PROCESSING OF TITANIUM-MAGNETITE CONCENTRATES FOR THE PRODUCTION OF IRON, TITANIUM DIOXIDE MODIFICATIONS AND TITANIUM

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Abstract. Conditions for the reduction of titanium-magnetite concentrates (main components are Fe 52–54 % and TiO_2 5–7 %) by natural gas for obtaining iron powder and titanium fraction were studied. Based on the theory of granulation in the drum apparatus, granules with 25 % of soda fluxing additive with optimum diameter, humidity, strength and porosity were obtained. It was found that the reduction reactions in the temperature range of 1143–1198 K are carried out if a mixture of hydrogen and carbon monoxide is added to the natural gas in amount of 15 vol %. Block-diagrams for processing titanium-magnetite concentrates for the production of iron powder α-Fe (purity 99 %), anatase and rutile modifications of titanium dioxide (99 % TiO_2) and titanium with a purity of 99% are presented.

Keywords: titanium-magnetite concentrates, natural gas, hydrogen, carbon monoxide, iron powder, titanium.

1. Introduction

Due to the intensive development of rich magnetite ores, their reserves are depleted. Therefore, the actual problem of modern metallurgy is the use of less technological types of iron ore, such as titanium-magnetite ores. Titanium-magnetites are a mixture of mainly two minerals: ilmenite $FeTiO_3$ and magnetite Fe_3O_4 with impurities of vanadium and chromium [1, 2]. Studies on the technology of processing titanium-magnetite ores are carried out to recover iron, titanium, chromium, vanadium, and other products [3-6]. Pyrometallurgical [7, 8], hydrometallurgical [9] and specific chemical methods for processing enriched titanium-magnetite ores to produce metallic iron and titanium-vanadium fractions are used [10, 11]. For several years, we have been developing

[12-14] processes for the complex processing of titanium-magnetite concentrates using the non-domain method of direct reduction of granules by natural gas in the solid phase to produce iron powder, titanium dioxide and vanadium. Depending on the ratio of ore and non-metallic minerals, the chemical composition of titanium-magnetite sandstones of various deposits varies widely. As a part of various samples of sandstones in Azerbaijan, we found (wt %): Fe total 6–12, sometimes to 22–38.5; TiO_2 0.7–1.7, sometimes to 3.2–5.9; Mn 0.5–0.7; V to 0.3–0.5; Cr 0.01–0.1; Al_2O_3 10–18; SiO_2 23–60; CaO 5–10; MgO 4–6; P_2O_5 0.1–0.3; SO_3 0.07–0.2; and CoO 0.005–0.01. Enrichment of titanium-magnetite sandstones using wet magnetic separation produces titanium-magnetite concentrates in which the total content of iron, titanium, vanadium and manganese reaches (wt %): Fe 52–54; TiO_2 5–7; V 0.8–1; and Mn 0.6–0.8.

The aim of this work is to generalize and develop our previous studies on processing titanium-magnetite concentrates to determine the conditions and technological schemes for obtaining iron, titanium, anatase, and rutile modifications of titanium dioxide.

2. Experimental

Depending on the ratio of ore and nonmetallic minerals the chemical composition of titanium-magnetite sandstones of various deposits varies widely. The objects of this study were titanium-magnetite concentrates (the major components are Fe 52–54 wt % and TiO_2 5–7 wt % with 25 % of soda fluxing additive), obtained from the procedure Adzhinaur sandstones from Azerbaijan described in [2]. Titanium-magnetite concentrates are used in the form of granules of 5–7 mm in diameter with a certain humidity, porosity and strength. The conditions for the preparation of granules are determined on the basis of the granulation theory in a drum apparatus [15]. The powder X-ray diffractometer D2 Phaser (Bruker) was used for XRF. A diffractogram for titanium-magnetite concentrate fluxed with soda is shown in Fig. 1.

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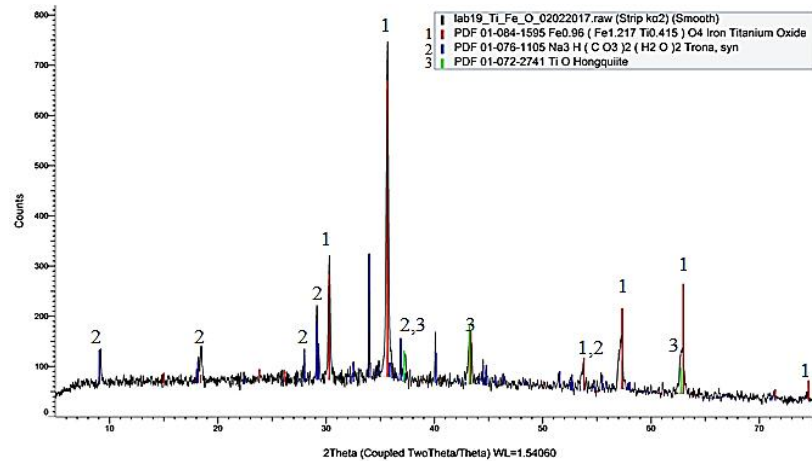**Fig. 1**. Diffractogram for titanium-magnetite concentrate fluxed with soda

2.1. Granulation of Titanium-Magnetite Concentrate Powders

Titanium-magnetite concentrates with 25 % of the anhydrous soda, after thorough mixing were granulated in a laboratory drum pelletizers of 15 cm in diameter and 100 cm in length. The pellets for reduction reactions were prepared from powders (with the diameter of 0.1–0.15 mm) of the titanium-magnetite concentrate. Water was used as a binder for tightening the powdered concentrate particles into lumps and ensuring subsequent pellet agglomeration during granulation. Spraying water ensures agglomeration of fine particles and laminating the surface formed nuclei in the moving bed. For modeling of the formation (lamination and compaction) of granules in a laboratory drum apparatus the following equation [15] was used:

$$a(t) = (a_0^2 + \gamma t)^{1/2} + a_0 \exp(-b_0 t)\sin\left(\frac{vt}{2}\right) \qquad (1)$$

where $\gamma = 2R\omega\lambda/\pi$, ($\gamma = 2$–2.5), $m^2 \cdot s^{-1}$; a is the current size of the granules, m; a_0 is an average size of the embryo (powder), m; b_0 is a parameter related to the density of the powdered material particles, s^{-1}; t is granule formation time, s; R is a radius of drum apparatus, m; λ is thickness of layering, m; ω is the rotation frequency of the drum apparatus, s^{-1}; and v is a characteristic number depending on shear viscosity, s^{-1}.

2.2. Reduction of Titanium-Magnetite Concentrates

2.2.1. Thermodynamic and kinetic analysis

Natural gas with the addition of 15 vol % of hydrogen and carbon monoxide was used as a reducing agent. The process of granules reduction from a titanium-magnetite concentrate basically consists of the following reactions:
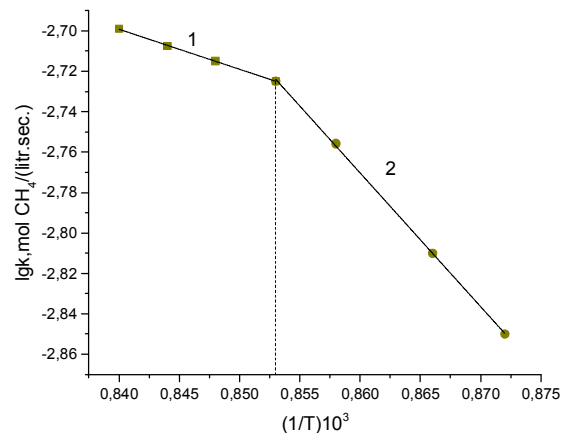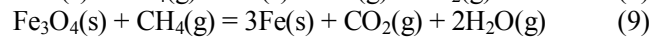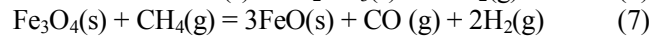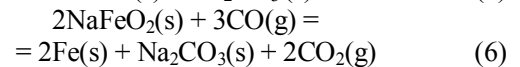
$$Fe_3O_4(s) + Na_2CO_3(s) =$$
$$= 2NaFeO_2(s) + FeO(s) + CO_2(g) \qquad (2)$$

$$FeTiO_3(s) + Na_2CO_3(s) =$$
$$= Na_2TiO_3(s) + FeO(s) + CO_2 \qquad (3)$$

$$2NaFeO_2(s) + H_2(g) + CO_2(g) =$$
$$= 2FeO\ (s) + Na_2CO_3(s) + H_2O(g) \qquad (4)$$

$$2NaFeO_2(s) + CO(g) =$$
$$= 2FeO(s) + Na_2CO_3\ (s) \qquad (5)$$

$$2NaFeO_2(s) + 3CO(g) =$$
$$= 2Fe(s) + Na_2CO_3(s) + 2CO_2(g) \qquad (6)$$

$$Fe_3O_4(s) + CH_4(g) = 3FeO(s) + CO\ (g) + 2H_2(g) \qquad (7)$$

$$FeO(s) + CH_4(g) = Fe\ (s) + CO(g) + 2H_2(g) \qquad (8)$$

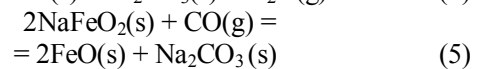$$Fe_3O_4(s) + CH_4(g) = 3Fe(s) + CO_2(g) + 2H_2O(g) \qquad (9)$$
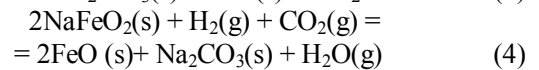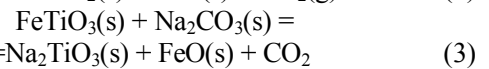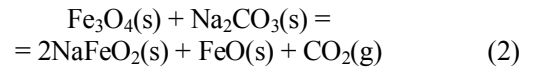

Fig. 2. Temperature regions of the kinetic curves of titanium-magnetite reduction by methane in the range of 1143–1198 K
For (1): $\lg k = (-1.03552)–(-1.98059)\ (1/T)$, (diffusion-kinetic region), (1173–1198 K), $E_a = 37.8$ kJ/mol;
For (2): $\lg k = 2.91935–6.61586\ (1/T)$, (kinetic region), (1143–1173 K), $E_a = 126.8$ kJ/mol

The temperature dependences of the Gibbs energies of these reactions are determined in [14]. It was found that magnetite starts to interact with soda to obtain ferrite(III) sodium (Eq. (2)) at 500–550 K. Sodium titanate prepared by Eq. (3) proceeds in a non-magnetic phase. Main reaction of magnetite reduction through wustite at relatively low temperatures proceeds poorly (Eqs. (7–9)). Equilibrium reactions (7–9) are shifted to the right side, starting with 1010 K ($\Delta G_T^0 < 0$).

The kinetic parameters of the reduction reactions of titanium-magnetite concentrates are determined from the methane consumption (in mol/(l·s)). In most cases, the reduction reactions of iron ore concentrates with natural gas are expressed by kinetic equations of the first order, which was confirmed by our methane consumption calculations. The logarithmic values of the rate constant of reactions as a function of temperature are shown in Fig. 2, from which it follows that the constructed graphs form straight lines with different slopes. This shows that the process of natural gas reduction of titanium-magnetites with flux additives obeys the Arrhenius law. The reduction of iron oxides to metal within the interval of 1143–1198 K (Fig. 2) takes place in two regions. In the temperature range of 1143–1173 K the process proceeds in the kinetic region. The apparent activation energy E_a, is 126.8 kJ /mol. Within 1173–1198 K the process moves to diffusion-kinetic region. In this case, the value of the apparent activation energy is $E_a = 37.8$ kJ/mol.

Fluxed with the addition of 25% soda granules of 3–7 mm in size were reduced using natural gas in a tube furnace in the temperature range of 1123–1273 K. The reactor and the entire system to supply natural gas were purged with nitrogen. The use of granules with optimum strength and porosity leads to an uniform distribution of the gas flow inside the reactor and sintering of iron powders does not occur. As can be seen from Fig. 3, with increasing reduction temperature of iron the metallization degree is increased and its maximum (98.5–98.7 %) is observed at 1173–1198 K. With further increase in the temperature to 1273 K the metallization degree slightly decreases to 94.7 %. This is due to the fact that the reduced iron particles on the surface of the pellets stick together, form crust and hinder the gas diffusion into the pellet to inhibit its complete reduction. These undesirable phenomena are practically absent in the temperature range of 1148–1198 K. With the increase in the natural gas reduction time at the feed rate of 0.1 l/min and the temperature of 1198 K, the degree of iron metallization is 98 % after 20 min. With further increase of reduction time to 1 h, the metallization degree of iron is kept at the maximum of 98.8 % with 1173 K. However, the excessive increase in the process time is not desirable and the optimum duration of the process is 30 min at optimal

temperatures of 1148–1198 K, natural gas rate of 0.1 l/min. Under such conditions the metallization degree of titanium-magnetite concentrate fluxed granules reaches 96.5–98 %.
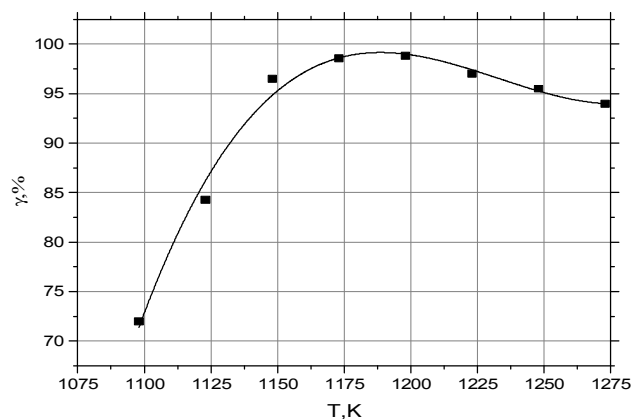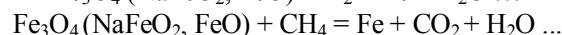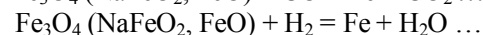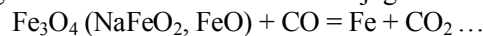

Fig. 3. The metallization degree of fluxed (25 % Na_2CO_3) granules of titanium-magnetite concentrate *vs*. reduction temperature at reduction time 30 min and the natural gas feed rate 0.1 *l*/min. Experimental data are denoted as (♦), curve is a polynomial
$$\gamma\,(\%) = -28222 + 69.09409\,T - 0.05612\,T^2 + 1.51758 \cdot 10^{-5}\,T^3$$

3. Results and Discussion

It was found that the reduction reactions in the temperature range of 1143–1198 K are carried out if a mixture of hydrogen and carbon monoxide is added to the natural gas in amount of 15 vol %. It has been established that the magnetite reduction reactions with methane, hydrogen and carbon monoxide are conjugated:
$$Fe_3O_4\,(NaFeO_2, FeO) + CO = Fe + CO_2 \ldots$$
$$Fe_3O_4\,(NaFeO_2, FeO) + H_2 = Fe + H_2O \ldots$$
$$Fe_3O_4\,(NaFeO_2, FeO) + CH_4 = Fe + CO_2 + H_2O \ldots$$

In these reactions, Fe_3O_4 ($NaFeO_2$, FeO) are the actors, CO and H_2 – inductors, CH_4 – acceptor. The first two reactions initiate the reduction of magnetite to methane. The induction factor $I = n(CH_4)/n(H_2+CO) \geq 5$. Block-diagrams for processing titanium-magnetite concentrates for the production of iron powder α-Fe (purity of 99 %), anatase and rutile modifications of titanium dioxide (99 % TiO_2) and titanium with the purity of 99 % are presented in Figs. 4 and 5.

As a result of the titanium-magnetite concentrates reduction by natural gas at 1143–1198 K, after the subsequent hot leaching of the reduced metallized pellets in water and wet magnetic separation of the pulp, an iron powder was obtained (Fig. 4). Reduction products were subjected to wet magnetic separation and divided into two fractions: magnetic and non-magnetic. Iron powder was obtained from the magnetic fraction after washing and

drying. After washing, filtering and drying, the titanium concentrate was extracted from the non-magnetic fraction to obtain technical titanium dioxide (Fig. 5).

3.1. Processing of Titanium Fraction

Titanium dioxide has three modifications: rutile, anatase and brookite. Rutile is a more stable form and is a densely packed structure of anatase (tetragonal). Anatase is a tetragonal structure and converts into the rutile modification at 1098 K. Brookite has an orthorhombic structure and is spontaneously converted into rutile at the temperature of about 1023 K. In the work [16] devoted to the complex processing of titanomagnetite ores, a rutile modification of TiO_2 was obtained.

In our work, 15 % hydrochloric acid is used to process the titanium fraction (Fig. 5). It was found that during the titanium fraction processing with a 15 % HCl solution at 358 K for 1 h the ions of iron, calcium and magnesium are dissolved in the form of chlorides. For desilication the titanium dioxide mixture was treated with a weak solution of sodium hydroxide at the boiling temperature of the solution. Polytitanic acid powder $xTiO_2 \cdot yH_2O$ was mixed with powder of pure chitosan in the weight ratio of 20:1, and calcined within the temperature range of 1123–1173 K to obtain technical titanium dioxide in the form of a mixture (94.5 % anatase and 4.5 % rutile modifications, Fig. 6).

Use of chitosan as a modifier is not random. Zima *et al.* [17] revealed the influence of bioactive natural polymer – chitosan as an organic reagent to form texture morphology and phase composition of products during hydrothermal treatment of TiO_2 powders.

Titanium from titanium dioxide was obtained by the method described in [17]. Chlorination of TiO_2 and then reduction of $TiCl_4$ with magnesium was carried out (Fig. 5). The diffractogram of the obtained product consists essentially of titanium lines (Fig. 7).
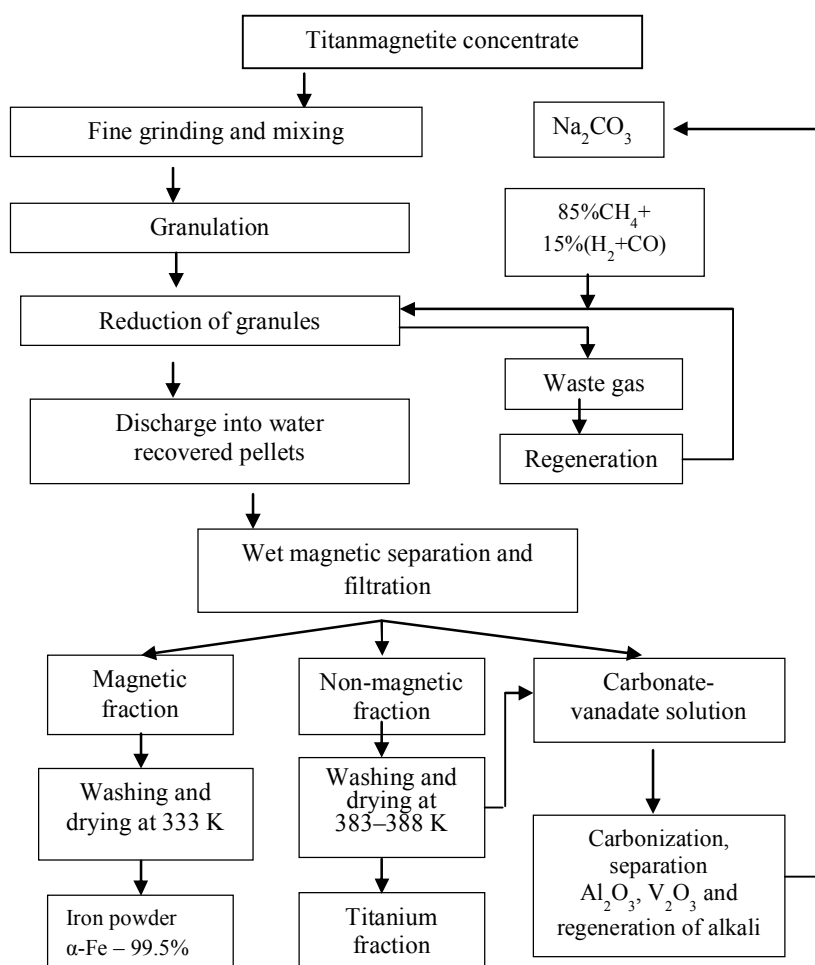

Fig. 4. Block-diagram for processing titanium-magnetite concentrate of Aginaur sandstones of Azerbaijan
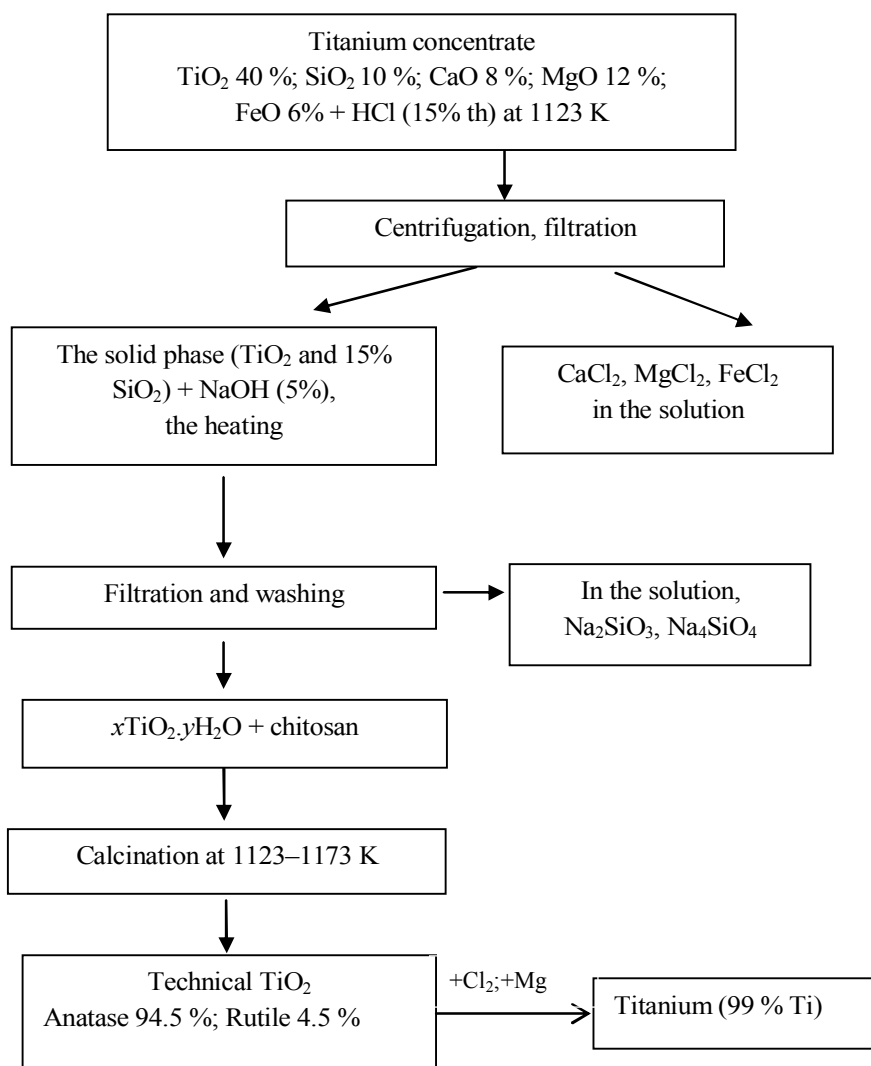
Titanium concentrate
TiO_2 40 %; SiO_2 10 %; CaO 8 %; MgO 12 %;
FeO 6% + HCl (15% th) at 1123 K

↓

Centrifugation, filtration

The solid phase (TiO_2 and 15% SiO_2) + NaOH (5%), the heating

$CaCl_2$, $MgCl_2$, $FeCl_2$ in the solution

↓

Filtration and washing → In the solution, Na_2SiO_3, Na_4SiO_4

↓

$xTiO_2.yH_2O$ + chitosan

↓

Calcination at 1123–1173 K

↓

Technical TiO_2
Anatase 94.5 %; Rutile 4.5 %   +Cl_2;+Mg → Titanium (99 % Ti)

Fig. 5. Block-diagram of titanium fraction processing

Pattern List #3

Show	Icon	Color	Index	Name	Scan
Yes			0	PDF 03-065-5714	TiO2_98.raw (Strip kα2) (X-Offset) #1
Yes			1	PDF 01-070-7347	TiO2_98.raw (Strip kα2) (X-Offset) #1

Compound Name	Formula	Quality	Y-Scale	I/Ic DB	S-Q	System	Space Group
Anatase, syn	Ti O2	Star (*)	95.55%	5.040	93.9%	Tetragonal	I41/amd (141)
Rutile	Ti O2	Star (*)	4.50%	3.620	6.1%	Tetragonal	P42/mnm (136)

a	b	c	Z	Volume
3.78500		9.51400	4	136.30
4.59300		2.96100	2	62.46

Fig. 6. Results of X-ray diffraction analysis of technical titanium dioxide with 94.5 %
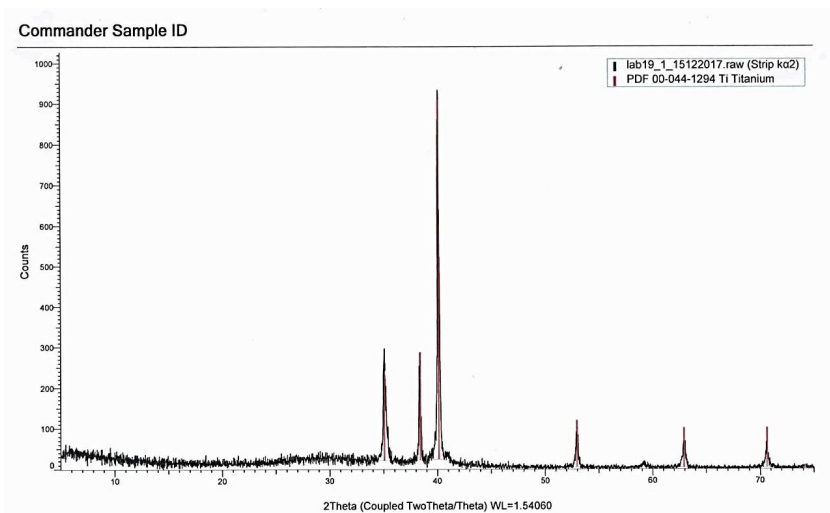of anatase and 4.5 % of rutile obtained from the titanium fraction of titanium-magnetite concentrate

Fig. 7. XRD pattern of titanium powder obtained from the titanium fraction

4. Conclusions

The conditions for the processing of titano-magnetite concentrates for the production of iron powder α-Fe (99 %), anatase and rutile modifications of technical titanium dioxide (99 % TiO_2) were determined. It was found that the reduction reactions in the temperature range of 1143–1198 K are carried out if a mixture of hydrogen and carbon monoxide is added to the natural gas in amount of 15 vol %. It has been established that the magnetite reduction reactions with methane, hydrogen and carbon monoxide are conjugated. Anatase modification of titanium dioxide is obtained only when using the bioactive natural polymer chitosan as a modifier.

Due to the depletion of reserves of rich magnetite ores the current problem of modern metallurgy is the use of less technological types of iron ore, for example, titanium-magnetite ores. The objects of the study were titanium-magnetite concentrates obtained from sandstones of Azerbaijan. At the same time, the revealed physical and chemical patterns and block-diagrams can be used for processing of titanium-magnetite concentrates of other sources for the production of iron, titanium and modifications of titanium dioxide.

Acknowledgements

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ПРИГОТУВАННЯ ТИТАНУ-МАГНІТНИХ КОНЦЕНТРАТІВ ДЛЯ ВИРОБНИЦТВА ЗАЛІЗА, МОДИФИКАЦІЙ ДИОКСИДУ ТИТАНУ І ТИТАНУ

Анотація. Вивчено умови відновлення концентратів титану-магнетиту (основні компоненти Fe 52–54 % та TiO$_2$ 5–7 %) природним газом для одержання порошку заліза та титанової фракції. З використанням теорії гранулювання в барабанному апараті та додаванням 25 % соди отримані гранули з оптимальним діаметром, вологістю, міцністю та пористістю. Встановлено, що в діапазоні температур 1143-1198 К відбуваються реакції відновлення, якщо суміш водню та монооксиду вуглецю додається до природного газу у кількості 15 об %. Приведені блок-діаграми приготування концентратів титану-магнетиту для виробництва порошку заліза α-Fe (чистота 99 %), анатаз- і рутил-модифікацій діоксиду титану (99 % TiO$_2$) та титану з чистотою 99 %.

Ключові слова: *концентрати титану-магнетиту, природний газ, водень, оксид вуглецю, порошок заліза, титан.*