UDC 66.099.2: 552.52

REDUCTION OF THE ADZHINAUR TITANOMAGNETITE CONCENTRATES OF AZERBAIJAN BY NATURAL GAS FOR THE PRODUCTION OF IRON POWDER AND TITANIUM DIOXIDE

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Received 25.12.2017

Based on the theory of granulation of powders in a drum apparatus using 3D modeling, granules with flux additions of 25% soda with optimum size, humidity, strength and porosity were obtained. It has been revealed that, when using such granules, the reduction reactions of titanomagnetite concentrates proceed in the kinetic-diffusion region, are conjugate: in reducing reactions, CO and H₂ are inductors and the CH₄ acceptor. The first two reactions initiate the reduction of magnetite to metal. Using chitosan as a bioactive modifier, anatase modification of titanium dioxide was obtained from powders of polytitanic acid xTiO₂·yH₂O.

**Keywords:** titanomagnetite concentrates, fluxed granules, conjugated reactions, chitosan.

**Introduction**

Titanomagnetites are a mixture of mainly two minerals: ilmenite FeTiO₃ and magnetite Fe₃O₄ with impurities of vanadium and chromium [1–3]. In titanomagnetite ores the following minerals are also present: rutile, anatase, brookite modifications of TiO₂, ilmenorutil FeO(Nb,Ta)₂O₆·5TiO₂, pseudobrookite 2Fe₂O₃·3TiO₂, arizonite Fe₂O₃·3TiO₂. By enrichment of titanomagnetite ores, including titanomagnetite sandstones, titanomagnetite concentrates for processing are obtained. Studies on the technology of processing titanomagnetite concentrates for the production of iron, titanium dioxide (rutile), chromium, and vanadium have been carried out for several decades, are relevant at the present time [4–10]. However, to date, insufficient attention has been paid to the formation of granules of titanomagnetite concentrates, to the reactions of their reduction with natural gas, to the production of anatase modification of titanium dioxide.

The aim of this work is to establish the conditions for the recovery of granules of a titanomagnetite concentrates of Adzhinaur sandstones of Azerbaijan with natural gas for the production of iron powders and anatase.

Depending on the ratio of ore and non-metallic minerals the chemical composition of titanomagnetite sandstones of various deposits varies widely. The objects of this study were titanomagnetite concentrates (the major components Fe – 54%, TiO₂ – 7% with 25% fluxing additives soda), obtained from the procedure Adzhinaur sandstones of Azerbaijan described in [11]. Titanomagnetite concentrates were used in the form of granules of 5–7 mm diameter with a certain humidity, porosity and strength. The conditions for the preparation of granules are determined on the basis of the theory of granulation in a drum apparatus [12]. For XRF recovery products there were used powder X-ray diffractometer D2 Phaser (Bruker).

**Granulation of powders of titanomagnetite concentrates**

If pelletization of concentrates of titanomagnetite Adzhinaur sandstones with fluxing additives previously prepared mixture of the concentrate with 25% of the anhydrous soda, after thorough mixing, was granulated in a laboratory drum pelletizers 15 cm in diameter and 100 cm long. The pellets for reduction reactions prepared from powders (with a diameter 0.1–0.15 mm) of the titanomagnetite concentrate. Used as a binder water 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 has been used Gudrat Kelbaliyev’s system of equations, particularly equation

\[ a(t) = (a_0 + \gamma t)^{1/2} + a_0 \exp(-b_0 t) \sin(\nu t/2). \]  

Here \( \gamma = 2R\omega\lambda/\pi \) (\( \lambda = 2 \sim 2.5 \)), \( a_0 \) – the current size of the granules; \( a_0 \) – average size of the embryo (powder), \( b_0 \) – parameter related to the density of the powdered material particles, \( t \) – granule formation time, \( R \) – radius drum apparatus, \( \lambda \) – the thickness of layering, \( \omega \) – the frequency of the rotation drum apparatus, \( \nu \) – is the characteristic number depending on shear viscosity.

Figures 1 and 2 as a histogram and analytical relationships are shown granule size distribution function and on the length of the drum granulator. However, for the convenience of these curves with the program OriginLab2017 approximated by polynomials.

Experimental and theoretical studies allow us to analyze the nature of the spread and distribution of granules by size and length of the granulator.

![Fig. 1. Histograms for the distribution function \( P(a,L) \) of granules of titanomagnetite concentrate, fluxed with soda, in according to the diameter \( (a, \text{mm}) \) of the granule along the length \( (L) \) of the drum granulator.](image1)

![Fig. 2. The evolution of the distribution function \( P(a,L) \) of granules of titanomagnetite concentrate according to the diameter \( (a, \text{mm}) \) of the granule along the length \( (L) \) of the drum granulator.](image2)
A major factor stabilizing structure of fluxed soda pellets with optimum moisture is its strength and resistance to fracture and deformation by the action of the external loads. Investigation of strength characteristics fluxed with sodium additives, pellet size been 5–6 mm, manufactured from the concentrate particle with size 0.1 mm, has shown their sufficient strength for subsequent recovery of natural gas in the filter bed tubular reactor in the preparation of iron powder. Based on experimental data the following dependence of the granule strength (Δ, kg/cm²) on the granulation time (τ, hours) and granule diameter (a, mm) was obtained:

\[ \Delta = (1.2685582 + 0.3212027 \times 10^{-10} - 4 \tau^2) a^{-1.3}. \]  
(2)

3D visualization of this relationship equation performed by a computer program OriginLab2015.

![3D visualization of equation (2) for the dependence of the granule strength (Δ) on the stabilization time (τ) and the size of granules (a).](image)

It was found that the strength and porosity of fluxed soda pellets with an optimal size (5–6 mm diameter) after 30 hours of exposure are stabilized.

**Thermodynamic and kinetic analyses**

To determine optimal temperature interval for obtaining iron calculated temperature dependence of the Gibbs free energy by the reaction concentrate recovery there was titano-magnetite of granules by natural gas according to equation

\[ \Delta G_T = \Delta H_{298} - T \Delta S_{298} - \Delta c_{p,298} T \left[ \ln \left( \frac{P}{T} \right) \right] + RT \ln K_{P,T}, \]
(3)

where \( \Delta G_T \), \( \Delta H_{298} \) and \( \Delta S_{298} \)– standard free energy, enthalpy and entropy of the reaction. Thermodynamic functions of forming the simple substances and compounds involved in the reactions are taken from reference [13, 14]. \( \Delta c_{p,298} \) – changing the molar isobaric specific heat of substances in the reactions, \( K_{P,T} \) – equilibrium constant for the reaction of gaseous substances. This value has little effect on the value, as in the flow regime of the reactor gaseous reaction products are removed.

The recovery process of granules of a titanomagnetite concentrate with natural gas basically consists of the following reactions:

\begin{align*}
\text{Fe}_3\text{O}_4 + \text{Na}_2\text{CO}_3 & \rightarrow 2\text{NaFeO}_2 + \text{FeO} + \text{CO}_2, \quad (4) \\
\text{FeTiO}_3 + \text{Na}_2\text{CO}_3 & \rightarrow \text{Na}_2\text{TiO}_3 + \text{FeO} + \text{CO}_2, \quad (5) \\
2\text{NaFeO}_2 + \text{H}_2 + \text{CO}_2 & \rightarrow 2\text{FeO} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}, \quad (6) \\
2\text{NaFeO}_2 + \text{CO} & \rightarrow 2\text{FeO} + \text{Na}_2\text{CO}_3, \quad (7) \\
2\text{NaFeO}_2 + 3\text{CO} & \rightarrow 2\text{Fe} + \text{Na}_2\text{CO}_3 + 2\text{CO}_2, \quad (8) \\
\text{Fe}_3\text{O}_4 + \text{CH}_4 & \rightarrow 3\text{FeO} + \text{CO} + 2\text{H}_2, \quad (9) \\
\text{FeO} + \text{CH}_4 & \rightarrow \text{Fe} + \text{CO} + 2\text{H}_2, \quad (10) \\
\text{Fe}_3\text{O}_4 + \text{CH}_4 & \rightarrow 3\text{Fe} + \text{CO}_2 + 2\text{H}_2\text{O}. \quad (11)
\end{align*}

The temperature dependences of the free Gibbs energies of the reactions (4 – 11), calculated from equation (3), are shown in Figure 4.

![The dependences of the free Gibbs energy of the reactions (4–11) on the temperature.](image)
From the Figure 4 it follows that 500–550 K magnetite starts to interact with soda to obtain ferrite (III) sodium (reaction 4). Sodium titanate prepared by the reaction (5) proceeds in a non-magnetic phase. Main reaction of magnetite recovery through wustite at relatively low temperatures proceeds poorly [reactions (9)–(11)]. Reactions equilibrium (9)–(11) is shifted to the right side, only from the 1010 K (ΔG^\text{II}_f<0). At the same time, we found that the reduction reaction with methane from 1010 K occurs when natural gas is added to a mixture of hydrogen and carbon dioxide. Thus to maximize metallization it is sufficient add to the natural gas to 15% by volume of hydrogen and carbon monoxide. This is because the reduction reaction of magnetite by methane, hydrogen and carbon monoxide are conjugated:

\[ \begin{align*}
  \text{Fe}_3\text{O}_4(\text{NaFeO}_2,\text{FeO})+\text{CO}=\text{Fe}+\text{CO}_2 & \quad (12) \\
  \text{Fe}_3\text{O}_4(\text{NaFeO}_2,\text{FeO})+\text{H}_2=\text{Fe}+\text{H}_2\text{O} & \quad (13) \\
  \text{Fe}_3\text{O}_4(\text{NaFeO}_2,\text{FeO})+\text{CH}_4=\text{Fe}+\text{CO}_2+ \\
  +\text{H}_2\text{O} & \quad (14)
\end{align*} \]

In these reactions CO and H2 are inducers CH4 acceptor. The first two reactions initiate recovery of magnetite by methane to metal. Inducing factor \(I=n(\text{CH}_4)/n(\text{H}_2+\text{CO})\geq5\). Revealed that the reduction process proceeds in the diffusion region, which is possible when high. Therefore, it is essential to obtain the desired granules density, strength and porosity to increase rate of penetration of methane molecules in all layers of the granules [24].

**Reduction of titanomagnetite concentrates**

**Receiving of iron powder**

Granules for reduction reactions were prepared from powders (with a diameter of 0.1–0.15 mm) of titaniferous magnetite concentrate. It is revealed that the raw pellet diameter of 4–6 mm, obtained from the concentrate particle size 0.1 mm strong enough on average about 0.5–1 kg/pellet depending on the size. Within 3 hours natural drying due to weathering of excessive moisture, their strength reaches a maximum of 1.2–3 kg/pellet, and thereafter decreases slightly again, is stabilized at a tenacity of about 0.5 kg/pellet (Figure 5).

Fluxed with addition of 25% soda granules 3–7 mm in size were reduced by natural gas in the horizontal tube furnace in the temperature range 850–1000°C. The reactor and the entire system to supply natural gas was purged with nitrogen. Use of the granules ensures a uniform distribution of gas flow within the reactor and permeability of recovered granule eliminates the dust discharge of fine and caking reducible material. Some recovery of fluxed granules titanomagnetite concentrate at variable temperatures and length of recovery are presented in the table. As can be seen in Figure 6 with increasing reduction temperature of iron metallization degree is increased and at 900–925°C maximum metallisation (98.5–98.7%) is observed. With further increase in temperature to 1000°C metallization ratio falls slightly to 94.7%. This is due to the fact that the recovered metallic iron particles on the surface of the pellets stick together, form crust and hinder the diffusion of gas into the pellet to inhibit its complete recovery. These undesirable phenomena are practically absent in the temperature range 875–925°C. With an increase in the duration of the recovery of natural gas at a feed rate of 0.1 l/min and a temperature 9250°C after 20 min, the degree of iron metallization of 98%. With further increase recovery duration until 1 hour metallization ratio of iron is kept at a maximum of 98.8% with 900°C.
However, excessive increase in the process time is not desirable and the optimum duration of the process takes 30 minutes when at optimal temperatures 875–925°C, natural gas velocity 0.1 l/min, the degree of metallization fluxed granules titanomagnetite concentrate reaches 96.5–98%. Reduction products were subjected to wet magnetic separation and divided into two factions: the magnetic and nonmagnetic. Because the magnetic fraction after washing and drying was obtained preconditioned iron powder (Figure 7). Of the non-magnetic fraction after washing, filtration and drying, the titanium extracted fraction for technical dioxide titanium.

![Diagram]

**Fig. 6.** Dependence of the degree of metallization ($\gamma$, %) of fluxed (25% Na$_2$CO$_3$) granules of titanomagnetite concentrate on the reduction temperature ($t$, °C) with natural gas at recovery duration $\tau=30$ min., the natural gas feed rate $V=ll/min$ and the volume of natural gas to restore gone $V=0.6$ m$^3$/kg. ⋄ – experiment; curve is a polynomial $\gamma, \% = 14.933 \cdot 10^{-6}t^3-0.043t^2 + 41.222t-13042$.

![Diagram]

**Fig. 7.** Scheme of anatase production from the titanium fraction.
Obtaining anatase from the titanium fraction

TiO₂ titanium dioxide has three modifications: rutile, anatase and brookite [https://en.wikipedia.org/wiki/Titanium_dioxide]. Rutile is a more stable form and is a densely packed structure of anatase (tetragonal). Anatase is a tetragonal structure and passes into the rutile modification at 915°C. Brookite has an orthorhombic structure and spontaneously converted into rutile at a temperature of about 750°C. Most of the work at the complex processing of titaniferous ores and titanium are rutile [3, 15]. Depending on the content of titanium in the ore phase they employ sulfate and chlorine methods [16, 17], direct leaching [18, 19], recovery and leaching [20, 22], dissolution of rutile [16], oxidizing roasting and fusion [8, 9, 15, 21].

In our work for the leaching of titanium fraction there was used 15% hydrochloric acid (Figure 7). It was found that when processing the titanium solution at 85°C for 1 hour iron ions, calcium and magnesium into solution in the form of chlorides. For desilication of titanium dioxide mixture was treated with a weak solution of sodium hydroxide at the boiling temperature of the solution. Polytitanic acid powder xTiO₂·yH₂O mixed with powder of pure chitosan in a weight ratio of 20:1, and calcined at temperatures up to 850–900°C technical titanium dioxide in a mixture of 94.5% of anatase and rutile 4.5 (Figure 7). Use of chitosan is not random as a modifier. The paper [23] revealed the influence of bioactive natural polymer – chitosan as an organic reagent on forming texture morphology and phase composition of products during hydrothermal treatment of TiO₂ powders.

Summary and Conclusions

Based on experimental data the following dependence of the granule strength (Δ, kg/cm²) on the granulation time (τ, hours) and granule diameter (a, mm) was obtained:

\[ \Delta = (1.2685582 + 0.3212027 \tau - 42.16162710 - 4 \tau^2) a^{1.13}. \]

3D modeling and visualization have been made of optimal conditions of forming granules titanomagnetite fluxed soda concentrates.

To restore fluxed pellets of 4–6 mm in size of titaniferous magnetite concentrate, the following optimal conditions were established with natural gas: \( T = 875+925^°C \), process time \( t = 30 \) min, the natural gas rate – 0.1 l/min, at a flow rate – 0.6 m³/kg. Under these conditions, the degree of metallization fluxed pellets of titaniferous magnetite concentrate reaches 96.5–98.5% without soot formation, clumping and sintering the pellets recovered.

Reduction reaction in the temperature range \( T=875+925^°C \) occurs in the case when natural gas is added to a mixture of hydrogen and carbon monoxide to 15% by volume. This is because the reduction reaction of magnetite and other compounds with methane, hydrogen and carbon monoxide are conjugated. In particular,

\[
\begin{align*}
\text{Fe}_3\text{O}_4 + \text{CO} &= \text{Fe} + \text{CO}_2, \\
\text{Fe}_3\text{O}_4 + \text{H}_2 &= \text{Fe} + \text{H}_2\text{O}, \\
\text{Fe}_3\text{O}_4 + \text{CH}_4 &= 3\text{Fe} + \text{CO}_2 + 2\text{H}_2\text{O}.
\end{align*}
\]

In these reactions CO and H₂ are inducers, CH₄ is an acceptor. The first two reactions initiated methane recovery of magnetite to metal. Inducing factor \( I = n(\text{CH}_4)/n(\text{H}_2 + \text{CO}) \geq 5 \). This factor occurs, if the reduction process proceeds in the kinetic area, what is possible at a high rate of penetration of the molecules into all layers of the granules.

When using bioactive natural polymer chitosan powders during hydrothermal treatment poltitanian acid \( x\text{TiO}_2\cdot y\text{H}_2\text{O} \) at temperatures 850–900°C technical titanium dioxide has been obtained as a mixture of 94.5% anatase and 4.5% rutile.

References


AZƏRBAYCANIN ACİNOHUR TİTANMAQNETİTİ KONSENTRATININ TÖBİİ QAQLA REDÜKSİYASI İLƏ DƏMİR TOZUNUN VƏ TİTAN DIÖZİSDİN ALINMASI

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Töz mətallərinin barabarn aparatinda qranulaşmışların fiziki-kimiyəvi və mexaniki nəzərəyəsindən istifadə edərkə Azərbaycanın Acınohur titanmaqnetiti konsentratlarının optimal tərkibdə, ölçülü və məsəməliyyət maliq qranulaşların alınma şəraitini müəyyən edilməsi və 3D analitik modelloşmaları hazırlanmışdır. Termodinamik və kinetik analizi titanmaqnetit fazasının metanla (aksətor) və konversiya məhşulları karbon monoksidini və hidrojenli (induktor) reduksiyası ilə dəmirin alınması reaksiyalarının qoşulmuş olduğu müəyyən edilmişdir. Bioaktiv xitozan maddindən istifadə edilmək əhəmiyyətli bir texnologiya və titan dioksiden inkiyata məzorafəzən danışdır. 

Açar səçər: titanmaqnetit konsentratlar, fləsiləmiş hissəciklər, reduksiya, əlaqəli reaksiya, xitozan.
ВОССТАНОВЛЕНИЕ АДЖИНАУРСКИХ ТИТАНОМАГНЕТИТОВЫХ КОНЦЕНТРАТОВ АЗЕРБАЙДЖАНА ПРИРОДНЫМ ГАЗОМ ДЛЯ ПОЛУЧЕНИЯ ЖЕЛЕЗНОГО ПОРОШКА И ДИОКСИДА ТИТАНА

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На основе физико-химической и механической теорий гранулирования в барабанном аппарате с использованием 3D-моделирования из порошков титаномагнетитового концентрата Аджинаурских песчаников Азербайджана получены гранулы с оптимальным размером, влажностью, прочностью и пористостью. Было обнаружено, что при использовании таких гранул реакции восстановления титаномагнетитовых концентратов природным газом с получением железного порошка протекают в кинетико-динамической области и являются сопряженными: в реакциях восстановления CO и H₂ – индукторы, а CH₄ – акцептор. Используя хитозан в качестве биоактивного модификатора из порошков политановой кислоты хTiO₂·yH₂O получена анатазная модификация диоксида титана.

Ключевые слова: титаномагнетитовые концентраты, офлюсованные гранулы, сопряженная реакция, хитозан.