metals

IMPACT FACTOR 2.5

CITESCORE 5.3

Article

Thermodynamic and Technological Studies of the Electric Smelting of Satpaevsk Ilmenite Concentrates

Maxat K. Myrzakulov, Saltanat K. Jumankulova, Madina B. Barmenshinova, Nikita V. Martyushev, Vadim Y. Skeeba, Viktor V. Kondratiev and Antonina I. Karlina

Special Issue

Smelting and Solidification Process of Special Steels

Edited by

Dr. Hongchun Zhu

MDPI

https://doi.org/10.3390/met14111211

metals

MDPI

Article

Thermodynamic and Technological Studies of the Electric Smelting of Satpaevsk Ilmenite Concentrates

Maxat K. Myrzakulov [1], Saltanat K. Jumankulova [2], 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
2 Mining and Metallurgical Institute, Satbayev University, Almaty 050013, Kazakhstan; s.jumankulova@satbayev.university (S.K.J.)
3 Department of Information Technology, 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
6 Stroytest Research and Testing Centre, Moscow State University of Civil Engineering, 26, Yaroslavskoye Shosse, 129337 Moscow, Russia
* Correspondence: martjushev@tpu.ru

Abstract: This work presents the results of thermodynamic and technological studies of the reducing electric smelting of low-quality and difficult-to-recover Satpaevsk ilmenite concentrates in the presence of sodium carbonate (Na_2CO_3) as a flux. In the course of thermodynamic studies, according to literature data and using the HSC Chemistry 8 program, the state diagrams of the FeO-TiO_2, FeO-Fe_2O_3-TiO_2, Na_2O-TiO_2, Na_2O-SiO_2, Ti-C-O and Fe-C-O systems and the possibility of reactions in the temperature range of 500–1600 °C (without smelting of titanium, 1678 °C), taking into account phase transitions, were studied. The article also presents the results of technological studies of the above process. In general, the research results showed the possibility of using sodium carbonate (Na_2CO_3) as a flux in the charge of the electric smelting of low-quality Satpaevsk ilmenite concentrates. It has been established that the addition of 4.5–5% of Na_2CO_3 allows for reducing the temperature and the duration of electric smelting, the viscosity of the melt, and the complete separation of the smelting products (cast iron from slag).

Keywords: ilmenite concentrate; titanium slag; electric smelting; thermodynamic analysis; sodium carbonate; cast iron; reaction; Gibbs free energy; experiments; state diagram

check for updates

Citation: Myrzakulov, M.K.; Jumankulova, S.K.; Barmenshinova, M.B.; Martyushev, N.V.; Skeeba, V.Y.; Kondratiev, V.V.; Karlina, A.I. Thermodynamic and Technological Studies of the Electric Smelting of Satpaevsk Ilmenite Concentrates. *Metals* **2024**, *14*, 1211. https://doi.org/10.3390/met14111211

Academic Editor: Hongchun Zhu

Received: 28 September 2024
Revised: 18 October 2024
Accepted: 22 October 2024
Published: 24 October 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Titanium is one of the most significant metals in modern industrial production due to its unique properties and strategic importance. It is used to create various alloys, among which the heat-proof and heat-resistant materials used in the aerospace, automotive and energy industries stand out. The process of obtaining titanium is a complex technological chain conditioned by the high melting temperature of this metal, which fluctuates in the range from 1672 to 1725 °C, as well as its high chemical activity in the reaction with gases (such as oxygen, hydrogen and nitrogen) and carbon. This makes titanium processing quite complex, requiring precise control at all stages.

Titanium is extracted from its ores, which are enriched before production. An important stage is the treatment of the ore with chlorine to obtain titanium tetrachloride ($TiCl_4$). $TiCl_4$ is then reduced using magnesium, as a result of which a titanium sponge is formed. This intermediate product is then crushed, pressed and sintered to form briquettes, which are then melted down into technical titanium [1,2]. The quality and the characteristics of the final product largely depend on the composition of the raw material. The presence of

different substances in ores and forms of titanium compounds determines the selected technology for its extraction and smelting. Therefore, for each specific deposit, it is necessary to individually develop technological processes based on the experience of working with ores, obtained from similar deposits. This emphasizes the need for a constant scientific approach and adaptation of technologies depending on changes in mining conditions and the characteristics of the raw material.

The raw material for the production of metallic titanium and its pure compounds is mainly ilmenite concentrates [3]. The quality of ilmenite concentrates depends on the content of titanium dioxide and impurities that complicate further treatment. The TiO_2 content in ilmenite concentrates from placer deposits usually ranges from 49 to 66%, and from primary deposits, it ranges from 40 to 48%. The lower the TiO_2 content, the more impurities in the concentrate, and the more difficult it is to obtain a high-quality product from it. The most common method of enriching the ilmenite concentrate by TiO_2 is a chemical method of electrothermal smelting [1]. This is a high-temperature (1650–1950 °C) process based on the reduction of iron oxides, accompanied by their release into a separate metal product (cast iron). As a result, titanium oxides form a separate product (the titanium slag with a TiO_2 content of 75–92%). Depending on the form and content of TiO_2, iron oxides and other impurities in the original ilmenite concentrate, various options for electrothermal smelting are used, including those with preliminary roasting, with the addition of fluxes, etc. [4,5]. The electric smelting of low-quality ilmenite concentrates from the Satpaevsk deposit (Kazakhstan)—containing no more than 50–51% of TiO_2, more than 25–30% of Fe_{tot} (in the form of Fe_2O_3 and FeO) and other impurities, such as silicon oxide, chromium and aluminum—occurs at a temperature of 1750–1850 °C. It proceeds with certain difficulties associated with the formation of a viscous and refractory melt. During non-flux smelting, a melt is formed that quickly solidifies at the slightest decrease in temperature, and when the temperature increases, it foams and spills over the edge of the furnace [3–5]. This leads to a disruption in the technological process and not only to the loss of valuable components but also to an increase in the consumption of electricity and the reducing agent [6,7].

The current work is aimed at improving the technology of titanium smelting, applicable to specific deposits with a certain ore composition. The work examines the possibility of smelting titanium by lowering the temperature from 1800–1850 to 1500–1600 °C by the end of the smelting by using the addition of sodium carbonate. However, as practice shows, a suitable technology for one deposit may require significant changes when applied to other deposits with different ore compositions [8]. In this regard, an important scientific task is to study and refine the existing methods of titanium smelting, taking into account the peculiarities of the ilmenite concentrate mined at the Satpaevsk deposit in Kazakhstan. Within this work, thermodynamic and technological studies of the titanium smelting process were performed to optimize the technology for its production from low-quality ilmenite concentrates of this deposit. To solve the identified problems during the smelting process, the efficiency of using sodium carbonate as a flux was studied. The studies will allow for adapting existing technologies to the conditions of the Satpaevsk deposit and increasing the extracted quantitative and qualitative indicators of titanium.

2. Methods and Materials

The general plan of the study consisted of two main stages.

In the first stage, a comprehensive assessment of all factors influencing the electric smelting of Satpaevsk ilmenite concentrates was made. For this purpose, literary data involving thermodynamic studies were analyzed using the HSC Chemistry 8 software. As a result of these studies, conclusions were drawn about the thermodynamic feasibility of the selected reaction based on the negative change in Gibbs energy.

In the second stage of the work, technological experiments on the electric smelting of the Satpaevsk ilmenite concentrate were conducted to confirm the obtained thermodynamic calculations. In these experiments, a flux additive in the form of sodium carbonate was used. These experiments allowed for detailing the practical application of theoretical conclusions

and evaluating the efficiency of the selected technology under conditions corresponding to real production processes.

2.1. Thermodynamic Studies

Thermodynamic studies were carried out using the HSC Chemistry 8 software developed by specialists from the Outotec Research Center. This package includes a database of thermodynamic characteristics of more than 28,000 substances and their properties. The study includes calculations of thermodynamic functions of possible chemical reactions in the FeO-TiO_2, FeO-Fe_2O_3-TiO_2, Na_2O-TiO_2 and Na_2O-SiO_2 systems in the temperature range of 500–1600 °C, considering phase transitions, as well as a study of the state diagrams of ternary systems (Ti-C-O, Fe-C-O) to determine the conditions for the formation of individual phases and to interpret the results of thermodynamic and technological studies. All thermodynamic quantities were selected in the ranges of the existence of different phases using the HSC Chemistry 8 software.

2.2. The Electric Smelting of the Ilmenite Concentrate

Technological studies of the electric smelting of the Satpaevsk ilmenite concentrate were conducted under laboratory conditions in the Nabertherm RHTH 120/150/...1600 (Lilienthal, Germany) furnace in the temperature range of 1400–1600 °C. The consumption of the reducing agent (anthracite) was determined by calculation and amounted to 8% of the concentrate mass; the consumption of the flux in the form of sodium carbonate was from 1.5 to 5%. The charge was prepared by mixing the calculated amounts of the concentrate, anthracite and flux. The composition of the concentrate is provided in Table 1. The ready-made charge was poured into a crucible and placed in the working zone of the furnace. Heating and holding the melt at the specified temperature occurred according to a predetermined scheme with automatic control of the parameters in the furnace control unit. The duration of the melts at the specified temperature varied from 30 to 60 min depending on the temperature of the start of charge melting. After the furnace was turned off, the crucible with the melt was cooled naturally up to room temperature, and the resulting product was separated into slag and cast iron. Slag and metal samples were then analyzed to determine their composition and structure. Based on the analysis results, the flux (sodium carbonate) consumption, temperature and duration of the process were adjusted in subsequent melts.

Table 1. The chemical composition of the ilmenite concentrates of Satpaevsk (Kazakhstan) and Volnogorsk (Ukraine) deposits.

Type of Concentrate	Content of Components in the Concentrate, Mass. %												
	TiO_2	FeO	Fe_2O_3	SiO_2	Al_2O_3	Cr_2O_3	MgO	MnO	CaO	P_2O_5	V_2O_5	ZrO_2	Nb_2O_5
Satpaevsk	51.15	16.57	27.51	2.10	1.25	0.20	0.20	0.35	0.20	0.05	0.20	0.20	0.02
Volnogorsk	66.65	27.12	–	1.12	1.23	0.51	1.50	1.02	0.35	0.05	0.20	0.22	0.03

2.3. X-Ray Analysis of Samples

The phase composition was studied using an ARL X'TRA X-ray diffractometer in CuK_α radiation. The sample under study was prepared by pressing; the survey was performed in comparison with an internal standard (germanium) in the angle range of $2\theta = 5 \div 150^\circ$. After introducing the corrections, the calculation was made according to the $2\theta_{meas} \rightarrow {}'_{meas} \rightarrow \alpha$ scheme. The measurement accuracy under the specified conditions at a recorder speed of 2400 mm/h was 0.02–0.04 deg., depending on the quality of the X-ray pattern lines.

3. Results and Discussion

3.1. Analysis of Theoretical Aspects of Titanium Smelting from Ilmenite Concentrate

Before the thermodynamic study, the chemical and phase composition of the Satpaevsk ilmenite concentrate and, according to the literature data, the state diagrams of some systems, such as FeO-TiO_2, FeO-Fe_2O_3-TiO_2, Na_2O-TiO_2 and Na_2O-SiO_2, were studied [9,10]. It should be noted that, at present, there are no complete data for private ternary systems, such as Fe-Ti-O [11].

Table 1 shows the results of the chemical analysis of the Satpaevsk ilmenite concentrate and the chemical composition of the Volnogorsk ilmenite concentrate (Ukraine) for comparison. Let us note that the ilmenite concentrate of the Volnogorsk deposit (Ukraine) is among the richest and purest since the content of the main component (TiO_2 is about 66%, and the total content of harmful components, such as SiO_2, Al_2O_3 and Cr_2O_3, is low.

Table 1 shows that the distinctive feature of the Satpaevsk ilmenite concentrate is the low content of titanium dioxide (51.15%), the presence of iron Fe_2O_3 oxide (27.51%) and a slightly high content of SiO_2 (2.10%). In the Satpaevsk ilmenite concentrate, the percentage ratio of iron oxides is FeO:Fe_2O_3 = 37.6:62.4 and FeO:Fe_2O_3 = 100:0 in the Volnogorsk concentrate. The total content of iron in the form of FeO (in terms of 27.51% of Fe_2O_3 to FeO) in the Satpaevsk concentrate is 28.95%, which is higher than that in the Volnogorsk concentrate (27.12%). The presence of other impurities (such as Al_2O_3, Cr_2O_3, MgO, MnO, CaO, etc.) is not greater than that in the Volnogorsk concentrate. The Satpaevsk ilmenite concentrate visually has a rich black color compared to that of the Volnogorsk one.

According to [12], the main ore minerals of the Satpaevsk concentrate are ilmenite and arizonite, and there are also very small amounts of rutile, anatase and iron hydroxides. Non-metallic minerals consist of quartz and small amounts of feldspar minerals: albite, anorthoclase and minerals such as zircon and leucoxene are also noted. The results of the X-ray phase analysis of the Satpaevsk ilmenite concentrate samples are given in Table 2 and they confirm these literary data.

Table 2. The phase composition of the Satpaevsk ilmenite concentrate.

The Name and the Formula of the Mineral	Content, %	The Name and the Formula of the Mineral	Content, %
Ilmenite, $FeO{\cdot}TiO_2$	35	Staurolite, $Fe(OH)_2{\cdot}2AlSiO_5$	1
Arizonite, $Fe_2O_3{\cdot}3TiO_2$	45	Quartz, SiO_2	1
Alumosilicate, $Al_2O_3{\cdot}SiO_2$	8	Leucoxene, $TiO_2{\cdot}nH_2O$	1
Chromite, $(Mg,Fe)_3(Al,Fe^{3+})_n{\cdot}(OH)_4$	6	Zircon, $ZrO_2{\cdot}SiO_2$	0.5
Tourmaline, $MnO{\cdot}TiO_2$	2	Rutile, TiO_2	0.5

The X-ray phase analysis showed that the Satpaevsk concentrate belongs to modified ilmenite concentrates, where titanium dioxide, in addition to ferric iron ($FeO{\cdot}TiO_2$, where TiO_2 is 18%), is also associated with ferrous iron ($Fe_2O_3{\cdot}3TiO_2$, where TiO_2 is 27%). The presence of natural spinelides from the magnetite series in the Satpaevsk ilmenite concentrate is also possible. Spinelides and solid solutions were studied in detail by McChesney and Moine, Akimoto, Lepp, Basta, Vincent and many others [13,14] as early as the second half of the last century (1950–1960). In their opinion, solid solutions, such as $Fe_2^{2+}TiO_4$ ulvospinel, with a melting point of 1470 °C, as well as titanium maghemite with γ-Fe_2O_3, formed during low-temperature oxidation of titanium magnetite and a series of Fe_2TiO_5-$FeTi_2O_5$ solid solutions can be found in the natural mineral of up to 44.35–51.8%. The rich black color and refractoriness of the Satpaevsk ilmenite concentrate are possibly associated with the presence of "natural" spinelides in it, and the obligatory appearance of "synthetic" spinelides is from reducing electric smelting, which has been proven by thermodynamic and technological studies.

Analysis of the diagrams of the FeO-TiO_2, FeO-Fe_2O_3-TiO_2 systems (Appendix A, Figure A1, the state diagram of the $FeOn$-TiO_2 system according to McChesney and

Moine [13]) shows that in the temperature ranges of 1200–1550 and 1350–1850 °C there are solid solutions based on pseudobrookite, hematite–ilmenite and magnetite–ulvospinel. In addition, depending on the content of components and the temperature in the FeO-Fe_2O_3-TiO_2 system, the following phases may be present: wustite, hematite, magnetite, 2FeO*TiO_2 ulvospinel, FeO*TiO_2 ilmenite, FeO*2TiO_2 pseudobrookite, rutile and their mixture.

According to the authors of [15], all of these compounds are solid solutions of complex composition, which are formed as a result of the unlimited dissolution of iron and titanium oxides in each other, for example, magnetite and hematite in ulvospinel and ilmenite or FeO*2TiO_2 pseudobrookite, formed at a temperature of 1115–1150 °C, can be a chemical compound or a solid solution of Ti_3O_5 in Fe_2O_3*TiO_2 pseudobrookite, etc.

In the diagram of the FeO-0.5Fe_2O_3-TiO_2 system (Appendix A, Figure A2) with an atomic proportion of 0.5Fe_2O_3, known high-temperature solid solutions are noted. According to the authors, ulvospinel can pass into ilmenite or into an aggregate of ilmenite, magnetite and metallic iron. Figure 1 shows a diagram of a part of the Fe-Ti-O system.

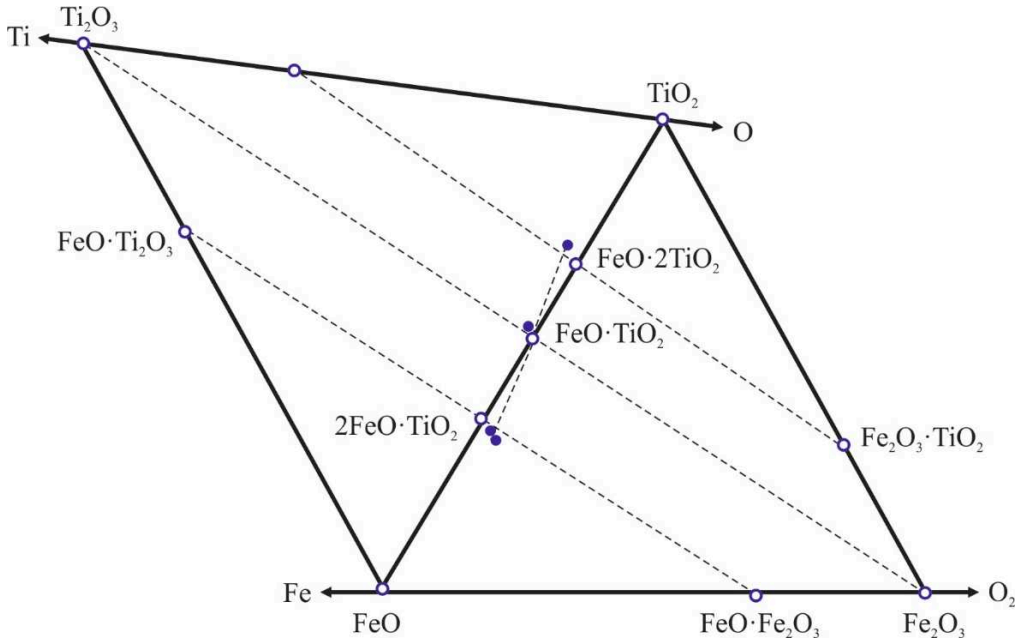


Figure 1. Diagram of a part of the Fe-Ti-O system. Adapted from Ref. [16].

According to the authors of [17,18], during the reducing electric smelting of ilmenite concentrates, there is difficulty in equalizing the phase composition, which is associated with the high rate of iron reduction and the accumulation of cast iron at the initial stage of the process. This leads to the fact that thermodynamic equilibrium cannot be achieved.

The distribution of iron and titanium between cast iron and slag is conditioned by the difference in the affinity of these metals for oxygen, which, in turn, depends on the partial pressure of carbon oxide in the pores of the charge. Therefore, the authors conclude that the consumption of the reducing agent and temperature are the key parameters determining the efficiency of the electric smelting process. This conclusion emphasizes the importance of monitoring these factors to achieve an optimal result in reducing electric smelting.

In Figures 2 and 3, diagrams of phase stability in the Ti-C-O and Fe-C-O systems are presented. We constructed them in the HSC Chemistry 8 software at a constant value of the partial pressure of oxygen of 1^{-20} bar and 5 bar, a change in temperature within 0–1600 °C and a changing partial pressure of CO and CO_2.

Figure 2 demonstrates that in the Ti-C-O system at a partial pressure of CO below 0.5 atm and a partial pressure of oxygen of 1^{-20} bar, the most stable compound is TiO_2 up to a temperature of 930 °C; the lower oxide Ti_6O_{11} is stable at 930–970 °C, Ti_3O_5 at 970–1280 °C and Ti_2O_3 at 1290–1320 °C. TiO exists above a temperature of 1320 °C. In the

Fe-C-O system, under these conditions, the stable compound is FeO up to a temperature of 960 °C, and only metallic iron and iron carbide are stable above 960 °C.

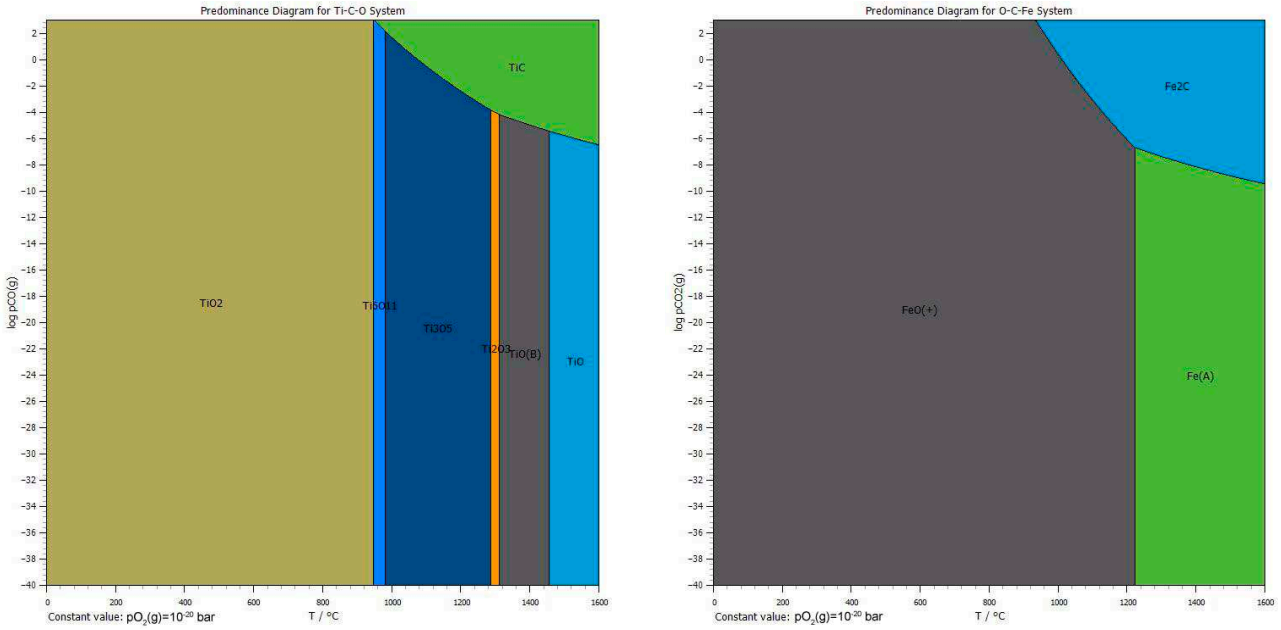


Figure 2. Diagram of phase stability in Ti-C-O and Fe-C-O systems at a constant value of partial oxygen pressure of 1^{-20} bar.

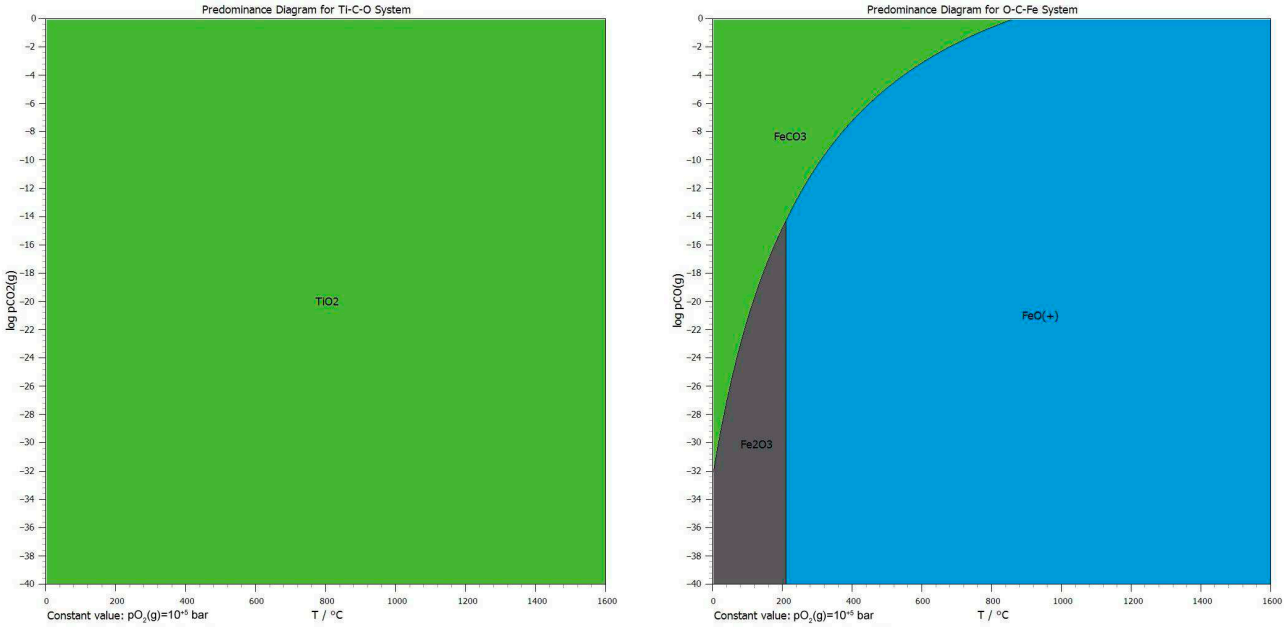


Figure 3. Diagram of phase stability in Ti-C-O and Fe-C-O systems at a constant value of oxygen partial pressure of 5 bar.

Figure 3 shows that in the Ti-C-O system at a partial pressure of CO below 0.5 atm and a partial pressure of oxygen of 5 bar, only TiO_2 is stable, and in the Fe-C-O system under these conditions and above a temperature of 850 °C, only FeO is a stable compound. It follows that during the reduction of iron oxides closer to a temperature of 1000 °C, metallic iron (cast iron) begins to appear. At the same time, the reduction of TiO_2 begins in parallel with the formation of lower titanium oxides, the most stable of which are Ti_6O_{11}, Ti_3O_5 anosovite, Ti_2O_3 tistarite and TiO, capable of forming refractory spinelides and solid solutions.

The authors of [9,19] classify titanium TiO_2 dioxide as an acidic oxide and network former since TiO_2 forms oxygen networks in the slag with a spatial bonding connected by bridges through oxygen atoms. The crystal structure of TiO_2 consists of spatially arranged TiO_6 octahedra, where titanium is sixfold coordinated with the surrounding oxygen anions. In different polymorphs of TiO_2, the edges of the octahedron are connected to each other in different ways, for example, in rutile through common corners, in anatase through edges and in brookite through edges and corners [17–19]:

As shown by Figure 4, the unit cell of Ti_3O_5 contains two Ti^{3+} sites and one Ti^{4+} site, and each Ti site is a distorted oxygen octahedron, where the Ti-O distances differ significantly from each other. Unlike TiO_2, in the octahedral sites of Ti_2O_3, the octahedra have a common face with each other through three edges in the plane and contain pairs of Ti^{3+} ions [20]. This means that with a decrease in oxygen in the Ti-O system, the crystal structure of the melt becomes more complex and stronger. In the presence of basic oxides, the network in the structure of TiO_2, Ti_3O_5 and Ti_2O_3 is broken, and, with an increase in the concentration of metal cations, free oxygen ions are formed. The difficulties that are encountered during the reducing electric smelting of ilmenite concentrates may be due to the presence of a complex crystalline structure of the titanium slag, which is formed along with the formation of lower oxides, such as Ti_3O_5 and Ti_2O_3. These oxides can promote the formation of refractory spinelides and solid solutions, including both acidic and basic oxides of the metals contained in the concentrate. As a result of these processes, the acidity of the melt increases, which in turn leads to an increase in its viscosity and melting point. These changes significantly complicate the electric smelting process, creating additional difficulties in controlling the technological parameters (such as acidity and alkalinity of the melt, chemical composition, melting point). Therefore, understanding the interaction of oxides during reducing electric smelting is critically important for optimizing the processes and increasing their efficiency.

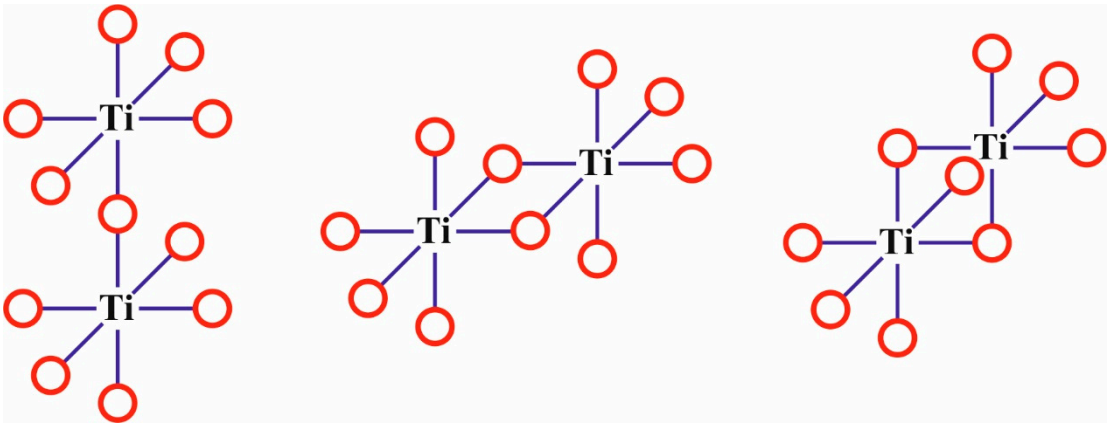


Figure 4. Crystal structures of Ti_3O_5 and Ti_2O_3. Adapted from Refs. [20–22].

The authors of [23–25] attribute the uncertain behavior of TiO_2 in slags to its variable valence and smelting conditions. With a lack of oxygen (under reducing conditions), the valence of titanium and the oxygen content in its oxides decrease, which leads to titanium starting to behave as the "main" oxide of the slag, turning into a reducing agent. Under conditions of a highly oxidizing environment, when the oxygen content in the slag is high, titanium is predominantly present in the form of the TiO_2 oxide and exhibits behavior similar to SiO_2.

Based on the above, several key conclusions can be made about the behavior of the components of the ilmenite concentrate and a possible mechanism for its reduction under electric smelting conditions can be proposed:

- At the initial stage of reducing electric smelting (at temperatures of up to 1000–1100 °C), when the oxygen content is still quite high, the solid-phase reduction of iron oxides with carbon and its oxide occurs.
- With an increase in temperature and a decrease in the oxygen content, the reduction of TiO_2 begins with the formation of lower oxides (Ti_3O_5 and Ti_2O_3), which begin to play the role of reducing agents.
- These lower oxides are capable of reducing oxides of other metals contained in the slag.
- The formation of refractory spinelides and the breaking of bonds in their crystal lattice depends on the content of acidic and basic oxides of other metals in the charge and in the ore, which ultimately influences the characteristics of the slag, such as acidity, viscosity, smelting capacity, etc.

An increase in slag acidity leads to an increase in its viscosity and complicates the separation of smelting products (the slag and cast iron) even at high temperatures (1650–1700 °C). This can lead to an increase in the iron content of the titanium slag. In production conditions, this may require very high temperatures (1850–1950 °C), which entails significant costs of electricity and a carbon-reducing agent for the final finishing. This, in turn, negatively influences the technical and economic indicators of the electric smelting process [26,27]. Taking into account the above behavior of the components and the regulation of the possible mechanism for the reduction of the ilmenite concentrate, these difficulties can be eliminated. In view of this, many researchers have proposed various solutions to this problem, including:

- A two-stage process consisting of the following operations: first, the solid-phase roasting of the ilmenite concentrate to reduce part of the iron oxides; then, the magnetic separation of the reduced part of the iron oxides and subsequently, ore-thermal smelting of the titanium-containing part of the cinder to produce the high-quality titanium slag (in a reducing atmosphere created by blowing argon).
- A single-stage process with the addition of fluxes, such as pure oxides (CaO, MgO, MnO, B_2O_3), chlorides (NaCl, KCl) and nitrides (AlN_3, BN, CNB) of metals, as well as titanium production waste (depositions of sludge collectors) and natural ores (boron, manganese ore, limestone, magnesite) [3–7,26].

These approaches can improve the efficiency of reduction and the electric smelting of ilmenite concentrates.

It should be noted that the addition of sodium carbonate (soda) to the electric smelting charge has not been well studied. In [27], in laboratory and pilot-industrial conditions, the authors tested the addition of soda to the electric smelting charge of iron-titanium concentrates containing about 55% of TiO_2, ~20% of Fe_{tot}, Al_2O_3, SiO_2 and Cr_2O_3. Despite the positive effect of soda on the process, the authors still propose using a combined flux consisting of 2% soda and 5% limestone. The authors do not explain the reason for this decision. This is probably due to either the high cost of soda at that time or the high content of acidic oxides (Al_2O_3, SiO_2) in the concentrate. Soda forms compounds in the form of aluminosilicates that pass into the slag; limestone (CaO) prevents this process and displaces Na_2O from aluminosilicates, thereby enhancing the catalytic effect of soda during electric smelting [28]. In [29], the authors also conducted several series of laboratory experiments with the ilmenite concentrate, containing (mass. %) TiO_2—45–47, Fe_2O_3—14–18, FeO—33–35, Al_2O_3—0.6, SiO_2—0.9 and Cr_2O_3—0.05, to compare the efficiency of various types of additives, including soda in an amount of 12% of the concentrate mass, while the consumption of the coke-reducer was 6%. The authors indicate that the addition of soda in the specified amount reduces the temperature of the end of the melting up to 1300 °C. At the same time, the slag was fluid, but the content of iron oxides in the slag was high (26%), and, accordingly, that of the titanium oxides was low (58%). Apparently, because of the lack of the coke-reducer (only 6%), the iron oxides were not completely reduced, and the high content of soda ash (12%) led to a decrease in the titanium content in the slag. In [30], the authors also tested many options for obtaining high-titanium slags from the lean concentrate ($TiO_2 \leq 46\%$) in the MAGMA-3 unit. In this case, preference is

still given to a one- and two-stage scheme without adding flux, where coke consumption is 10–15%, a temperature within 1600–1650 °C is used, and 12–15% of iron oxides are left in the slag. When smelting richer concentrates ($TiO_2 \geq 55\%$), it is suggested to add lime (10–15% of the concentrate mass), soda ash (5–10%) and coke (6–13%). This allows for reducing the temperature up to 1360–1500 °C and the FeO content in the slag up to 3–4%.

As a result of studying the literature data, we conclude that the two-stage process clearly leads to an increase in capital costs in production. Therefore, electric smelting with fluxes in the form of sodium carbonate (soda) is more acceptable for processing the Satpaevsk ilmenite concentrate into titanium slag. In this case, the soda consumption can be about 3% of the mass of the original concentrate. Several technological experiments were performed to study the effect of soda on temperature, duration of the electric smelting process and the composition of the products.

The results of the thermodynamic analysis conducted in the temperature range of 500–1600 °C, considering phase transformations, are provided in Appendix B. Reactions 1–4 consider the reduction of ilmenite without the addition of soda. They prove that the formation of metallic iron develops only from a temperature of 900–1000 °C, and up to this temperature, only the formation of FeO is possible in the system. The comparison of the negative values of the change in Gibbs energy in reactions 2–3 shows that during the reduction of ilmenite, accompanied by the formation of FeO and TiO_2, the combustion of solid carbon occurs with gaseous oxygen (in the form of atmospheric oxygen) and not with active oxygen (in the form of oxides). The formation of lower titanium Ti_2O_3 oxide (reaction 4) is possible only above 1000 °C.

The negative value of the change in Gibbs energy implies that reactions with the addition of Na_2CO_3 have significant differences from the reactions without the additive, especially at low temperatures. According to the state diagram of the Na_2O-TiO_2 system [7], in the system, in addition to $Na_2O{\cdot}3TiO_2$, which melts incongruently at 1130 °C, and $4Na_2O{\cdot}5TiO_3$, which melts congruently at 1027 °C, $Na_2O{\cdot}TiO_2$, which melts congruently at 1030 °C, was also found. Reactions 5–13 show the formation of these sodium titanates under two conditions:

(1) As a result of the interaction of ilmenite and soda;
(2) As a result of the interaction of pure sodium (Na_2O) and titanium (TiO_2) oxides.

In the first variant, the change in Gibbs energy becomes negative at temperatures above 600–700 °C and, with increasing temperature, has large negative values, especially in reactions of ortho- and polytitanates formation. In the second variant, the reactions are impossible since, with increasing temperature (when the temperature increases above 900–1000 °C), a decrease in the negative values of the change in Gibbs energy is noted. A comparison of the changes in Gibbs energy of reactions 7–8 allows the conclusion that, when using solid carbon as a reducing agent, the reaction proceeds predominantly with the formation of carbon monoxide, but the formation of carbon dioxide is not excluded.

Reactions 14–19 show interactions among Na_2O, Al_2O_3 and SiO_2. In them, the change in Gibbs energy has a large negative value only in reaction 19. Consequently, compared with the other reactions of the sodium aluminate and silicate formation, the reaction, accompanied by the formation of sodium alumosilicate, is more probable and develops at low temperatures. Since the content of Al_2O_3 and SiO_2 in the Satpaevsk ilmenite concentrate is insignificant, the loss of flux (sodium carbonate) with this reaction will be insignificant.

In view of this, the addition of sodium carbonate to the charge of the electric smelting of low-grade and refractory ilmenite concentrates can contribute to a more effective reduction and separation of iron into a separate phase at relatively low temperatures. Sodium carbonate, interacting with oxides, promotes the formation of low-melting sodium alumosilicate in the presence of a significant amount of silicon and aluminum oxides in the ore. This, in turn, prevents the interaction of lower titanium oxides with these components until refractory compounds are formed. Adding soda reduces the melting point of slags and their viscosity.

In addition, the introduction of sodium carbonate lowers the start temperature of all possible reactions by at least 200–300 degrees. This allows the final temperature of the electric smelting process to be reduced from the range of 1600–1800 °C to 1300–1500 °C. Therefore, the use of sodium carbonate not only increases the efficiency of the reduction smelting process but also contributes to improving the physical and chemical properties of the resulting slags.

3.2. The Experimental Smelting of Titanium from the Ilmenite Concentrate

In the technological studies, we used the Satpaevsk low-grade ilmenite concentrate, the type and composition of the phases of which are shown in Figure 1 and in Tables 1 and 2. Twenty experiments (melts) were conducted under the conditions; Table 3.

Table 3. Conditions for conducting technological studies.

Group Number	Melt Number	Flux Consumption (Na_2CO_3), %	Consumption of the Reducing Agent (Anthracite), %	Temperature, °C	Time, min
I	1–5	1.5	8	1400–1600	45–60
II	6–11	3	8	1400–1600	45–60
III	12–16	5	8	1400–1500	30–45
IV	17–20	4.5	8	1400–1500	30–45

In group I of the experiments, the complete melting of the charge was not observed at 1400 °C for 60 min. Melting occurred at t = 1500 °C, but after holding for τ = 60 min, only a viscous melt was formed; upon cooling, the product was magnetic, and no separation of cast iron and the slag occurred. At 1600 °C, after holding for 45–60 min, a more liquid melt was formed, but part of the iron remained in the slag in the form of iron oxides. The results of the semi-quantitative X-ray phase analysis are shown in Figures 5 and 6. The composition of the slags obtained in experiment group I is given in Table 4.

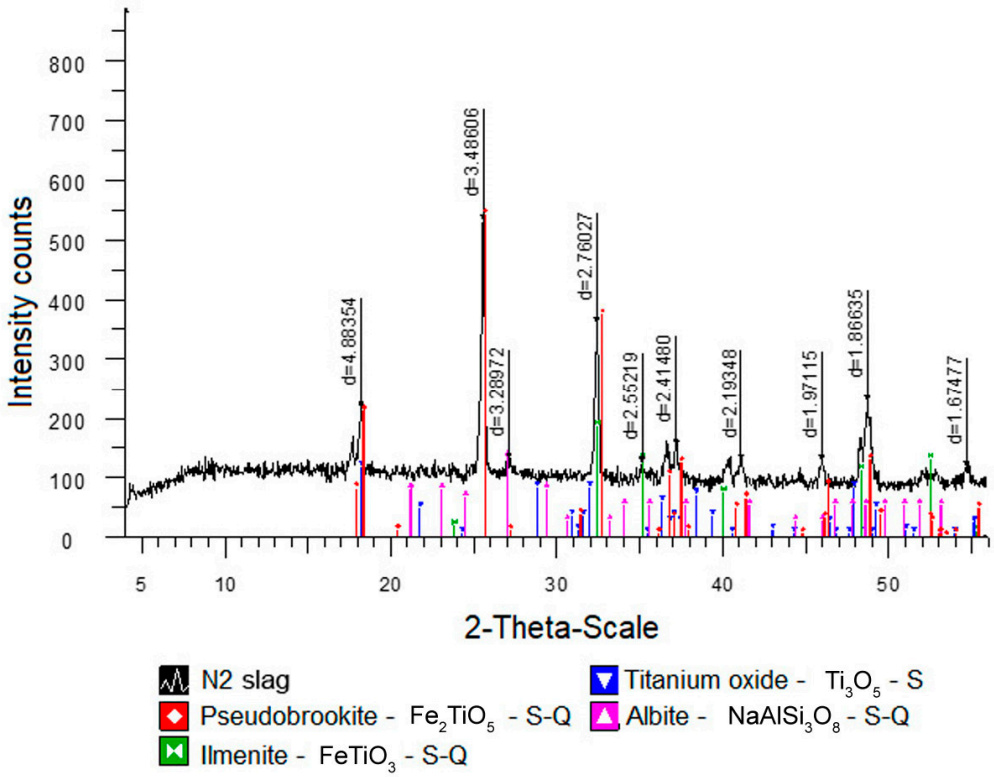


Figure 5. Diffractogram of sample No. 2 (slag).

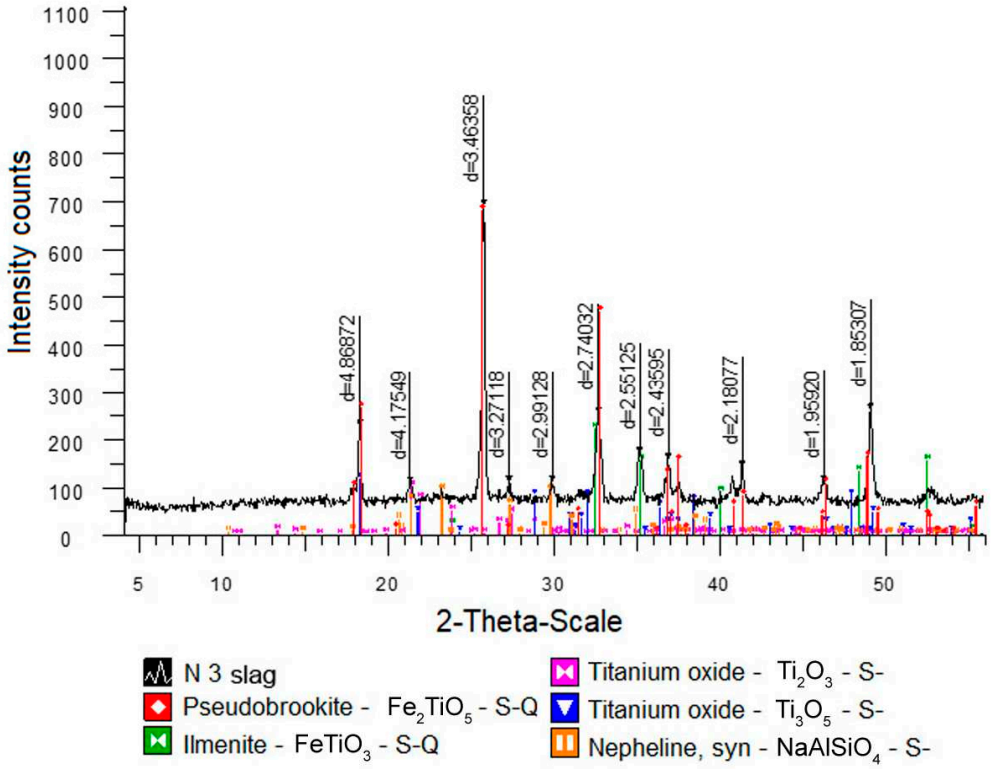


Figure 6. Diffraction pattern of sample No. 3 (slag).

Table 4. Composition of products from experiment group I (with 1.5% addition of Na_2CO_3).

Experimental Conditions	Slag Composition, %						
	TiO_2	FeO	Na_2O	Al_2O_3	Si_2O	MnO	P_2O_5
at 1400 °C, 60 min	56.85	24.27	2.15	6.45	5.76	3.72	0.57
at 1500 °C, 60 min	63.12	18.66	2.31	5.89	5.52	3.65	0.45
at 1600 °C, 45 min	64.52	16.85	2.25	6.25	5.86	3.62	0.41
at 1600 °C, 60 min	67.26	14.25	2.24	6.15	5.75	3.44	0.52

Based on the experiment (Figures 5 and 6 and Table 4), we conclude that with the addition of 1.5% sodium carbonate to the charge of the electric smelting of Satpaevsk low-grade ilmenite concentrates at a temperature of 1400–1500 °C, the pseudobrookite and ilmenite phases are the main components present. Apparently, at this temperature, iron is reduced in the solid phase, and with the appearance of the liquid phase, the formation of lower titanium oxides begins. At 1600 °C, the reduced part of iron is not released into a separate phase and remains in the melt. The formation of synthetic sodium alumosilicates (albite and nepheline) is apparently associated with the partial interaction of the crucible material (alundum) with sodium carbonate.

Group II of the experiments was conducted under the same conditions, but the amount of flux additive in the form of sodium carbonate was 3% of the concentrate mass. The composition of the slags obtained in the experiments of group II is presented in Table 5 and Figure 7. In this group of experiments, good results were obtained at a temperature of 1500 °C with a holding time of 45–60 min. In this case, the melt was fluid. Iron was well separated in the form of a large piece at the bottom of the crucible. At 1400 °C and a melting time of 60 min, small iron beads were found in the product. Apparently, owing to high viscosity and insufficient temperature, these beads did not have time to combine with each other and separate from the slag as a separate phase. At 1600 °C with a

holding time of 45–60 min, the composition of the products changed little. The presence of sodium alumosilicate in all slag samples is evident from the interaction of Na_2CO_3 with the crucible material.

Table 5. The composition of products from group II of the experiments (with 3% addition of Na_2CO_3).

Experimental Conditions	Slag Composition, %						
	TiO_2	FeO	Na_2O	Al_2O_3	Si_2O	MnO	P_2O_5
at 1400 °C, 45 min	59.42	21.79	2.18	6.25	6.17	3.78	0.09
at 1400 °C, 60 min	61.92	20.24	2.12	6.12	5.21	3.55	0.55
at 1500 °C, 45 min	72.25	10.61	2.22	5.36	5.10	3.67	0.44
at 1500 °C, 60 min	72.50	9.53	2.21	5.91	5.49	3.67	0.34
at 1600 °C, 45 min	68.65	11.64	2.45	6.37	6.21	3.78	0.55
at 1600 °C, 60 min	70.17	11.31	2.36	6.12	6.04	3.55	0.09
The average composition of cast iron, %							
	C	Ti	Si	Mn		Fe	
at 1500 °C, 45–60 min	2.47	1.07	0.58	0.12		Res.	

Note: Based on the chemical analysis data of the products, only the main components are provided in the table. The composition of slags is recalculated in terms of metal oxides.

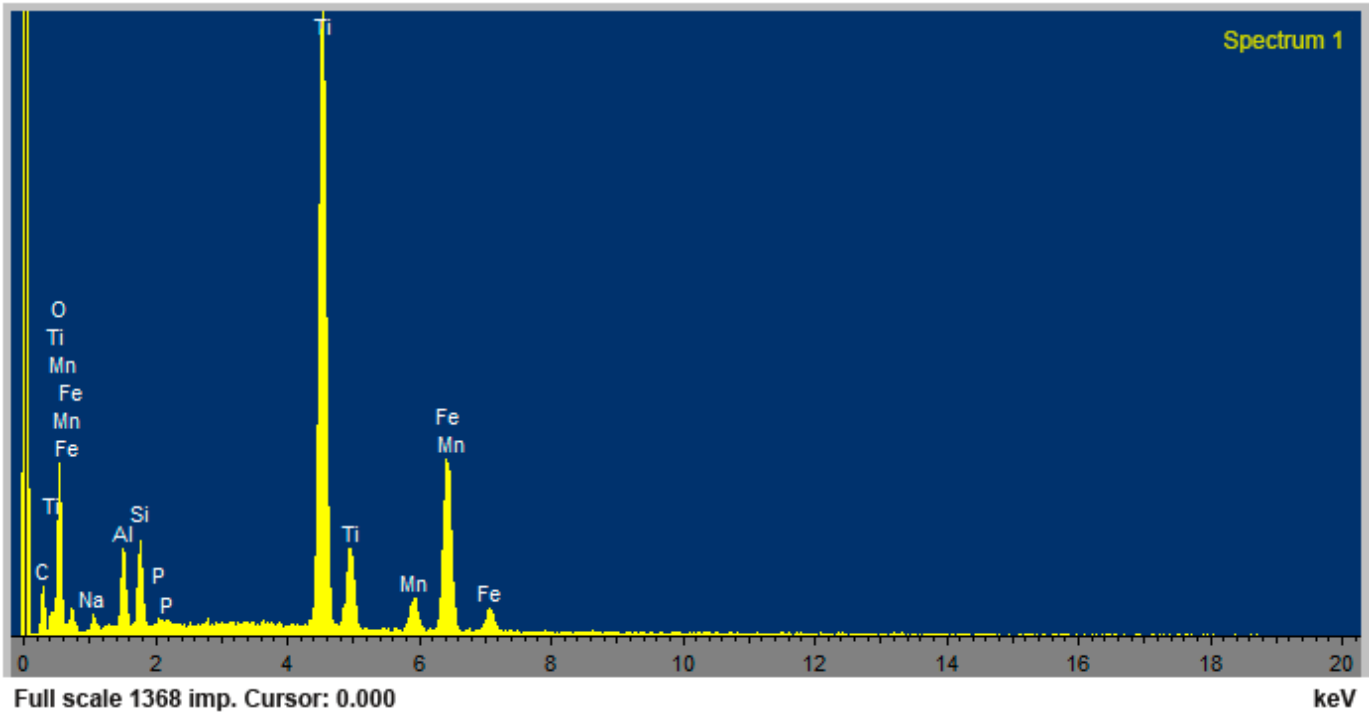


Figure 7. Diffraction pattern of sample No. 8 (slag under the condition: Na_2CO_3 addition of 3%, t = 1500 °C, τ = 45 min).

Since the previous experiments demonstrated the formation of sodium alumosilicates as a result of the reaction of the charge with the crucible material, in group III of the experiments, the temperature was reduced to 1400–1500 °C, and the holding time decreased to 30–45 min. As the amount of flux was high, the Na_2CO_3 additive was 5% of the Satpaevsk concentrate mass. The results of the group III experiments are presented in Table 6 and Figure 8. At 1400 °C and a holding time of 30 min, a product with numerous large and small iron beads was obtained, but they could not combine due to insufficient time. After holding for 45 min at 1400 °C and for 30 min at 1500 °C, products with good phase separation

were obtained. When held for 45 min at 1500 °C and 30 min at 1600 °C, part of the melt reacted strongly with the crucible material; the crucible melted, and the melt flowed into the furnace from the bottom of the crucible (there were product losses).

Table 6. The composition of slags from group III experiments (with 5% addition of Na_2CO_3).

Experimental Conditions	Slag Composition, %									
	TiO_2	FeO	Na_2O	Al_2O_3	Si_2O	MnO	MgO	CaO	P_2O_5	Cl
at 1400 °C, 30 min	71.27	10.38	4.4	5.56	5.35	1.91	0.2	0.15	0.09	0.25
at 1400 °C, 45 min	76.00	6.17	4.06	5.25	5.10	1.99	0.30	0.32	0.23	0.19
at 1500 °C, 30 min	77.20	4.95	4.23	5.48	5.36	1.85	0.17	0.20	0.11	0.15
at 1500 °C, 45 min	55.40	12.82	3.52	9.90	8.16	3.27	0.63	0.49	0.34	0.61
at 1600 °C, 30 min	52.83	15.13	3.15	10.50	8.21	3.14	0.60	0.66	0.30	0.65

Note: According to the chemical analysis data, the composition of slags is provided in terms of metal oxides.

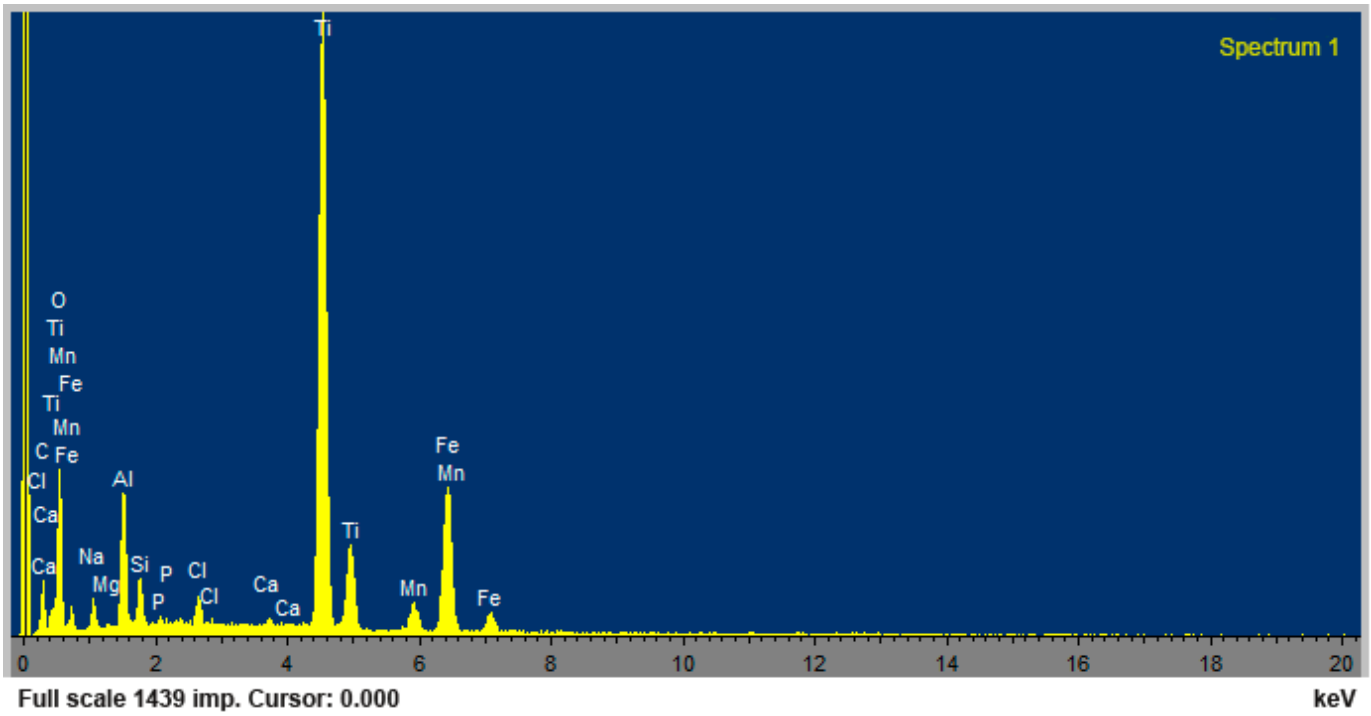


Figure 8. Diffraction pattern of sample No. 12 (slag under the condition: Na_2CO_3 additive of 5%, t = 1450 °C, τ = 30 min).

Table 6 and Figure 8 shows that by adding 5% of Na_2CO_3 as a flux at a temperature of 1500 °C for 30 min, it is possible to obtain the titanium slag with a maximum TiO_2 content (77%) and a low FeO content (up to 5%).

The experiments of group IV were designed to determine the optimal smelting mode, taking into account the results of the previous groups of experiments (I–III), including the optimal amount of Na_2CO_3 additive. Therefore, the Na_2CO_3 additive was taken at 4.5% of the mass of the Satpaevsk concentrate. Melting was carried out at temperatures of 1400–1500 °C for 30–45 min. The results of the experiments of group IV are given in Table 7.

Table 7. The composition of slags in experiment group IV (with 4.5% addition of Na_2CO_3).

Experimental Conditions	Slag Composition, %							
	TiO_2	FeO	Na_2O	Al_2O_3	Si_2O	MnO	CaO	ZrO_2
at 1400 °C, 30 min	71.82	8.73	4.21	5.65	5.48	2.1	0.41	0.65
at 1400 °C, 45 min	76.87	5.91	4.31	4.72	4.50	1.81	0.42	0.47
at 1500 °C, 30 min	78.12	4.76	4.34	4.82	4.61	1.96	0.34	0.1
at 1500 °C, 45 min	68.50	7.84	3.98	7.93	7.39	2.39	0.49	0.55

Note: According to the chemical analysis data, the composition of slags is given in terms of metal oxides.

The best results with the addition of 4.5% Na_2CO_3 of the concentrate mass were achieved by melting the charge at a temperature of 1500 °C for 30 min (Table 8). In this case, it is possible to obtain slag with a TiO_2 content of 78% and FeO of ~5% (4.76%). When holding the charge for 45 min at a temperature of 1500 °C, owing to a significant reaction of the charge with the crucible material, the melting process is disrupted, and product losses occur. When holding the charge for 30 min at a temperature of 1400 °C, due to a lack of time and temperature, the melting products (the slag and cast iron) are not completely separated from each other into separate phases. The melting product contains iron beads that have not had time to combine with each other. At 1400 °C and holding for 45 min, it was possible to reduce FeO in the slag up to 5.9%, which we also consider to be good results. The diffraction pattern and microphotographs of slag samples obtained from group IV of the experiments are shown in Figures 9–11. In the microstructure of the slag samples (Figure 11), the homogeneous gray region 1 represents the glassy titanium-containing phase. The gray–white region 2 belongs to perovskite, and the white region 3 represents the residual metallic iron phase.

Table 8. Composition of the metallic phase (cast iron) of samples No. 18–19 (the Na_2CO_3 additive of 4.5%).

Experimental Conditions	Chemical Composition of Cast Iron, %		
	Fe	Ti	C
at 1400 °C, 45 min	99.24	0.76	traces
at 1500 °C, 30 min	100	–	traces

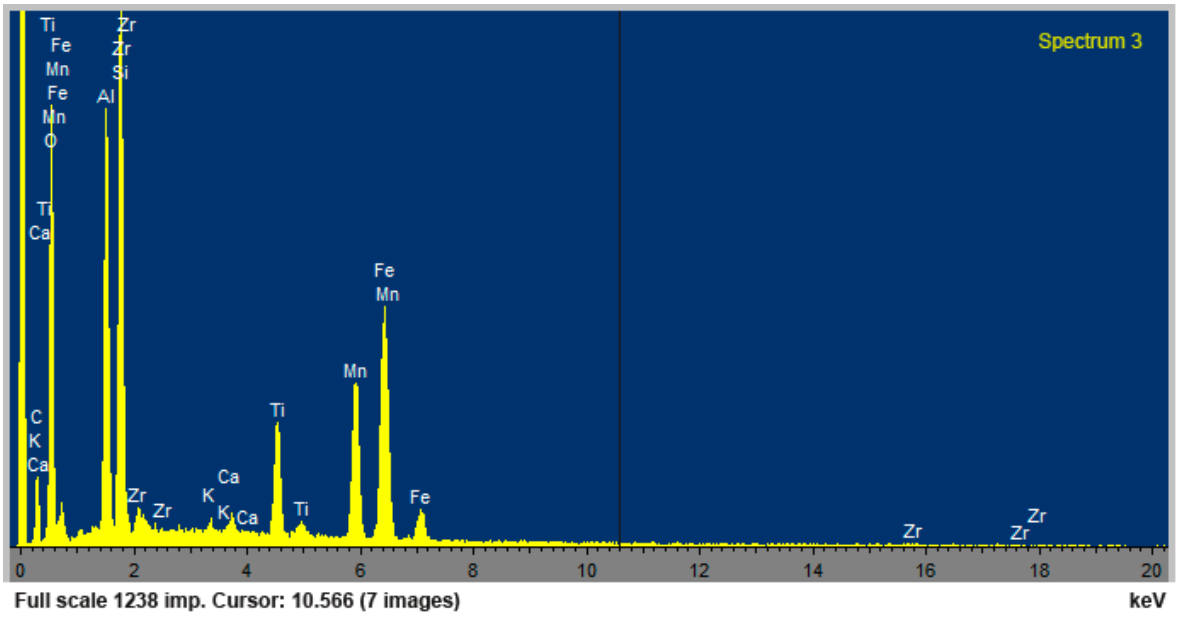


Figure 9. Diffraction pattern of sample No. 17 (slag under the condition: Na_2CO_3 additive of 4.5%, t = 1400 °C, τ = 30 min).

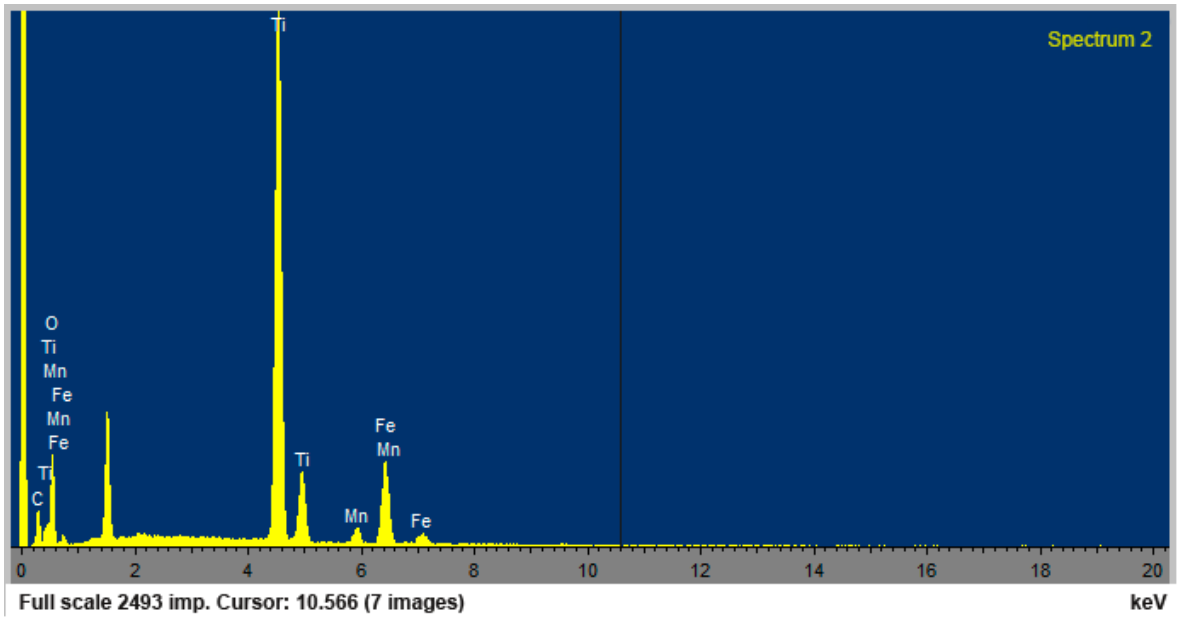
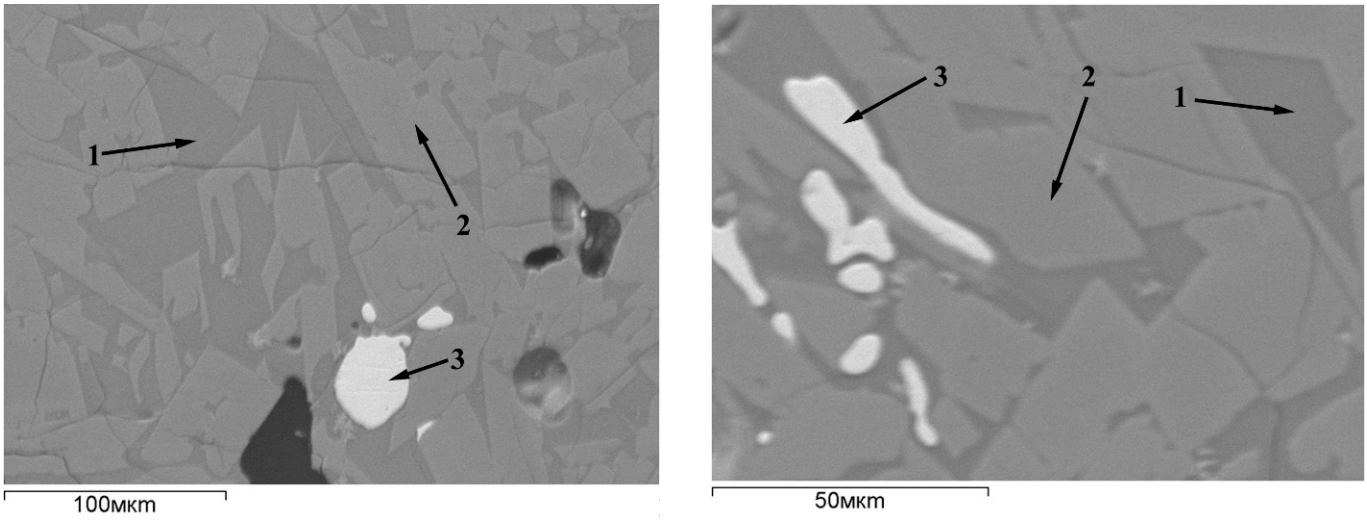


Figure 10. Diffraction pattern of sample No. 19 (slag under the condition: Na_2CO_3 additive of 4.5%, t = 1500 °C, τ = 30 min).



(**a**) (**b**)

Figure 11. Microphotographs of samples No. 18–19 (slag under the condition: Na_2CO_3 additive of 4.5%, (**a**)—t = 1400, τ = 45 min; (**b**)—t = 1500 °C, τ = 30 min).

The metallic phase (cast iron) obtained from experiments 18–19 is presented as a large iron ingot. The composition is represented by almost pure iron, with a small content of titanium (in sample No. 18) and traces of carbon (Table 8).

The diffraction patterns and micrographs of the samples of the metallic phase (cast iron) from group IV of the experiments are shown in Figures 12–14. The microstructure clearly shows inclusions of lamellar graphite 2 against the background of a light-grey iron matrix 1.

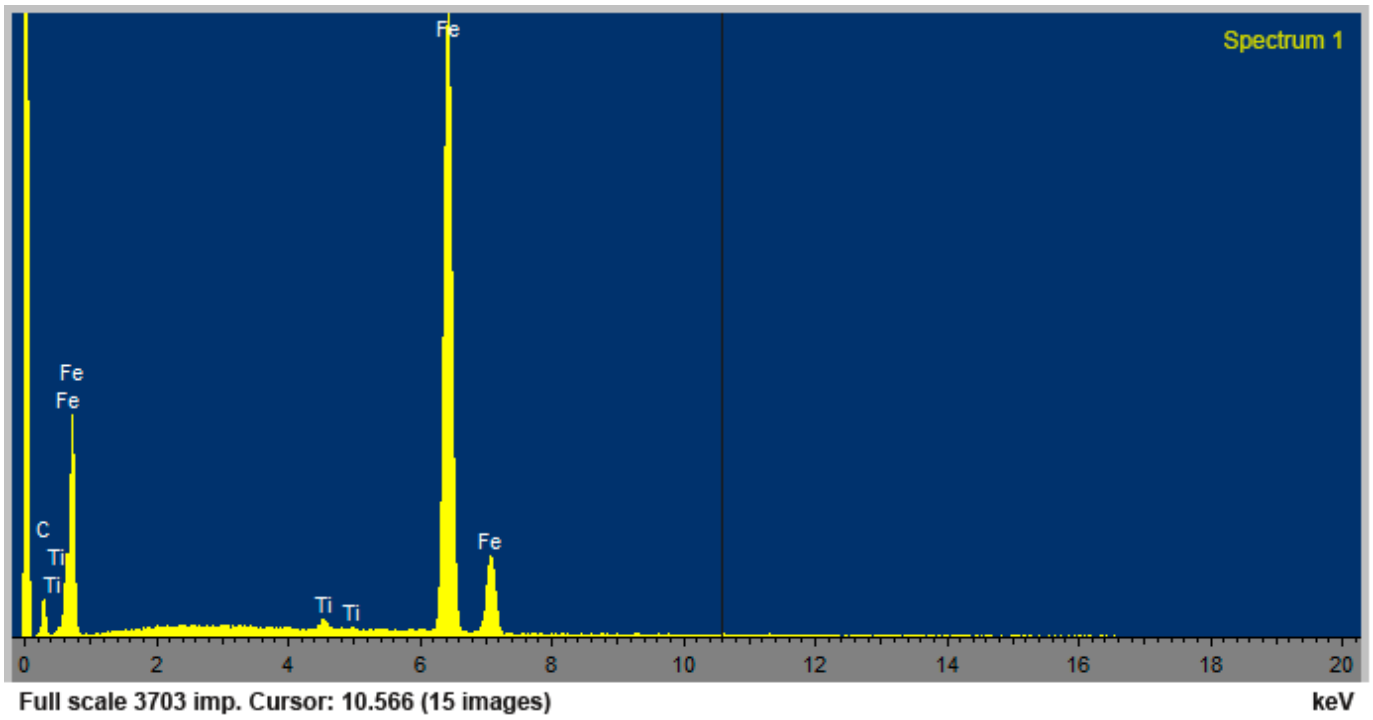


Figure 12. Diffraction pattern of the metal (cast iron) of sample No. 18 (with addition of 4.5% Na_2CO_3, t = 1400 °C, τ = 45 min).

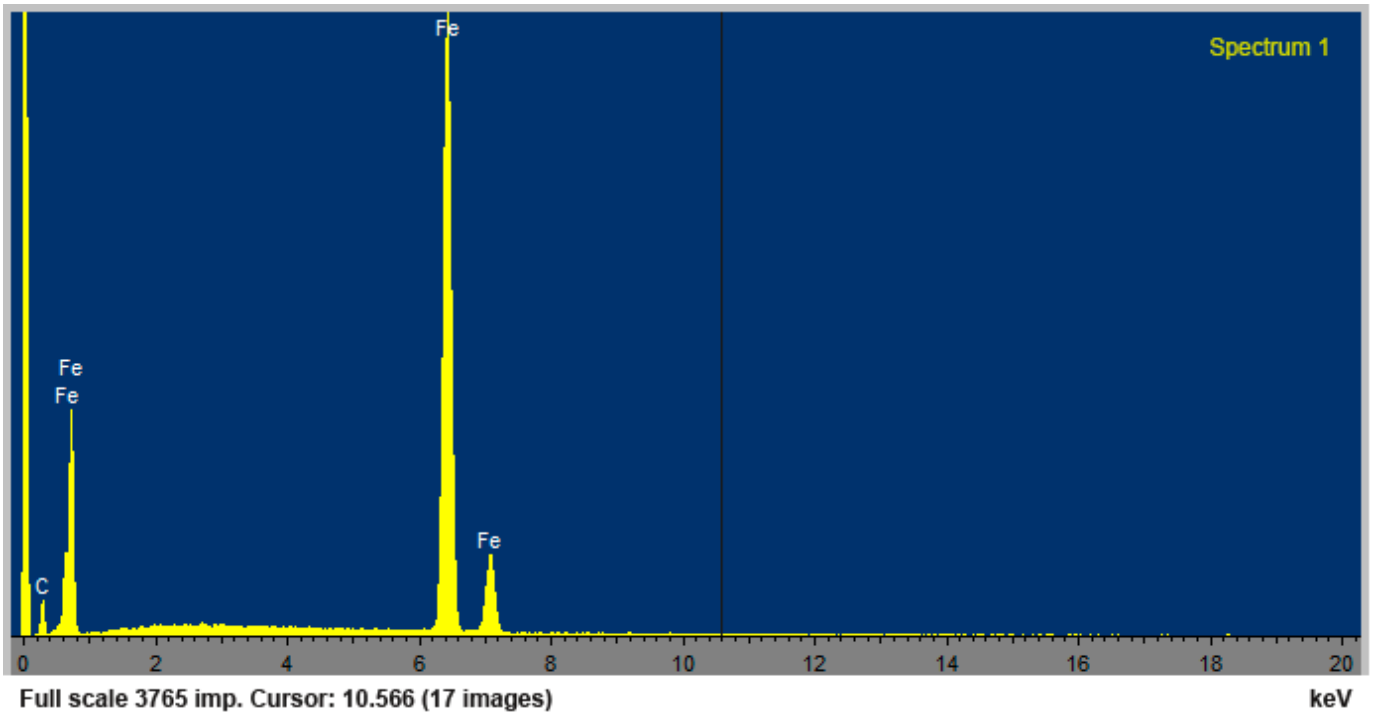


Figure 13. Diffraction pattern of the metal (cast iron) of sample No. 19 (with the addition of 4.5% Na_2CO_3, t = 1500 °C, τ = 30 min).

When adding Na_2CO_3, the consumption of the reducing agent (anthracite) was constant (8% of the concentrate mass), and no additional anthracite consumption was required for slag finishing. This consumption of the reducing agent was 2–2.5 times lower than in traditional smelting (without adding the flux), where the consumption of the reducing agent is at least 13% for the main smelting and about 4–10% for slag finishing.

It is worth noting that when adding sodium carbonate as a flux, it is necessary to use crucibles made of basic oxides (for example, magnesite ones) or to use insulating lubricants. Since the basicity of the charge increases with the addition of Na_2CO_3 when using crucibles made of acidic oxides (for example, alundum), the crucible wall is quickly corroded.

In general, the results of the technological studies show the catalytic and liquifying effect of sodium carbonate in the electric smelting of low-grade and hard-to-recover ilmenite concentrates, such as Satpaevsk concentrates. This led to a decrease in temperature from 1800–1850 to 1500 °C and in the smelting time from 60 to 30 min, and it also ensured a complete separation of the metal phase (cast iron) from the slag. It is obvious that such a decrease in temperature by 300–350 °C and a 2-time decrease in smelting time will lead to a decrease in energy consumption and the cost of the commercial titanium slag.

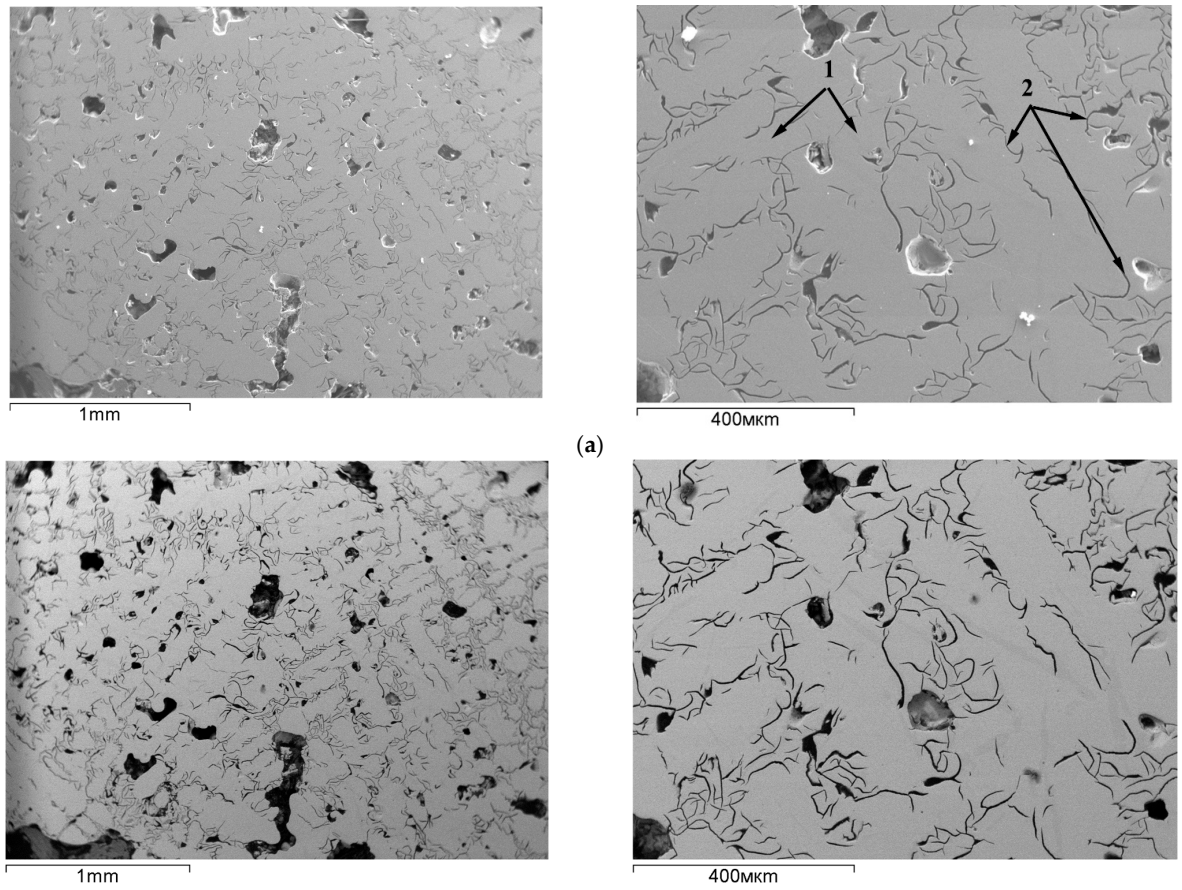


Figure 14. Microphotographs of the metal (cast iron) of sample No. 19 (with the addition of 4.5% Na_2CO_3, t = 1500 °C, τ = 30 min): (**a**) secondary electron mode; (**b**) backscattered electron mode.

4. Conclusions

In summary, our thermodynamic and technological studies of the process of the reducing electric smelting of Satpaevsk low-grade and refractory ilmenite concentrates with the addition of sodium carbonate (soda) to the charge under laboratory conditions confirmed the efficiency of this process (in the temperature range of 1500–1600 °C). At the same time, the difficulties arising during the electric smelting of Satpaevsk concentrates without adding fluxes were eliminated, including the temperature at the end of smelting being reduced from 1800–1850 to 1500 °C and the time from 60 min to 30 min. The FeO content in the slag was reduced to 5%. The viscosity of the slag was also reduced due to the lowering of the slag melting temperature. This ensures good separation of the smelting products into individual phases (cast iron and slag). When adding 4.5–5% Na_2CO_3 to the charge, the slag contained a large amount of TiO_2 (77–78%) and a small amount of FeO

(~5%). In this case, there was no difficulty in separating the smelting products. Due to the high fluidity and low viscosity of the melt, the metal phase (cast iron) was well separated from the slag in the form of a large ingot. Based on the above data, it can be concluded that the addition of sodium carbonate (Na_2CO_3 or soda) in the amount of 4.5–5% of the mass of the Satpaevsk ilmenite concentrate to the electric smelting charge has a positive effect on the smelting process and allows for achieving high technical and economic indicators. Such a solution to this problem also leads to a significant reduction in the consumption of expensive anthracite, which is used as a reducing agent. It makes up only 8% of the concentrate mass. In addition, the use of sodium carbonate minimizes additional costs for slag finishing.

Nevertheless, one of the main disadvantages of this process is the risk of rapid wear and tear of the crucible walls or furnace lining, especially if they are made of acidic materials when the temperature increases above 1500 °C and the processing time exceeds 45 min. This can lead to a breakdown of the melting and, as a result, to the loss of titanium. In view of this, it is necessary to take into account the optimal parameters of the temperature and time regime of the process to ensure its stability and cost-effectiveness.

Author Contributions: Conceptualization, M.K.M.; methodology, S.K.J. and M.B.B.; validation, V.V.K. and A.I.K.; formal analysis, S.K.J. and M.B.B.; investigation, V.V.K. and A.I.K.; data curation, V.V.K. and A.I.K.; writing—original draft preparation, N.V.M. and V.Y.S.; writing—review and editing, N.V.M. and V.Y.S.; supervision, N.V.M.; project administration, M.K.M.; funding acquisition, S.K.J. and M.B.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author/s.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A Phase Diagram of Fe-Ti Compound Systems

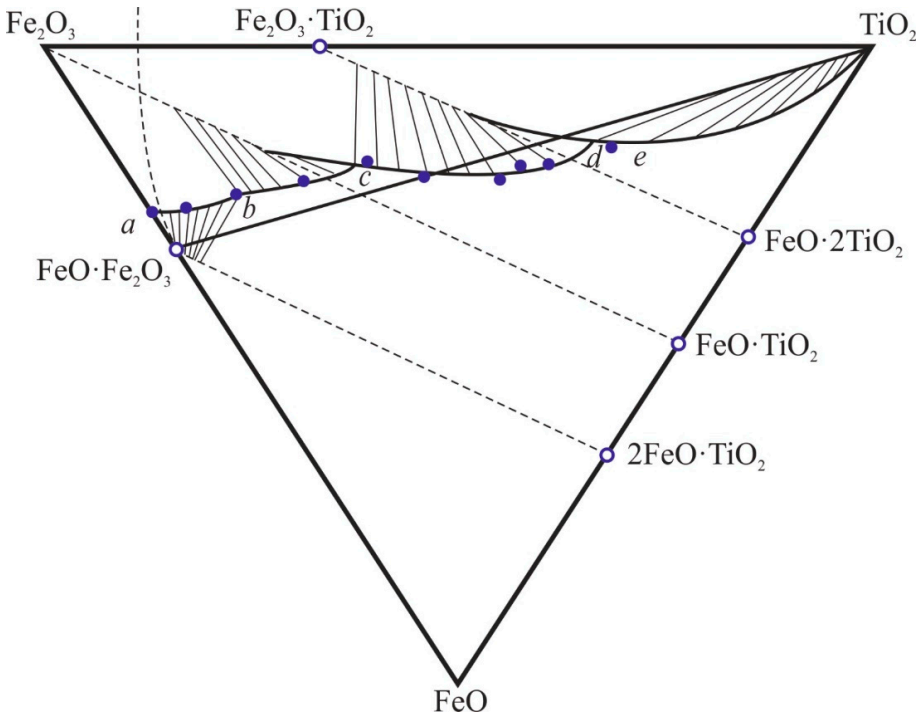


Figure A1. Phase relationship in the FeO-Fe_2O_3-TiO_2 system, according to McChesney and Moine. Adapted from ref. [16].

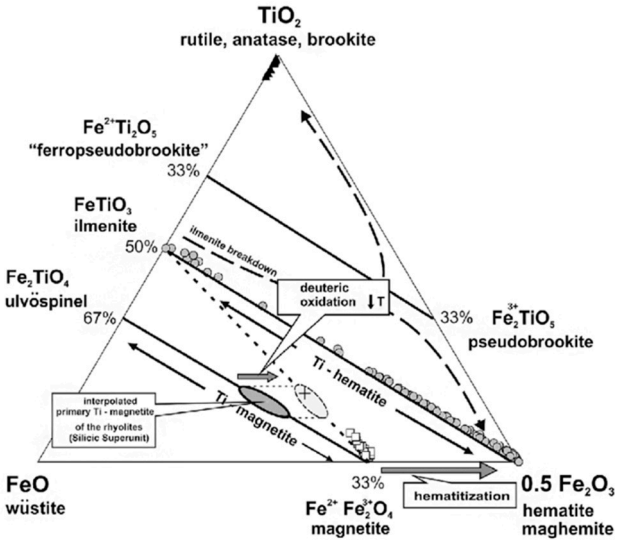


Figure A2. Diagram of the FeO-0,5Fe_2O_3-TiO_2 system. Adapted from ref. [17].

Appendix B Values of the Gibbs Free Energy of the Reactions

No.	Reactions	Values of ΔG (kJ·mol) at Temperatures (°C)											
		500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600
1	$FeO{\cdot}TiO_2 + C = Fe + TiO_2 + CO$	53.42	37.79	22.17	6.49	−9.19	−24.87	−40.44	−55.88	−71.20	−85.55	−95.02	−104.59
2	$FeO{\cdot}TiO_2 + C + O_2(g) = FeO + TiO_2 + CO_2$	−375.23	−375.86	−376.48	−377.09	−377.70	−378.28	−378.85	−379.39	−379.90	−379.89	−376.14	−372.07
3	$FeO{\cdot}TiO_2 + C + O_2(a) = FeO + TiO_2 + CO_2$	−347.10	−315.05	−274.78	−226.23	−169.38	−104.20	−30.66	51.26	141.58	240.82	352.20	472.30
4	$2FeO{\cdot}TiO_2 + 3C = 2Fe + Ti_2O_3 + 3CO$	231.58	182.27	132.89	83.32	33.64	−16.09	−65.65	−115.02	−164.20	−211.47	−249.04	−286.83
5	$FeTiO_3 + Na_2CO_3 + 2C = Na_2O{\cdot}TiO_2 + Fe + 3CO$	63.45	4.60	−55.32	−116.18	−175.81	−235.49	−295.76	−356.62	−418.07	−480.07	−542.72	−606.62
6	$Na_2O + TiO_2 = Na_2O{\cdot}TiO_2$	−188.47	−187.90	−187.26	−186.48	−185.57	−184.36	−182.47	−178.29	−173.02	−167.77	−162.57	−157.43
7	$2FeTiO_3 + Na_2CO_3 + 3C = Na_2O{\cdot}2TiO_2 + 2Fe + 4CO$	43.75	−41.58	−129.08	−218.71	−308.10	−401.95	−502.52	−604.54	−707.92	−812.56	−918.56	−1027.11
8	$2FeTiO_3 + Na_2CO_3 + C = Na_2O{\cdot}2TiO_2 + 2Fe + 2CO_2$	−17.59	−87.87	−119.60	−174.12	−228.60	−287.74	−353.79	−421.45	−490.65	−561.27	−633.42	−708.24
9	$Na_2O + 2TiO_2 = Na_2O{\cdot}2TiO_2$	−226.53	−224.31	−221.74	−218.79	−215.48	−212.96	−217.08	−218.90	−219.57	−220.19	−220.77	−221.29
10	$3FeTiO3 + Na_2CO_3 + 4C = Na_2O{\cdot}3TiO2 + 3Fe + 5CO$	56.69	−57.19	−174.74	−295.72	−417.65	−541.62	−667.84	−807.24	−949.59	−1094.39	−1241.75	−1393.40
11	$Na_2O + 3TiO_2 = Na_2O{\cdot}3TiO_2$	−238.01	−236.25	−234.09	−231.50	−228.50	−224.95	−220.48	−221.66	−225.20	−229.10	−233.33	−237.86
12	$5FeTiO_3 + 4Na_2CO_3 + 9C = 4Na_2O{\cdot}5TiO_2 + 5Fe + 13CO$	98.01	−108.65	−430.56	−702.16	−969.63	−1238.00	−1509.29	−1783.43	−2060.37	−2339.98	−2622.65	−2911.38
13	$2FeTiO_3 + 2Na_2CO_3 + C = 2Na_2O{\cdot}TiO_2 + 2Fe + 3CO_2$	34.88	−29.55	−96.42	−165.47	−232.37	−299.66	−368.42	−438.62	−510.24	−583.22	−657.72	−734.94
14	$Na_2O + Al_2O_3 = Na_2O{\cdot}Al_2O_3$	−185.84	−186.89	−187.78	−188.43	−188.86	−188.88	−188.14	−184.99	−180.65	−176.22	−171.72	−167.16
15	$2SiO_2 + Na_2CO_3 + C = Na_2O{\cdot}2SiO_2 + 2CO$	−1.76	−33.01	−65.35	−97.19	−128.35	−160.18	−191.80	−223.23	−254.46	−285.51	−316.39	−347.11
16	$3SiO_2 + Na_2CO_3 + C = Na_2O{\cdot}3SiO_2 + 2CO$	−17.89	−49.69	−81.03	−111.97	−140.16	−167.49	−194.70	−221.88	−249.09	−276.41	−303.88	−331.57
17	$SiO_2 + 2Na_2CO_3 + 2C = 2Na_2O{\cdot}SiO_2 + 4CO$	108.88	48.10	−11.72	−70.48	−124.07	−175.42	−226.19	−280.19	−333.51	−386.19	−438.29	−489.83
18	$2SiO_2 + 3Na_2CO_3 + 3C = 3Na_2O{\cdot}2SiO_2 + 6CO$	136.86	44.10	−47.54	−137.95	−220.85	−300.74	−379.76	−458.09	−535.87	−613.21	−690.23	−767.02
19	$Al_2O_3 + Na_2O + 6SiO_2 = 2NaAlSi_3O_8$	−341.61	−347.23	−352.23	−358.57	−363.74	−368.52	−372.63	−374.46	−375.23	−376.06	−376.98	−378.01

References

1. El Khalloufi, M.; Drevelle, O.; Soucy, G. Titanium: An Overview of Resources and Production Methods. *Minerals* **2021**, *11*, 1425. [CrossRef]
2. van Vuuren, D.S. A critical evaluation of processes to produce primary titanium. *J. S. Afr. Inst. Min. Metal.* **2009**, *109*, 455–461.
3. Malek, B.; Serp, J.; Doreau, F.; Miguirditchian, M.; Vandenhende, M.; Pradeilles, N.; Lepetitcorps, Y.; Maitre, A. Production of Metallic Titanium by Electrowinning in Molten Salts of Titanium Oxycarbide Anode. *Mater. Proc.* **2021**, *5*, 63. [CrossRef]
4. Belonozhko, N.D.; Kozlov, V.A.; Pavlov, A.V.; Batrakova LKh Shayakhmetova, R.A. Effect of additives on the processes of reducing roasting and selective extraction of Fe and Ti from ilmenites. *Complex Use Miner. Resour.* **2000**, *3–4*, 34–40.
5. Ulasyuk, S.M.; Pavlov, A.V.; Kantemirov, M.D.; Onaev, M.I. Electromagnetic desiliconization of ilmenite concentrate from the Satpayevskoye deposit. *Complex Use Miner. Resour.* **2002**, *6*, 39–41.
6. Kantemirov, M.D. Features of roasting-magnetic enrichment of ilmenites of different degrees of alteration. *Ind. Kazakhstan* **2004**, *1*, 63–65.

7. Fkh, T.; Trebukhov, S.A.; Ksh, A.; Nitsenko, A.V.; Burabayeva, N.M. Problematic processing of low-quality ilmenite concentrates. *Complex Use Miner. Resour.* **2018**, *4*, 77–86.
8. Yang, G.; Xu, B.; Wan, H.; Wang, F.; Yang, B.; Wang, Z. Effect of $CaCl_2$ on microstructure of calciothermic reduction products of Ti_2O_3 to prepare porous titanium. *Metals* **2018**, *8*, 698. [CrossRef]
9. Noguchi, H.; Natsui, S.; Kikuchi, T.; Suzuki, R.O. Reduction of $CaTiO_3$ by electrolysis in the molten salt $CaCl_2$-CaO. *Electrochemistry* **2018**, *86*, 82–87. [CrossRef]
10. Osipov, A.A.; Korinevskaya, G.G.; Osipova, L.M.; Muftakhov, V.A. Titanium coordination in TiO_2–Na_2O–SiO_2 glasses of $xTiO_2 \cdot (100 - x)$ $[2Na_2O \cdot 3SiO_2]$ $(0 \leq x \leq 30)$ composition based on Raman spectroscopy. *Glass Phys. Chem.* **2012**, *38*, 357–360. [CrossRef]
11. Yang, G.; Xu, B.; Lei, X.; Wan, H.; Yang, B.; Liu, D.; Wang, Z. Preparation of porous titanium by direct in-situ reduction of titanium sesquioxide. *Vacuum* **2018**, *157*, 453–457. [CrossRef]
12. Selifonov, E. Mineral resource base of the titanium industry of Kazakhstan. *Miner. Resour. Kazakhstan* **2005**, *10–11*, 22–29.
13. Topoev, A.N.; Valieva, D.S. Features of the geological structure of the ilmenite deposit Bektemir (Eastern Kazakhstan). *Geol. Kazakhstan* **1999**, *5–6*, 66–70.
14. Korneliussen, A.; McEnroe, S.A.; Nilsson, L.P.; Schiellerup, H.; Gautneb, H.; Meyer, G.B.; Storseth, L.R. An overview of titanium deposits in Norway. *Geol. Surv. Nor.* **2000**, *436*, 27–38.
15. Lorkiewicz, W.; Malina, D.; Tyliszczak, B.; Sobczak-Kupiec, A. Manufacturing of titanium and its alloys. In *Sustainable Production: Novel Trends in Energy, Environment and Material Systems*; Springer: Berlin/Heidelberg, Germany, 2020; pp. 61–74.
16. Erlksson, G.; Pelton, A.D.; Woermann, E.; Ender, A. Measurement thermo dynamic evaluation of phase in the Fe-Ti-O system. *Berichte Bunsenges./Phys. Chem. Chem. Phys.* **1996**, *100*, 1839–1849. [CrossRef]
17. Ondrejka, M.; Broska, I.; Uher, P. The late magmatic to subsolidus T-fO_2 evolution of the Lower Triassic A-type rhyolites: Fe–Ti oxythermometry and petrological implications. *Acta Geol.* **2015**, *7*, 51–61.
18. Leyens, C.; Peters, M. *Titanium and Titanium Alloys: Fundamentals and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2003.
19. Benčina, M.; Iglič, A.; Mozetic, M.; Junkar, I. Crystallized TiO_2 Nanosurfaces in Biomedical Applications. *Nanomaterials* **2020**, *10*, 1121. [CrossRef] [PubMed]
20. Xu, B.; Sohn, H.Y.; Mohassab, Y.; Lan, Y. Structures, preparation and applications of titanium suboxides. *RSC Adv.* **2016**, *6*, 79706–79722. [CrossRef]
21. Tian, M.; Liu, C.; Ge, J.; Eres, G. Recent progress in characterization of the core–shell structure of black titania. *J. Mater. Res.* **2019**, *34*, 1138–1153. [CrossRef]
22. Moellmann, J.; Ehrlich, S.; Tonner, R.; Grimme, S. A DFT-D study of structural and energetic properties of TiO_2 modifications. *J. Phys. Condens. Matter* **2012**, *24*, 424206. [CrossRef]
23. Yan, Z.; Zheng, S.; Zhang, Y.; Zhou, Z.; Qiao, S. Sodium carbonate roasting and mild acid leaching of vanadium titanomagnetite concentrates: Vanadium extraction and residue sodium decrease. *Process Saf. Environ. Prot.* **2024**, *185*, 1132–1144. [CrossRef]
24. Eriksen, J.M.; Robles, E.C.; Rosenqvist, T. Equlibrium between liquid Fe-Ti-O slags and metallic iron. *Steel Res. Int.* **2007**, *78*, 671–675. [CrossRef]
25. Faust, R.; Stanicic, I.; Gastaldi, J.; Ansari, E.; Brorsson, J.; Mattisson, T.; Ryden, M.; Knutsson, P. Thermodynamic Modeling and Experimental Investigation of the System Fe-Ti-O-K for Ilmenite Used as Fluidized Bed Oxygen Carrier. *Energy Fuels* **2024**, *38*, 14569–14576. [CrossRef]
26. Fedorov, S.A.; Udoeva, L.Y.; Vusikhis, A.S.; Pikulin, K.V.; Cherepanova, L.A. Joint processing of perovskite and ilmenite concentrates. Part 1. Chemical-mineralogical (material) characteristics of perovskite and ilmenite concentrates. *Izv. Ferr. Metall.* **2024**, *67*, 27–36. [CrossRef]
27. Smirnov, K.; Gamov, P.A. Specific features of metal reduction from ilmenite concentrate. In Proceedings of the 16th International Conference on Industrial Manufacturing and Metallurgy (ICIMM 2021), Nizhny Tagil, Russia, 17–19 June 2021; Volume 2456, p. 020052. [CrossRef]
28. Tleugabulov, S.M.; Tleugabulov, B.S.; Koishina, G.M.; Altybaeva, D.K.; Tazhiev, E.B. Smelting reduction of a monocharge. *Metallurgist* **2016**, *60*, 31–37. [CrossRef]
29. Shabanov, E.Z.; Baisanov, A.S.; Toleukadyr, R.T.; Inkarbekova, I.S. Study of phase transformations during heating of briquetted mono-charge from chromium-containing materials and carbon reducing agents. *CIS Iron Steel Rev.* **2023**, *25*, 26–30. [CrossRef]
30. Subasinghe, H.C.S.; Ratnayake, A.S. Mechanical activation and physicochemical factors controlling pyrometallurgical, hydrometallurgical, and electrometallurgical processing of titanium ore: A review. *J. S. Afr. Inst. Min. Metall.* **2023**, *123*, 399–414. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.