

Article

Reductive Smelting of Neutralized Red Mud for Iron Recovery and Produced Pig Iron for Heat-Resistant Castings

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Abstract: The chemical and mineral composition of the red mud from the Ural Aluminum Plant were studied by XRF, XRD, and Mössbauer spectroscopy. Experiments on reductive smelting of red mud were carried out in a range of temperatures (1650–1750 °C) to recover iron from the aluminum production waste with maximum efficiency. It was found that it is possible to obtain pig iron with a high content of titanium, phosphorus, and vanadium, and low sulfur content. The efficiency of iron recovery at 1750 °C was found to be around 98%. Thermodynamic calculations were carried out to assist in finding the optimal conditions for the process (e.g., carbon content, furnace temperature, slag liquidus temperature). It was also found that the pig iron phase obtained at 1650 to 1700 °C is not separated from the slag phase into ingot compared with the sample obtained at 1750 °C. Pig iron obtained at 1750 °C can be used to produce molds for the steel-casting equipment.

Keywords: red mud; Mössbauer spectroscopy; reductive smelting; thermodynamic modeling; slag; pig iron

1. Introduction

The accumulation and storage of the alumina production waste, red mud (RM), represents one of the most critical ecological problems for the aluminum industry. Depending on the composition of the initial bauxite ore and its processing technology, 1.0 to 1.4 tons of RM can be formed from the production of 1 ton of alumina [1,2]. At the moment, RM in Russia is barely utilized but stored in slurry storages. Currently, about 600 million tons of RM are already accumulated at aluminum plants in Russia [3]. The construction and operation of slurry storages require significant costs that leads to an increase of the cost value of alumina and, consequently, of metallic aluminum. There is also a high risk of ecological disasters: Dams breaks and weathering process make this problem even more severe [4].

RM contains up to 60% iron compounds [5], which implies the practicality of their processing using reductive smelting with extraction of iron into a separate phase and reception of slag suitable for further extraction of Al, Ti, and rare metals by hydrometallurgical methods [6–8]. A high content of alkali in RM (up to 12% Na_2O [9]) leads to furnace lining destruction caused by high RM reactivity during the melting process. Despite this fact, most studies are devoted to the pyrometallurgical processing of the initial RM [10–12], because the alkali present in RM significantly reduces its melting point and improves the separation of slag and metal [13,14]. However, from our point of view, it would be more practical to regenerate the alkali for recirculation by autoclave leaching of bauxite [15,16], since during the smelting of red mud with high sodium content, the alkali goes into the gas phase, and its further regeneration is very difficult [17].

The most valuable components in slag obtained after RM reductive smelting are aluminum, titanium, and scandium [18,19]. Because of the high content of silicon dioxide (10–15 wt. %) in the slag, it is impractical to process it by alkaline technology, as part of the alkali will be lost due to a chemical reaction with silica. The most perspective slag treatment is a leaching process by hydrochloric acid to obtain aluminum chloride solutions [20,21]. Then, aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and scandium (Sc) compounds may selectively be extracted from these solutions [22–27]. Silicon dioxides and titanium oxides will concentrate in a solid residue. The residue can be leached with sulfuric acid to extract titanium into the solution [28,29]. Thus, the proposed way of RM processing consists of reductive smelting of neutralized RM to obtain pig iron and further hydrometallurgical treatment of the produced slag by hydrochloric acid to extract valuable products: Sandy grade alumina (Al_2O_3), scandium concentrate, titanium concentrate, and wollastonite (CaSiO_3), as shown in Figure 1.

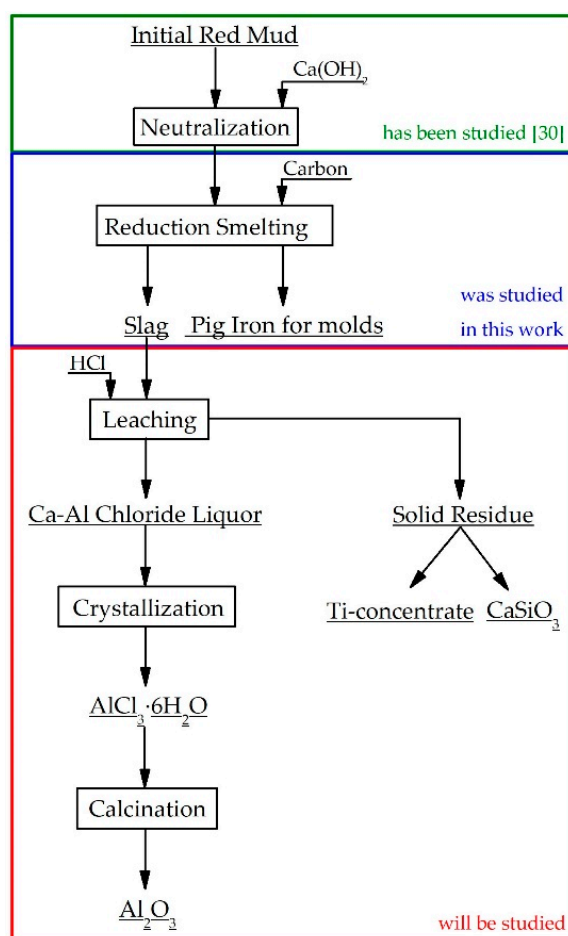


Figure 1. A flowsheet of the recycling treatment of red mud.

In the present paper, the second stage of the abovementioned treatment, reductive smelting of the neutralized RM, was investigated to obtain: (1) The maximum amount of the pig iron, (2) complete separation of the metal and slag, and (3) analysis of the resulting pig iron with a description of potential applications.

2. Materials and Methods

2.1. Raw Materials

Table 1 shows the chemical composition of the neutralized RM from Ural Aluminum Plant (56.304530, 61.980334; Kamensk-Uralsky, Russia). Sodium was removed from RM on the plant by leaching with a lime slurry at 90 °C for a duration of 3 h [30], which can be described by the following equation [31,32]:

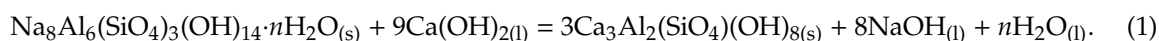


Table 1. The average chemical composition (wt %) of RM from Ural Aluminum Plant (Kamensk-Uralsky, Russia).

Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	MgO	MnO	Na ₂ O	P ₂ O ₅	S	LOI *
36.9	8.71	11.8	3.54	23.8	1.01	0.95	0.27	0.42	0.14	12.46

* LOI—loss on ignition.

2.2. Thermodynamic Modeling

Liquidus projections were calculated using FactSage software (version 7.1) [33]. The amount of reducing agent for complete reduction of iron-containing phases was calculated using HSC Chemistry software (version 6.00) [34].

2.3. Reductive Smelting of Red Mud

Reductive smelting of the neutralized RM was carried out in a vertical resistance tube (Tammann) furnace, as shown in Figure 2.

A RM and carbon mixture (5) was filled into carbon crucibles (4), which were placed into a Tammann furnace (1) with a graphite heater (2) on a graphite platform (3). The furnace dimensions (height/diameter/tube diameter) are 360/300/74 mm. The furnace temperature was controlled by an automatic PID-controller (8) and by a W-Re thermocouple (type: WR20 with $\pm\Delta T = 0.005T$) (7) in an Al₂O₃ shield (6), which was lowered into the graphite crucible (4). To reduce the oxygen potential in the gas phase and to avoid erosion of the carbon heater due to burning, Ar gas was introduced into the tube with a 0.5 L/min flow rate through a gas inlet (9) in the lower part of the furnace.

The mixture with 27.6 g of RM and 2.4 g of carbon graphite was used for reductive smelting. The furnace was heated up to 1300 °C with a maximal rate during 1 h, then a required temperature within the range 1650–1750 °C was reached with the 10 °C/min rate and kept for 10 min. After that, the furnace was switched off and the crucibles were cooled down with the furnace.

The slag chemical composition was analyzed using an X-ray fluorescence spectrometer (XRF) ZXS Primus II (Rigaku, Tokyo, Japan). The mineralogical composition of the samples was determined by X-ray diffraction analysis (XRD) on a MiniFlex 600 (Rigaku, Tokyo, Japan). Quantitative analysis of phase fractions was performed by the Rietveld method using PDXL-2 program (Rigaku). The elemental composition of pig iron was determined on an atomic emission spectrometer GDS-850A (LECO Corporation, St. Joseph, MI, USA) while the carbon and sulfur content were analyzed on a CS-600 (LECO Corporation, St. Joseph, MI, USA). Samples (~1 g) were placed in ceramic crucibles and then loaded into an induction furnace. The C and S concentrations were determined by infrared absorption of gaseous CO₂ and SO₂ during sample combustion in oxygen atmosphere.

The Mössbauer analysis of RM and pig iron were obtained using a spectrometer MC1104EM (KORDON, Rostov-on-Don, Russia) at temperatures of 296 ± 3 and 77.5 ± 0.5 K in a vacuum cryostat. The ^{57}Co nuclei with 47 mCi activity in a Rh matrix (RITVERC JSC, St-Petersburg, Russia) was used as the γ -radiation source. The Mössbauer spectra were analyzed using SpectrRelax 2.4 software (MSU, Moscow, Russia). The values of chemical shifts are presented relative to α -Fe.

Surface visualization and chemical element distribution in arbitrarily selected segments of the slag and metal samples were performed by a scanning electron microscope (SEM) Vega III (Tescan, Brno, Czech Republic).

Microindentation hardness testing was carried out using an optical microscope METAM RV-23M with a microhardness tester PMT-3 (all equipment from LOMO, St. Petersburg, Russia). The pig iron sample was etched with a solution of 3% nitric acid (HNO_3) in ethanol ($\text{C}_2\text{H}_5\text{OH}$) to reveal the microstructure and determine the phase composition. The force applied to the diamond indenter was 0.49 N, with a duration of 10 s.

The Vickers hardness number was calculated using the following equation by ISO 6507-1-2007: Metals and alloys. Vickers hardness test. Part 1. Test method:

$$HV = 0.189 \times (F/d^2), \quad (2)$$

where F is the force applied to the diamond indenter, N; and d is the average length of the diagonal left by the indenter, mm.

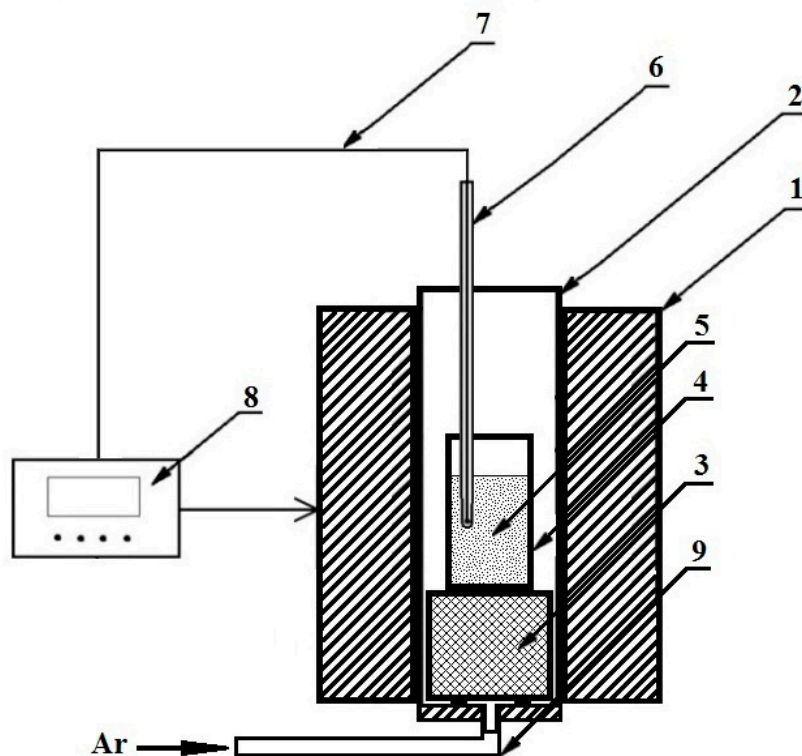


Figure 2. Schematic of the Tamman resistance furnace (1—furnace; 2—graphite heater; 3—graphite stands; 4—crucible; 5—mixture of RM with carbon; 6—thermocouple shield; 7—W-Re thermocouple; 8—automatic temperature controller; 9—gas inlet).

3. Results

3.1. Composition of the Neutralized Red Mud

Figure 3 shows the results of the XRD analysis of RM collected from Ural Aluminum Plant. It can be seen that the RM consists mainly of hematite (α - Fe_2O_3), katoite ($\text{Ca}_3\text{Al}_2\text{SiO}_4(\text{OH})_8$), calcite (CaCO_3),

and quartz (SiO_2). It also contains small amounts of portlandite ($\text{Ca}(\text{OH})_2$) and goethite ($\alpha\text{-FeOOH}$). Titanium is distributed between titanate (CaTiSiO_5) and di-iron titanate (Fe_2TiO_5).

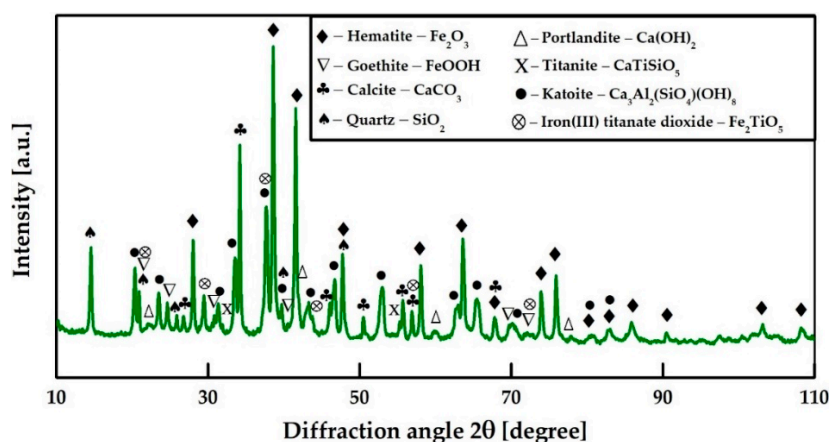


Figure 3. XRD analysis of the neutralized RM from Ural Aluminum Plant (Kamensk-Uralsky, Sverdlovsk region, Russia).

The Mössbauer spectrum of this RM sample was analyzed in a previous work [35]. In this study, a more complete and correct description of the RM sample from Ural Aluminum Plant was obtained using the complex Mössbauer analysis.

The RM Mössbauer spectra obtained at 296 and 77.5 K (Figure 4) have a similar nature and contain a sextet distorted by broadening into the interior of the spectrum, two additional resonance lines asymmetric in intensity in the interior of the spectrum, with a width comparable to sextet lines, and a relatively wide resonance line in the center of the spectrum.

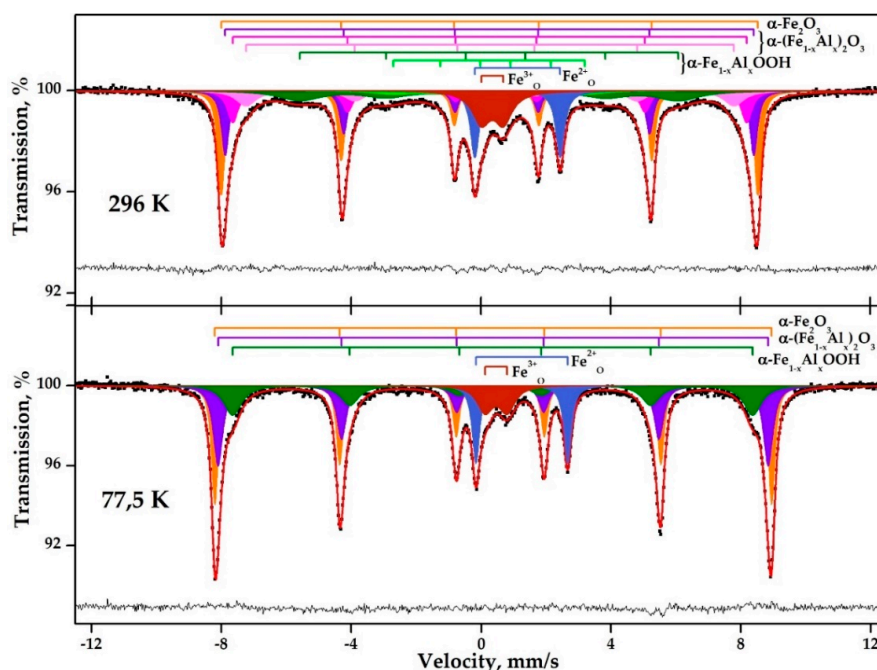


Figure 4. Mössbauer spectra of the RM sample obtained at 296 and 77.5 K.

The difference between the low-temperature and high-temperature spectra is as follows: The presence of sharp shoulders on lines 1 and 6 of the sextet (see #1–6, Table 2); the absence of absorption between 1–2–3 and 4–5–6 resonant sextet lines; and a noticeable increase in the intensity

of the resonance lines of the sextet. At the same time, the intensity of the paramagnetic part of the spectrum (an asymmetric doublet and a wide resonance line in the center) has not changed. This makes it possible to exclude the occurrence of superparamagnetism in this sample, a phenomenon that is characteristic of nano-scale iron-containing particles. Therefore, the asymmetry of the resonance lines at room temperature is only due to the locally inhomogeneous environment of the Fe atoms in at least one of the present phases.

The shoulders in the low-temperature spectra and the resonance lines reaching the baseline indicate a superposition of the spectra of at least two magnetically ordered phases, and one of them at room temperature was obviously responsible for the distortion of the background line in the central part of the spectrum.

In the model description, the Mössbauer spectrum obtained at room temperature can be fully characterized by a superposition of six sextets, divided into two groups of four and two sub-spectra, and two doublets (see Table 2). The low-temperature spectrum is described by a superposition of three sextets (grouped as two plus one) and two doublets.

The intensity and appearance of the paramagnetic part of the spectrum practically do not change in the studied temperature range. One of the doublets, characterized by high values of isomeric shift and quadrupole splitting (#7, Table 2), corresponds to Fe^{2+} ions in a high-spin state in an octahedral oxygen environment [36]. Obviously, these iron atoms correspond to a layered aluminosilicate mineral. The second doublet (#8, Table 2) corresponds to Fe^{3+} ions in a high-spin state in an octahedral oxygen environment [36]. It has a large line width, which may indicate a lower degree of crystallinity of the phase containing it (as compared, for example, with #7, Table 2). The absence of temperature dependence for its intensity does not allow us to interpret this subspectrum as being related to iron (III) hydroxide [37]. Since its quadrupole splitting value does not change with temperature, and the line width decreases, the assignment of this doublet to superparamagnetic particles [38] is also excluded. Obviously, this broadened doublet may contain subspectra of Fe_2TiO_5 with paramagnetic properties up to 55 K [39,40].

Table 2. Mössbauer spectra parameters of red RM obtained at 296 and 77.5 K.

Temperature, K	#	Compound or Site	δ	$\Delta = 2\varepsilon$	Γ_{exp} (mm/s)	a_+	a_-	H_{eff} (kOe)	S# (at%)
296	1	$\alpha\text{-Fe}_2\text{O}_3$	0.37	−0.21	0.26	−	−	513.2	25
	2	$\alpha\text{-(Fe}_{1-x}\text{Al}_x)_2\text{O}_3$	0.37	−0.22	0.27	−	−	505.4	16
	3		0.37	−0.20	0.39	−	−	491.3	11
	4		0.37	−0.18	0.72	−	−	467	10
	5	$\alpha\text{-Fe}_{1-x}\text{Al}_x\text{OOH}$	0.35	−0.20	1.55	−	−	362	14
	6					−	−	183	4
	7	Fe^{2+}O	1.13	2.64	0.32	−	−	−	10
	8	Fe^{3+}O	0.35	0.68	0.67	−	−	−	10
77.5	1	$\alpha\text{-Fe}_2\text{O}_3$	0.48	−0.21	0.26	−0.016	−0.007	530.8	32
	2	$\alpha\text{-(Fe}_{1-x}\text{Al}_x)_2\text{O}_3$	0.48	−0.21	0.37	−	−	524.5	30
	3	$\alpha\text{-Fe}_{1-x}\text{Al}_x\text{OOH}$	0.47	−0.23	0.67	−	−	496.7	20
	4	Fe^{2+}O	1.25	2.83	0.30	−	−	−	11
	5	Fe^{3+}O	0.46	0.69	0.58	−	−	−	8

δ —isomer shift, $\Delta = 2\varepsilon$ —quadrupole splitting, $a_{+/-}$ —the second-order terms in quadrupole perturbation [41], Γ_{exp} —line width, H_{eff} —hyperfine magnetic field, and S#—relative area of a subspectrum #.

The magnetically split part of the spectrum can be described by two groups of sextets related to compounds of a different nature. The relatively narrow and asymmetric resonance lines of the high-temperature spectrum, representing a distinctly broadened sextet, can be described by

a superposition of four sextets, which differ mainly in the magnitude of the magnetic splitting and line width (#1–4, Table 2). The parameters of the external sextet of this group (#1, Table 2) are in very good agreement with the parameters of hematite— $\alpha\text{-Fe}_2\text{O}_3$ [42,43]. Internal sextets, which differ mainly in larger line widths, their lower intensity, and lower magnitude of magnetic splitting, obviously belong to defective forms of hematite, differing in various degrees of substitution of iron atoms by atoms of another nature (#2–4, Table 2). Given the origin of the sample, it is possible to assume, with a high degree of certainty, isomorphic substitution of a part of iron atoms by aluminum atoms [44]. The substitution of a part of atoms in the iron sublattice by aluminum atoms leads to a proportional impurity content and to a decrease in the magnitude of the magnetic splitting in proportion to the impurity content [45]. As the sample temperature decreases to 77.5 K, the discussed part of the spectrum is described by two sextets of different widths. In this case, the magnetic field of the outer sextet of a smaller width does not reach the value characteristic of hematite [43], which confirms the version of isomorphic substitution of part of the iron atoms. In the studied temperature range, the sample does not undergo the Morin transition [46], which confirms the distortion of the hematite structure by the impurity atoms present in the iron sublattice. We also note that an increase in the content of hydroxyl groups in the oxygen positions of aluminum-hematite can also lead to a decrease in the Morin transition temperature [47]. In this compound, a strong magnetic dipole and electric quadrupole interactions are observed (obviously caused by distortion of the crystal lattice of aluminum-hematite by impurity atoms), which required this part of the spectrum to be described by taking into account the terms second-order of quadrupole perturbation [41] (a_+ , a_- ; see Table 2).

3.2. Thermodynamic Calculations

It can be seen from Table 1 that Fe_2O_3 , CaO , Al_2O_3 , SiO_2 , and TiO_2 are the major components of the RM. After reductive smelting, the total iron is reduced to a metallic phase while the other oxides occur in a slag phase. Thermodynamic modeling of the slag phase was carried out for complete (no Fe in slag) and partial (2.5 mass % of FeO added to slag) reduction of iron.

Liquidus projections for the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ system calculated in the temperature range of 1300 to 1800 °C are shown in Figure 5a. The slag chemical composition obtained after reductive smelting of the neutralized RM [35] was recalculated to four components (26.04 mass % Al_2O_3 , 20.46 SiO_2 , 45.21 CaO , 8.29 TiO_2) and is also shown in Figure 5a. It was assumed that all iron-containing phases are completely reduced and the Fe content in the slag is zero.

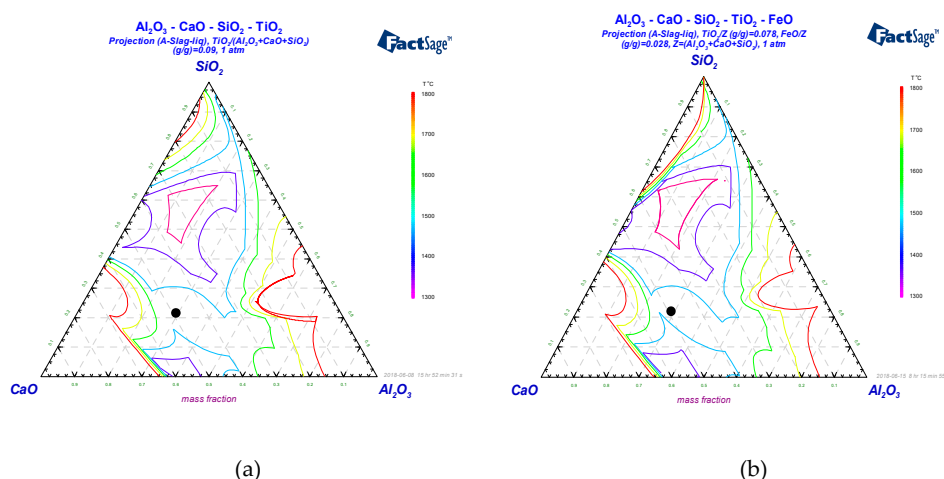
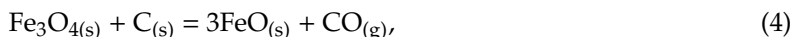
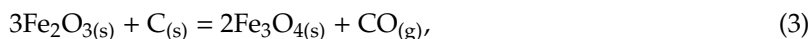


Figure 5. Liquidus projections for (a) the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-8.21 wt % TiO}_2$ and (b) the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-7.5 wt % TiO}_2\text{-2.5 wt % FeO}$ slag systems (the slag chemical composition is marked by a black dot).

Figure 5a indicates that the RM melting point under complete reduction of iron is about 1600 °C while the presence of iron oxide in slag under reducing conditions shifts the liquidus towards lower temperatures (Figure 5b).

Figure 5b shows the same liquidus projections calculated for the CaO-Al₂O₃-SiO₂-FeO-TiO₂ system with 2.5 mass% of FeO and 7.5 mass% of TiO₂. This five-component system represents a more realistic situation of incomplete reduction of iron due to non-equilibrium conditions.

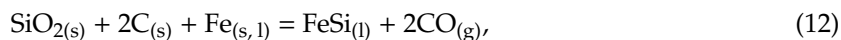
The iron oxide reduction process may be represented as the following reactions:



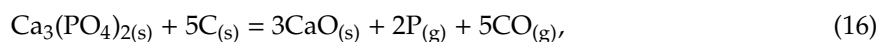
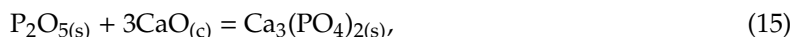
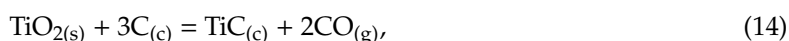
At the same time, at temperatures >700 °C, carbon monoxide is regenerated by the Boudouard–Bell reaction, and Equation (5) is actually a total reaction of:



Silicon oxides can be reduced by solid carbon only at temperatures above 1400 °C by the following reactions:



Titanium and phosphorus oxides can be reduced by the reactions:



So, reduced silicon, titanium, and phosphorus can pass into metal according reactions, as shown in Equations (12)–(14) and (17).

Equilibrium calculations of complete iron reduction while considering the silicon dioxide, phosphorus, and titanium oxides reduction were performed by a Gibbs energy minimization method using the HSC Chemistry program. The normalized composition of the neutralized RM from Table 1 was used for calculations. The proportions of iron-containing phases calculated as a function of the carbon amount are shown in Figure 6. Calculation was performed for 100 kg of RM.

Figure 6 shows that as the amount of carbon in the system increases from 3 to 10 kg (per 100 kg of RM), the content of pure iron increases from 0% to 100%, and the concentrations of the other iron-containing phases decreases to zero. With a lack of carbon in the system, the formation of wustite (FeO) and hercynite (FeAl₂O₄) occurs in the system. It can be seen that at least 10 kg of carbon per 100 kg of neutralized RM is necessary for complete recovery of iron compounds.

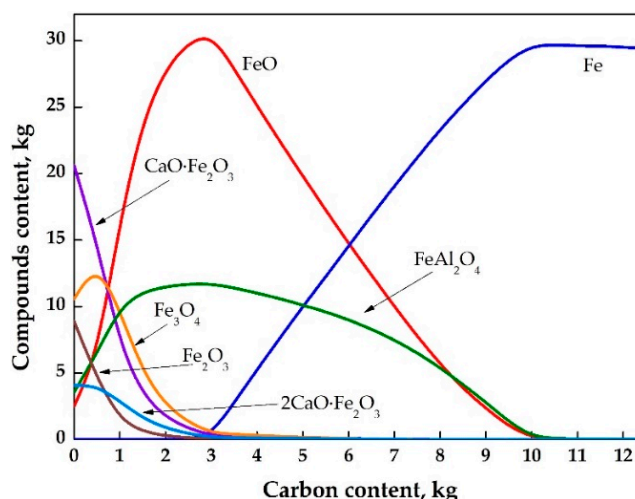


Figure 6. The equilibrium compositions of iron-containing phases as a function of the added carbon in the system at 1600 °C.

3.3. Reductive Smelting of the Neutralized Red Mud

A series of experiments were carried out at different temperatures in the range 1650–1750 °C to study the effect of the furnace temperature on metal extraction and the metal/slag separation process. Figure 7 shows the change in the iron content in the slag at different furnace temperatures. At 1650 °C, the slag phase contains ~8 wt % of iron, which is not separated into ingot (see Figure 8a). By increasing the temperature up to 1700 °C, the metal ingot is formed at the bottom of the crucible, but a part of the iron remains in the slag (Figure 8b). A further increase of temperature by 50 °C leads to an almost complete iron reduction and formation of large metal ingots on the bottom of the crucible (Figure 8c).

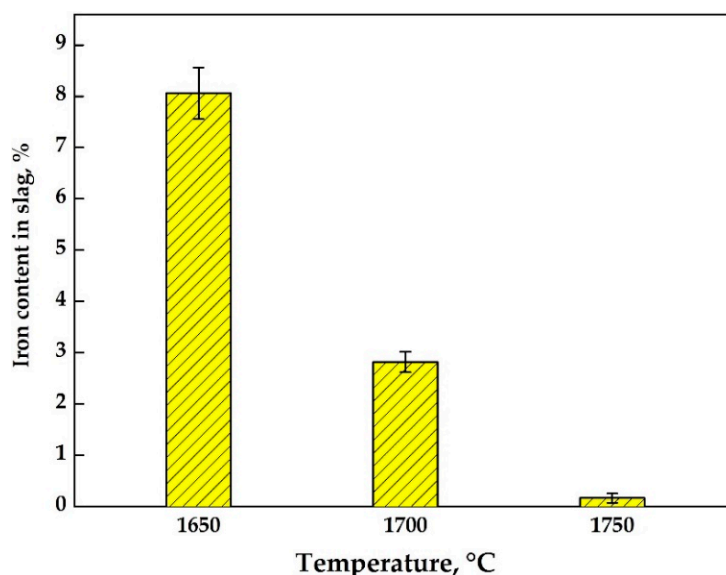


Figure 7. The iron content (wt %) in slag after reductive smelting of RM at different temperatures.

An increase of the temperature from 1650 to 1750 °C results in increasing the CaO and Al₂O₃ content in slag (Table 3). At the same time, the SiO₂ content in slag decreases, due to silicon reduction by Equations (10)–(13). The TiO₂ content in slag increases at temperatures of 1650 to 1700 °C, which indicates that the formed of titanium carbide remains in slag phase. At 1750 °C, TiO₂ reduces to titanium carbide, which further dissolves in a metallic phase.

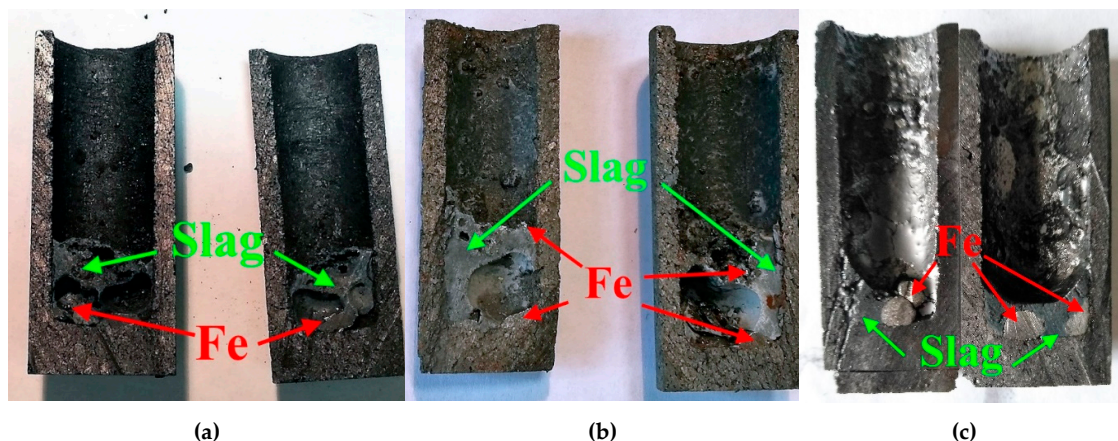


Figure 8. Samples of metal and slag obtained after reduction smelting of RM at (a) 1650 °C, (b) 1700 °C, and (c) 1750 °C.

Table 3. The slag chemical composition after reductive smelting of the RM (wt %).

Temperature	T.Fe *	CaO	Al ₂ O ₃	SiO ₂	TiO ₂	MgO	MnO	P ₂ O ₅	S
1650 °C	8.06	43.34	18.18	22.23	3.75	1.53	0.31	0.084	0.31
1700 °C	2.82	50.41	21.46	14.46	6.64	1.71	0.13	0.032	0.33
1750 °C	0.16	61.79	24.37	11.47	0.2	0.57	0.02	0.03	0.29

* T.Fe is the total concentration of iron (element) in the slag.

Figure 9 represents the phases found in slag by XRD analysis. The main slag phase present at 1650 °C is gehlenite (Ca₂Al₂SiO₇). It also contains minor amounts of larnite (Ca₂SiO₄), third and fifth calcium aluminates (Ca₃Al₂O₆ and Ca₅Al₆O₁₄), perovskite (Ca₂TiO₃), and hatrurite (Ca₃SiO₅). At 1700 °C, as the SiO₂ content in slag decreases due to silicon reduction into the metal, and the slag composition shifts from the gehlenite primary phase field towards the larnite primary phase field, which leads to an increase of its content in the slag. Gehlenite and perovskite are not present in slag at 1750 °C, and the main slag phase is di-calcium silicate (γ-Ca₂SiO₄). This may be explained by the shifting of the slag composition to the larnite primary phase field [48].

It can be concluded on the basis of XRD analysis that titanium carbide is likely formed as a result of the following reactions between perovskite and carbon:

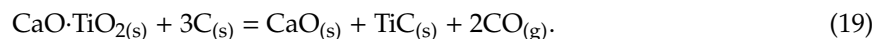


Table 4 provides values of the Gibbs free energy calculated for Equation (18) at different temperatures. It can be seen that the TiC formation is likely to occur in slag at temperatures higher than 1600 °C.

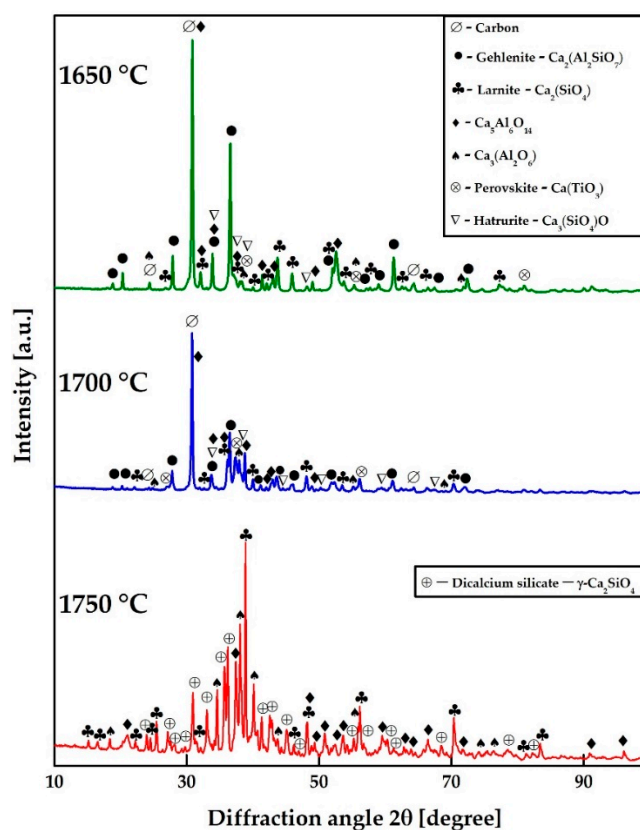


Figure 9. XRD analysis of slag after reductive smelting of RM at 1650, 1700, and 1750 °C.

Table 4. Thermodynamic calculations for Equation (19).

T, °C	ΔG , kJ·mol ^{−1}
1500	22.756
1550	6.914
1600	−8.887
1650	−24.650
1700	−40.376
1750	−56.068
1800	−71.725

To explain the behavior of titanium in the reduction smelting process of the RM, the slag and metal samples obtained at 1650 and 1750 °C were analyzed by SEM (Figure 10). Figure 10a indicates that titanium is distributed over the whole slag volume, but the majority is concentrated around the molten metal drops. In this case, titanium is not dissolved in the metallic phase and it may prevent the coagulation of metal drops into one large ingot. With the temperature increasing to 1750 °C, most of the titanium is present in the metal phase as carbide (Figure 10b,c).

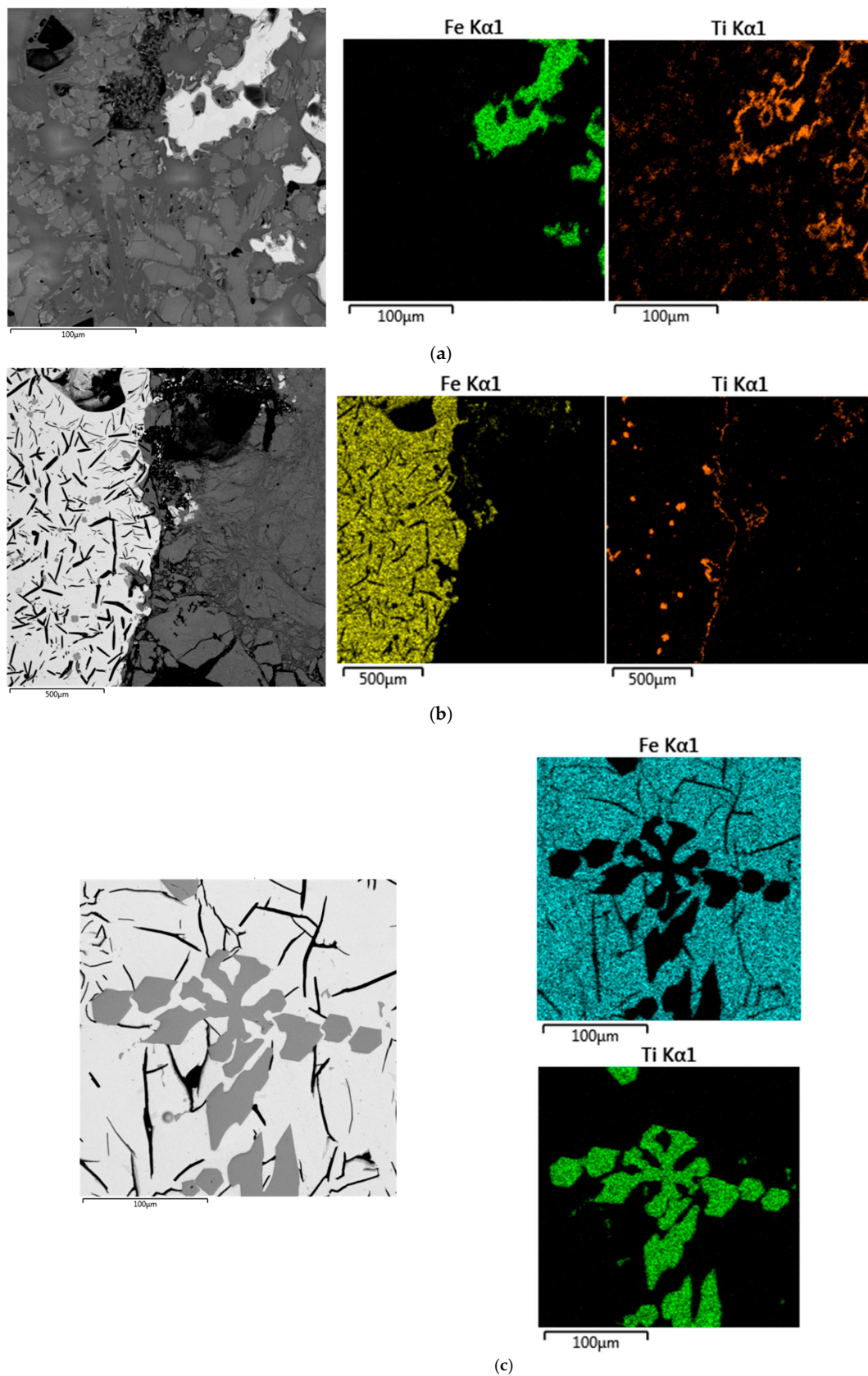


Figure 10. SEM images of the slag and pig iron samples: reduction smelting at 1650 °C (a), reduction smelting at 1750 °C (b), titanium carbide in pig iron (c) (the mapping shows distribution of Fe and Ti).

3.4. Composition of Pig Iron

The chemical composition of the metallic phase obtained in reductive smelting of the RM at 1700 and 1750 °C are presented in Table 5. The chemical composition can be attributed to the pig iron having a higher content of titanium, phosphorus, and manganese, and a low sulfur content. It can be seen that the metallic phase obtained at 1700 °C contains much lower phosphorous and titanium as well as other elements.

Table 5. Chemical composition of pig iron after reductive smelting of the RM at 1700 and 1750 °C (wt %).

Temperature	Si	Mn	Ti	V	P	S
1700 °C	0.35	0.45	0.45	0.05	0.32	<0.005
1750 °C	1.17	1.35	1.12	0.49	0.96	<0.005

Figure 11 represents the phase composition of pig iron obtained at 1750 °C. The XRD phase analysis showed that graphite is present in pig iron in both a free and bound form, and titanium occurs in the form of titanium carbide.

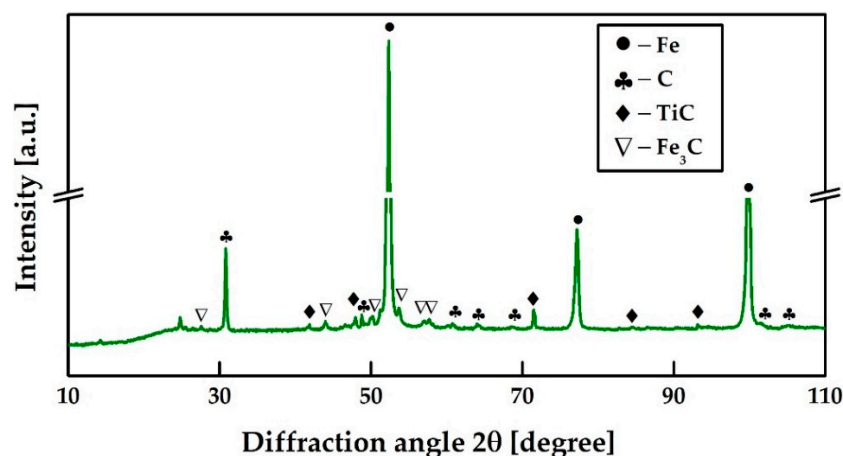


Figure 11. XRD analysis of the pig iron after reductive smelting of the RM at 1750 °C.

The Mössbauer spectrum of a pig iron sample obtained at room temperature is a distorted broadened sextet (Figure 12). The asymmetric broadening of the resonance lines to the center of the spectrum is observed for one, two, and six lines, as three, four, and especially five lines are relatively symmetrical. One, two, and six sextet lines are clearly split into at least two, and on the inner side of the first resonance line, an additional shoulder is observed. The intensity of the internal lines is comparable with the intensity of the external lines of the sextet, and the intensities of lines two and five even exceed them. All this data indicates that the sample spectrum is a superposition of several subspectra of sextets describing the iron atoms in the alloy, surrounded by a different number of impurity atoms. The Mössbauer spectrum of the pig iron sample can be described by a superposition of seven narrow subspectra of sextets with related parameters, a sextet with a small splitting, but wide lines, and one low-intensity doublet (Table 6).

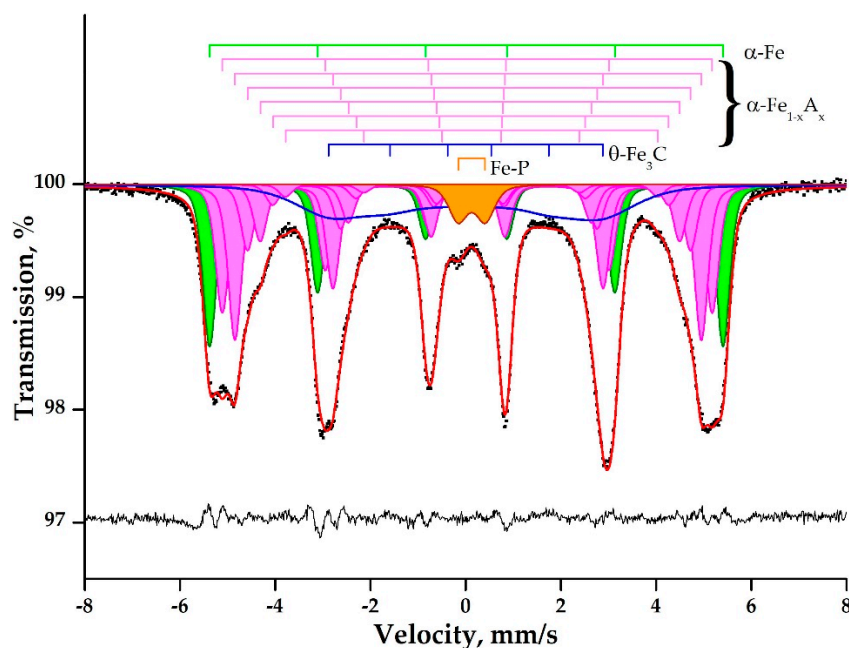


Figure 12. Mössbauer spectra of pig iron sample obtained at 296 K.

Table 6. Mössbauer spectra parameters of pig iron obtained at 296 K.

#	Compound or Site	δ	$d\delta$	$\Delta = 2\varepsilon$ (mm/s)	Γ_{exp}	H_{eff} (kOe)	dH	S# (at %)
1	$\alpha\text{-Fe}$	0.013				334.4		20.7
2	$\alpha\text{-Fe}_{1-x}\text{A}_x$	0.032				319.0		16.5
3		0.051	0.0188	0.001	0.343	303.6	15.36	19.9
4		0.070				288.3		8.4
5		0.089				272.9		7.3
6		0.108				257.6		2.6
7		0.126				242.2		1.7
8	$\theta\text{-Fe}_3\text{C}$	0.04	-	-0.04	1.63	178.6	-	19.9
9	Fe-P	0.13	-	0.55	0.45	-	-	3.0

$d\delta$ and dH —step of changing the Mössbauer parameter for satellite spectra.

The internal sextet (#8, Table 6) includes a combination of subspectrum with very close hyperfine parameters for compounds of iron with carbon: $\theta\text{-Fe}_3\text{C}$ [49,50], and/or phosphorus: $(\text{Fe}_{1-x}\text{A}_x)_2\text{P}$, where A is a transition metal [51]. The doublet (#9, Table 6) is characterized by a small isomeric shift, for example, characteristic of iron compounds in a tetrahedral or pyramidal environment with phosphorus [52,53] or for complex solutions of the type $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{P}$ [54].

The parameters of the external narrow sextet (#1, Table 6) correspond to $\alpha\text{-Fe}$ [55], and were the starting parameters for calculating the parameters of the satellite subspectra. The following six satellite subspectra correspond to the iron atoms in the "alloy" lattice, $\alpha\text{-Fe}_{1-x}\text{A}_x$, which are surrounded by one, two, or more atoms of a different nature. Their parameters are similar to those of subspectrum #1, with the only difference being that their chemical shift and effective magnetic field are successively different from the original ones by $n \cdot d\delta$ and $-n \cdot dH$, where n is the serial number of the satellite, and dF is the change in the Mössbauer parameter (see Table 6). Taking into account that the obtained step, dH , is approximately two times smaller than that usually observed for iron alloys with various metals and nonmetals, it can be assumed that the observed satellite subspectra describe the changes in magnetic fields of iron atoms under the action of impurity atoms from at least two nearest coordination spheres [55,56].

3.5. Pig Iron Application

At the steel mill EVRAZ ZSMK (53.878267, 87.269946; Novokuznetsk, Russia), the steel-casting equipment (bottom pallets for through molds and molds for forging ingots) is made from pig iron. Titanium and vanadium alloying is normally used to increase the durability of the molds at the plant [57,58]. It has previously been shown [59] that the titanium carbide particles enhance wear resistance of the steel composite. The influence of the content of titanium and vanadium in pig iron on the tensile strength can be described by the equations:

$$\sigma = -3.71 + 291.7 \times V, \quad (20)$$

$$\sigma = -5.00 + 325.0 \times Ti, \quad (21)$$

where σ is the tensile strength of pig iron, kg/mm²; V, Ti is the element content in pig iron, %.

An increase in the strength properties of cast iron leads to a decrease in the erosion of molds by a falling stream of metal. The alloying process used in the EVRAZ ZSMK increases the heat resistance of molds by 7% to 12% [60]. However, a high content of vanadium and titanium in pig iron leads to low fluidity. In EVRAZ ZSMK, ferrophosphorus (P ~17 wt %) is used to increase the fluidity (in the ratio of 800 kg flux per 90-ton ladle). Industrial tests have shown that shrinkage effects and micropores are practically absent in castings doped with phosphorus due to better filling of the molds [61]. This effect was observed when the phosphorus content in pig iron was above 0.21 wt % [62].

The pig iron obtained in our study contains high amounts of Ti, V, and P (Table 5). The SEM analysis of the pig iron microstructure showed triple phosphide eutectic (Fe₃P) in addition to titanium carbide (Figure 13).

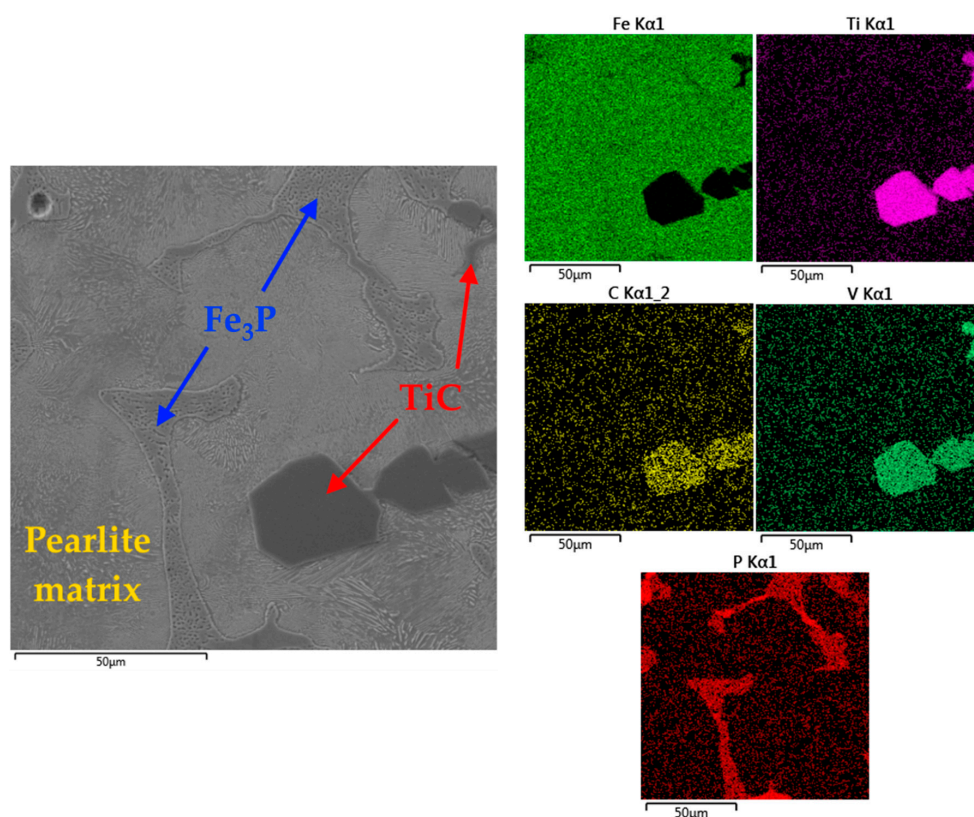


Figure 13. SEM images of the pig iron sample obtained at 1750 °C (the mapping shows distribution of Fe, Ti, C, V, and P).

Analysis of the main phases of pig iron included titanium carbide, and phosphide eutectic and pearlite matrix was used in microindentation hardness testing (Figure 14). After measuring the diagonals of the indenter prints, the average size for each of the phases was determined. Using Equation (2), the value of the Vickers hardness was calculated (Table 7). TiC has an extremely high hardness index (5130HV50/10). Fe₃P has a Vickers hardness almost three times higher (934HV50/10) compared to the pearlite matrix (336HV50/10). Thus, this pig iron has all the characteristics necessary to increase the mold lifecycle: High strength and good fluidity due to the presence of phosphide eutectic. Since, nowadays, expensive ligatures containing titanium, vanadium, and ferroalloys are used to produce pig iron with similar properties to EVRAZ ZSMK, the use of RM as a raw material will reduce the costs of the production of molds.

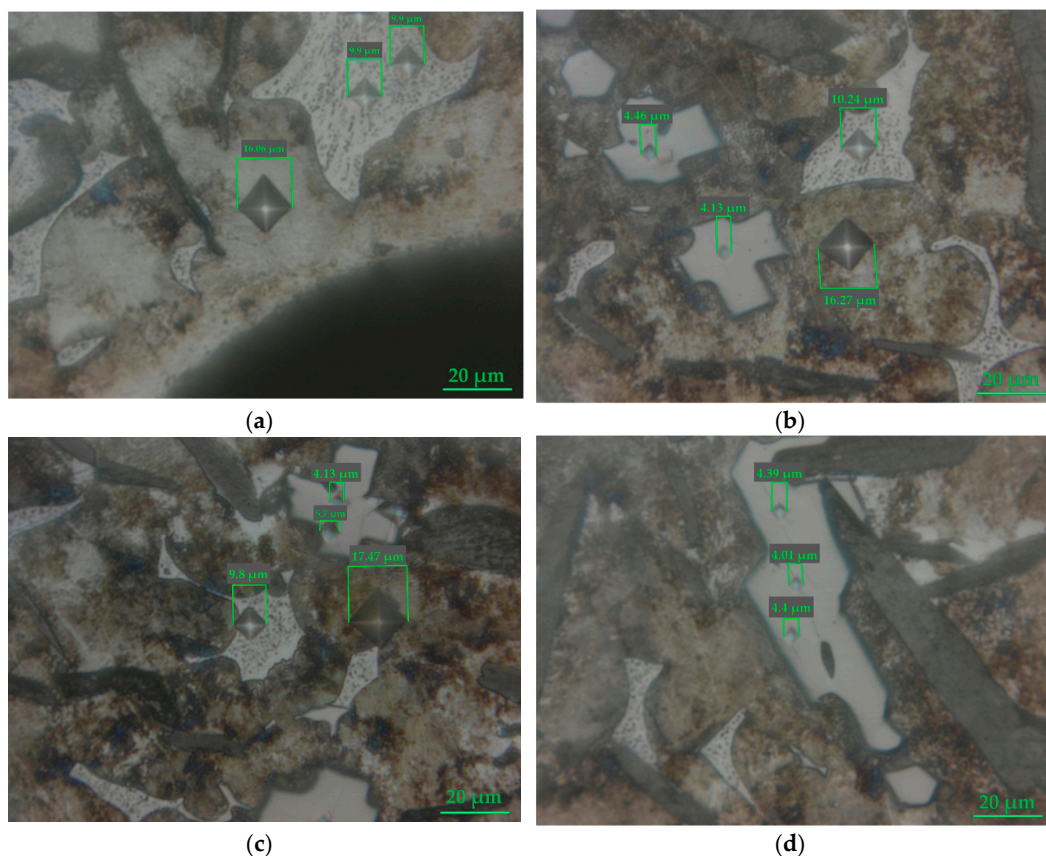


Figure 14. Micrographs of microindentation hardness testing of the pig iron sample obtained (a–d) at 1750 °C (0.49 H, $\tau = 10$ s).

Table 7. Microindentation hardness data of pig iron phase.

Phase	Impression Diagonal, μm	Average Diagonal, μm	Vickers Hardness
TiC	4.46; 4.13; 4.13; 4.39; 4.01; 4.4	4.25	5130
Fe ₃ P	9.9; 9.9; 10.24; 9.8;	9.96	934
Pearlite	16.06; 16.27; 17.47	16.60	336

4. Conclusions

It was experimentally proven that it is possible to obtain pig iron using reductive smelting of the neutralized RM at a temperature of 1750 °C. The metallic phase (pig iron) contains high amounts of titanium, phosphorus, and vanadium and a low amount of sulfur. The iron extraction optimum at 1750 °C was found to be more than 98%. The obtained pig iron can successfully be used at EVRAZ ZSMK as a raw material to produce molds with higher wear resistance.

The research will be continued to determine optimal parameters for better slag–metal separation. A perspective way is to adjust the slag composition by adding a flux containing Al_2O_3 , which can be made economically feasible if aluminum dross is used. The second part of the research will be focused on hydrometallurgical processing of slag to extract alumina, wollastonite, and titanium concentrate.

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