric anhydride (B_2O_3) is a significant decrease in the softening temperature (~1200–1280 °C) and the melting of the charge (~1400–1450 °C) [28,29]. Despite the fact that the addition of nitrides of Al, Ca, and B_2O_3 provided a significant reduction in the viscosity of the slag, there is the consequence of rapid crystallisation with little cooling (i.e., due to the formation of "short" slag). There are also conditions for complete deposition of metal corollas and separation of the individual metal phase (despite the formation of large corollas at the bottom of the crucible, there are medium and small corollas that have not merged with each other). At higher temperatures (over 1400 °C), the electrical conductivity of all melts is relatively the same, which may be due to the formation of the metallic phase. It should be noted that the addition of aluminium oxide in maximum amounts significantly increases the electrical conductivity of the melt at high temperatures. The results of phase and chemical analyses show that despite the reduction of iron content in the slag, the titanium content increases insignificantly. This is due to the fact that iron in the slag is replaced with metals (aluminium, calcium, etc.) of fluxing additives.

Adding boron nitride and CNB revealed a more significant decrease in softening temperature (~1180 °C) and the melting of the charge (~1400 °C). Moreover, at 1450–1500 °C, there is a complete melting and separation of phases, which is a consequence of reducing the viscosity of the slag and improving conditions for complete deposition of metal corollates [30]. In this case, the residual FeO content in the slag decreased to 3.96–4.59% without a significant decrease in the TiO_2 content in the slag [31].

Figure 3 shows that in the high temperature range (1100–1200 °C), there is the greatest resistance melt with the addition of boron nitride and carbonitride. As the temperature increases above 1200 °C, the electrical resistance of the melts decreases; then, above 1400 °C, the electrical resistance of all melts is almost the same. This suggests that with the appearance of a conductive phase, i.e., solid solutions or metallic iron, the electrical conductivity of the entire slag increases.

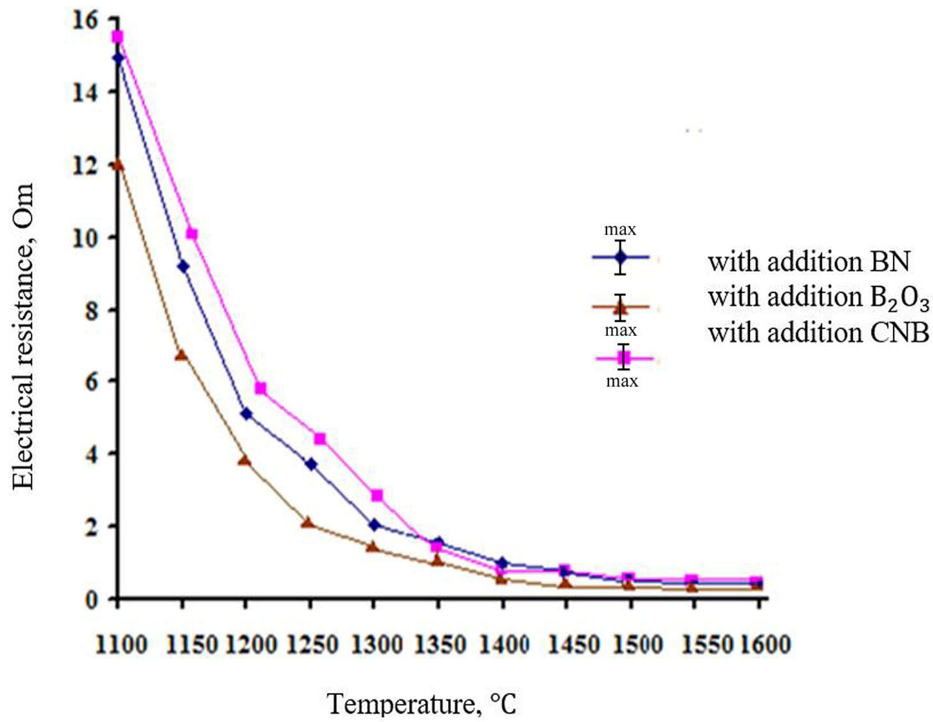

Figure 3. The relation of electrical resistance to temperature melts with the addition of B_2O_3, BN, and CNB.

Therefore, the results of studying the effect of fluxing additives on the melting temperature of the charge, electrical conductivity, and melt viscosity show that, in the temperature range of 1150–1700 °C, the best indicator has the charge with the addition of boron oxide, nitride, and CNB. With the remaining additives at high temperatures, the rate of reduction in viscosity and electrical conductivity decreases [32,33]. This suggests that more suitable fluxing additives in smelting the Satbayev concentrate are boron oxide, nitride, and CNB, as they significantly reduce the melting temperature of the charge and the resulting melts have the best properties, which contributes to improving the conditions of the reducing electrical smelting. Previous experiments allow concluding that boron oxide, nitride, and CNB have a positive effect on the degree of the transition of iron into the metallic phase without much reduction of titanium in the slag. When adding other fluxes, there is a considerable quantity of corresponding oxides, which dilute slag and reduce the content of titanium in slag.

4. Comparative Analysis of the Developed Technology for Obtaining Titanium Slag from Low-Grade Ilmenite Concentrates

The results of the study, presented in this paper, are focused on the development of the effective technology of producing titanium slag from low-grade Kazakhstan ilmenite concentrates, characterised by a high content of refractory components. Satpayev ilmenite, containing 48–55% of TiO_2, was used as the feedstock in the study. The problem of smelting titanium from such concentrate is the complexity of separating it into slag and cast iron. Unlike the majority of studies and industrial productions [4,9,17,25], using high-quality ilmenite concentrates with a TiO_2 content of 55–65%, the authors work with a concentrate containing only 48–55% of TiO_2. Traditional flux smelting methods, using calcium, magnesium, and manganese oxides or alkali and alkaline earth metal chlorides, have turned out to be ineffective for this raw material due to its high energy and capital intensity. In this context, the novelty of the work lies in using fluxing additives: oxides and nitrides of aluminium, calcium, and boron, as well as boron carbonitride. Literature data confirm the applicability of some of these additives [17,23,34,35], but their combination and influence on the smelting process of low-grade concentrates have not been previously studied.

Unlike most studies [36,37] focused on optimising the smelting of high-grade concentrates, this study directly addresses the problem of processing low-grade raw materials. This is a significant contribution, since expanding the raw material base is an urgent task for the titanium industry. Many publications [9,17,25,34,36] describe experiments with various fluxes, but often the studies are conducted using relatively pure and low-melting materials. The presented work shows how to overcome the difficulties associated with the high melting point and slag viscosity that are typical of low-grade concentrates. The use of boron nitride and CNB appears to be particularly effective. This is confirmed by a significant decrease in the melting point of the charge (up to 1400 °C versus over 1600 °C without additives), a decrease in melt viscosity, and, most importantly, improved separation of slag and metal phases. A high degree of iron extraction into pig iron (up to 98%) is also a significant advantage.

Moreover, the authors conduct a comparative analysis of various fluxing additives, not limited to just one additive. The work examines the influence of oxides and nitrides of aluminium, calcium, and boron, comparing their effectiveness. This provides a more complete picture of the mechanisms of action of fluxes and allows choosing the best option for a particular type of raw material. The results of the work show that the mechanism of action of fluxes is complex and multifactorial. It is based on the combined effect of several factors: lowering the melting point, changing the viscosity of the melt, improving the iron reduction process, and modifying the slag phase. The use of boron nitride and CNB becomes the most effective due to their ability to form low-melting compounds and reduce the viscosity of the melt to the greatest extent. A more detailed study of the mechanisms of the interaction of fluxes with the components of the ilmenite concentrate is required for further optimisation of the technological process. Many studies focus on optimising individual process parameters, such as temperature [38] or holding time [39], without a systematic study of the effect of various fluxes. In this paper, a comprehensive analysis was conducted to determine the optimal process parameters for the maximum extraction of titanium into slag and iron into cast iron. This provides a more comprehensive understanding of the effect of the fluxing additives on all the aspects of the smelting process.

The conducted X-ray diffractometric analysis allowed identifying crystalline phases in slag and cast-iron samples that were obtained under different conditions. The analysis revealed changes in the phase composition of the slag with the addition of various fluxes. When using boron nitride and CNB, a decrease in the iron oxide content in the slag was observed, which corresponds to a more effective reduction of iron. The influence of fluxes on the formation of low-melting phases contributed to a decrease in the viscosity of the melt. It was tracked by changes in the composition and amount of crystalline phases. The results of the chemical analysis showed that the addition of boron nitride and CNB made it possible to maintain the high TiO_2 content in the slag while increasing the extraction of iron into cast iron compared to other fluxes. This result is important since maintaining the high TiO_2 content in the slag is important for the subsequent stages of obtaining metallic titanium. A decrease in the melting point and an increase in the electrical conductivity of the melts with the addition of boron nitride and CNB indicate the formation of a metallic phase (cast iron), as well as a change in the oxide ratio.

In comparison with the works aimed at optimisation of the existing technologies [23,34,36–39], this study offers a different approach, solving the problem of processing previously unsuitable raw materials. This allows expanding the raw material base for titanium production. The authors not only propose new fluxing additives but also conduct a study of their influence on the smelting process using modern methods of analysis. An important peculiarity of this work is that the study was conducted, taking into account the conditions of the existing production at the JSC "Ust-Kamenogorsk Titanium and Magnesium Plant". This allows considering the results more practically applicable since real technological limitations and capabilities are taken into account. The sequence of studies, from laboratory experiments to planned pilot tests, is an important advantage. This allows gradually scaling up the technology, minimising risks, and ensuring a gradual transition from laboratory conditions to industrial production.

5. Conclusions

(1) Obtaining titanium slag demonstrated the lack of effective and economically feasible methods for processing low-grade ilmenite concentrates, containing from 48% to 55% of TiO_2. Under these conditions, flux electric welding remains the most applicable process. Studies have shown that the proposed fluxing materials—oxides and nitrides of aluminium (Al), calcium (Ca), and boron (B)—can be successfully used as fluxes due to their stability in reducing medium, high electrical resistance at high temperatures, and ability to have a catholic effect, acting as a lubricant on the walls of the apparatus.

(2) According to the results of the experiments, conducted in the area of extremum, it is found that the specified fluxing materials have different effects on the degree of reduction and separation of iron into a separate phase (into cast iron). For completeness of the processes, it is possible to increase the holding time up to 120 min and the temperature only up to 1600 °C. Also, it is revealed that the addition of the above fluxes decreases reducing agent consumption, i.e., the addition of anthracite to the charge in the area of maximum leads to foaming, the formation of viscous slag, and the increased content of refractory titanium carbide in the slag.

(3) Experiments that are aimed at determining the optimum parameters revealed that the most effective results are achieved with the addition of boron nitride and boron carbonitride (CNB) (up to 3% of the initial concentrate mass). The optimum conditions for achieving maximum iron-to-iron conversion include a process temperature of 1550–1600 °C, a reducing anthracite consumption of 8–10% of the concentrate mass, and a process duration of 90 min. These results are supported by the data obtained from previous laboratory studies. The addition of boron oxide is also a promising approach for smelting titanium slag from the ilmenite concentrate of the Satbaevskoe deposit, being superior to aluminium and calcium oxides in terms of efficiency.

(4) The results of studying the influence of fluxing additives on the melting point, electrical conductivity, and viscosity of the melt show that, in the temperature range of 1150–1700 °C, the best characteristics are demonstrated by the charge with the addition of boron oxide, nitride, and CNB. Other additives have less pronounced effects on viscosity and conductivity reduction at high temperatures. Consequently, boron oxide, nitride, and CNB are preferred fluxing additives for smelting the Satbayev concentrate, as they significantly reduce the melting temperature of the charge and improve the properties of the melts, helping to optimise reductive electro-melting conditions. It is also revealed that these fluxes have a positive effect on the degree of the transition of iron into the metallic phase without significantly reducing the titanium content in the slag.

(5) Balance melting confirmed that when using ilmenite concentrates with Al_2O_3, CaO, B_2O_3, CNB, and CaN_3 additives, titanium recovery in slag is 98–99% and iron recovery in pig iron is 92–95%. The estimated efficiency of ilmenite recovery using an-

thracite is 92%. The use of these additives allows reducing the process temperature by 100–150 °C and provides the formation of liquid slag, which simplifies the separation of pig iron and slag and reduces energy consumption by 2–3% in industrial conditions.

(6) The third stage of research and development (R & D), planned for 2025, includes the study of the behaviour of new additives in the chlorination of titanium slag, pilot tests of the electric smelting of the ilmenite concentrate with new fluxing materials, as well as the preparation of the technological task.

Evaluating the completeness of solving the set tasks showed that, according to the results of the second research stage and developing the possibility of implementing the electric smelting of Satbaev ilmenite concentrates with new fluxing additives (based on oxides and nitrides of Al, Ca, B, and boron carbonitride), CNB was theoretically substantiated and experimentally confirmed. This will allow expanding the raw material base of titanium production in Kazakhstan due to the use of local substandard materials and will improve the technical and economic indicators of electric smelting. The approximate technical and economic efficiency of the introduction of the developed technology of titanium slag production from domestic low-grade and hard-to-extract ilmenite concentrates, using new fluxing additives, is estimated not only by the reduction of transport costs for transportation of imported raw materials.

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