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NONEQUILIBRIUM THERMODYNAMICS OF OXIDATIVE RECOVERY REACTIONS VANADIUM CONTAINING TITANOMAGNETITE CONCENTRATES

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***Abstract**: Non-equilibrium and equilibrium thermodynamic conditions of direct reduction of magnetite to free iron and oxidation of vanadium (3) to vanadium (5) in granules fluxed by soda vanadist titanomagnetite concentrates using a mixture of natural gas and hydrogen were determined. To determine temperature dependences of Gibbs free energy of redox reactions, the Temkin-Schwartsman equation was modified with due regard for the Gibbs free energy of formation of magnetite-based substitution solid solutions and the vapor pressure of the components in the flow system where the mixture of methane and hydrogen is continuously fed while gaseous reaction products are removed . 3D modeling of the Gibbs free energy difference of reactions proceeding under equilibrium and non-equilibrium conditions was carried out. On the basis of the free energy of the system deviation from the equilibrium state, it revealed that the greatest effect of reducing the temperature of redox reactions is observed in terms of low values of the reaction products pressure As a result of the thermodynamic analysis, the temperature range of 950-970K was chosen to produce metallic iron and sodium vanadate.*

***Keywords**: thermodynamics, equilibrium and non-equilibrium reactions, titanomagnetite, iron, vanadium.*

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Introduction

Owing to the depletion of rich magnetite ore reserves, the research has been developed on technology of titanium ore processing to produce iron, titanium, chromium and vanadium [1-4]. To determine optimal conditions of oxidation-reduction reactions, thermodynamic calculations are widely used [5-8]. In [5], thermodynamic calculations and experiments showed principal possibility of one-stage processing of ilmenite concentrate for obtaining artificial rutile of commercial quality. In the works [6-8], natural gas was used as a reducing agent in the course of processing of titanium-magnetite concentrates fluxed with soda. In particular, in [6–8], on the basis of the physicochemical theory of granulation in a drum apparatus in line with thermodynamic-kinetic analysis, it was found that the reduction reactions of titanium-magnetite concentrates with natural gas to produce iron powder proceed in the kinetically-diffusion region and are conjugate: in the reactions of reduction of CO and H_2 - inductors, and CH_4 - acceptor.

In [8], the equilibrium thermodynamic conditions for the direct reduction of magnetite to free iron and the oxidation of vanadium oxide (3) to vanadium oxide (4) and vanadium oxide (5) in granules with fluxed soda vanadium titanomagnetite concentrates were determined. The purpose of this work is to determine and model non-equilibrium thermodynamic conditions for the reduction of magnetite to iron and the oxidation of V^{3+} to and V^{5+} in titanium-magnetite concentrates using a mixture of natural gas and hydrogen. Note that a subject of the study are titanomagnetite concentrates, in which the content of the target components is as follows: Fe(total)- 51-54 mass. %, TiO_2 - mass. 5-7% and 1-1.5 mass% V_2O_5 and V_2O_3.

Thermodynamic equations of oxidative reduction reactions. The total oxidation reaction of vanadium oxide (3) to vanadium (5) and the reduction of magnetite to iron has the following form:

$$3Fe_3O_4(s)+V_2O_3(s)+2CH_4(g)+2H_2(g)+Na_2CO_3(l)= \\ 9Fe(s)+2NaVO_3(l)+3CO_2(g)+6H_2O(g) \quad (1)$$

Titanium dioxide TiO_2, not involved in the redox process, is not included in the reaction equation. To determine the temperature dependences of the Gibbs free energy of the reaction (1) in the temperature range 900-1200K, Temkin-Schwartsman equation [9] was used with due regard for thermodynamic functions of the formation of solid solutions and the vapor pressure values of gaseous components:

$$\Delta G_T = \Delta H^0_{298} - \Delta S^0_{298}T - T(\Delta a\left(ln\left(\frac{T}{298}\right) - \frac{298}{T} - 1\right) + \Delta b\left(\frac{T}{2} + \frac{298^2}{2T} - 298\right) +$$

$$\Delta c^*(\frac{T^2}{6} + \frac{298^3}{3T} - \frac{298^2}{2}) + \Delta c(\frac{T^{-2}}{2} + \frac{298^{-1}}{-T} + \frac{298^{-2}}{2}) -$$

$$RT[xlnf(x) + (1-x)\ln(1-x)] + RT\sum \nu_i lnP_i \quad (2)$$

Equation (2) allows for the temperature dependence of the specific heat in the form as follows:

$$C_p = a + bT + c^*T^2 + cT^{-2}$$

ΔG_T ,ΔH^0_{298},ΔS^0_{298}-free energies, standard enthalpies and entropies of the reaction (1);

ν_i – stoichiometric coefficients;

P_i-partial pressures of components in a non-equilibrium state (reaction proceeds in the reactor under the flow regime of the gas mixture).

$RT[xlnf(x) + (1-x)\ln(1-x)]$ – is the free energy of formation of solid solutions due to the replacement of ions V^{3+} in the crystal cell Fe_3O_4 of ions Fe^{3+} accompanied by the formation of solid solutions $xFe_3O_4 + (1-x)V_2O_3 \rightarrow Fe_{3x}V_{2(1-x)}O_{3+x}$,

n- the total number of unlike cations in the solid solution;

The last term $RT\sum \nu_i lnP_i$ of equation (2) allows for the deviation from the standard state. Therefore, the following equation presents the temperature dependence of the standard Gibbs free energy in the equilibrium as follows:

$$\Delta G_T = \Delta H^0_{298} - \Delta S^0_{298}T - T(\Delta a\left(ln\left(\frac{T}{298}\right) - \frac{298}{T} - 1\right) + \Delta b\left(\frac{T}{2} + \frac{298^2}{2T} - 298\right) +$$

$$\Delta c^*(\frac{T^2}{6} + \frac{298^3}{3T} - \frac{298^2}{2}) + \Delta c(\frac{T^{-2}}{2} + \frac{298^{-1}}{-T} + \frac{298^{-2}}{2}) -$$

$$RT[xlnf(x) + (1-x)\ln(1-x)] \quad (3)$$

Thermodynamic parameters of simple substances and compounds involved in the reactions arise from [10]. The following values were used in the calculations: $\Delta H^0_{298}(V_2O_3) = -1218.7\pm2.5$ kJ/mol; $\Delta H^0_{298}(NaVO_3)$=–1148.6±2.5; $\Delta H^0_{298}(Fe_3O_4)$=–1117.2±2.5; $\Delta H^0_{298}(Na_2CO_3)$=–1129.4±2.5; $\Delta H^0_{298}(CH_4)$=–74.8±0.5; $\Delta H^0_{298}(CO_2)$=–393.5±0.5;

$\Delta H^0_{298}(\mathrm{H_2O}, gas)$=–241.8±0.5, $S^0_{298}(V_2O_3) = 98$.32±1.5 J/(mol.K); $S^0_{298}(NaVO_3)$=99.98±1.5; $S^0_{298}(Fe_3O_4)$=146.21±2.5; $S^0_{298}(Na_2CO_3)$=134.97±2; $S^0_{298}(CH_4)$=186.19±2.5; $S^0_{298}(CO_2)$=213.6±0.5; $S^0_{298}(\mathrm{H_2O}, \text{газ})$=188.74±2.5, $S^0_{298}(\mathrm{H_2})$=130.61±1.5, $S^0_{298}(Fe)$=27.15±0.5, $\mathrm{C}^0_{298}(V_2O_3) = 103$.2±0.5J/(mol.K); $\mathrm{C}^0_{298}(NaVO_3)$= 97.6±0.5; $\mathrm{C}^0_{298}(Fe_3O_4)$=150.8±1.0; $\mathrm{C}^0_{298}(Na_2CO_3)$=112.3±1.5; $\mathrm{C}^0_{298}(CH_4)$=35.8±0.5; $\mathrm{C}^0_{298}(CO_2)$=37.1±0.5; $\mathrm{C}^0_{298}(\mathrm{H_2O}, \text{газ})$=33.6±0.5, $\mathrm{C}^0_{298}(\mathrm{H_2})$=28.8±0.5,$\mathrm{C}^0_{298}(Fe)$=25.2±0.5.

In this temperature range the sodium carbonate and sodium metavanadate melt as follows: $T^m(Na_2CO_3)$=1137K, $T^m(NaVO_3)$=963 K. Therefore, when determining the temperature dependence of the Gibbs free energy of the reaction (1) by equation (2, 3), the enthalpy and entropy of melting of these compounds were used:

$\Delta H^m(Na_2CO_3)$=28080 J/mol,
$\Delta H^m(NaVO_3)$=28310 J/mol,
$\Delta S^m(Na_2CO_3)$=24.77 J/(mol.K),
$\Delta S^m(NaVO_3)$=31.38 J/(mol.K).

Results and discussion

Figure 1 presents the results of calculations using equations (2 and 3).

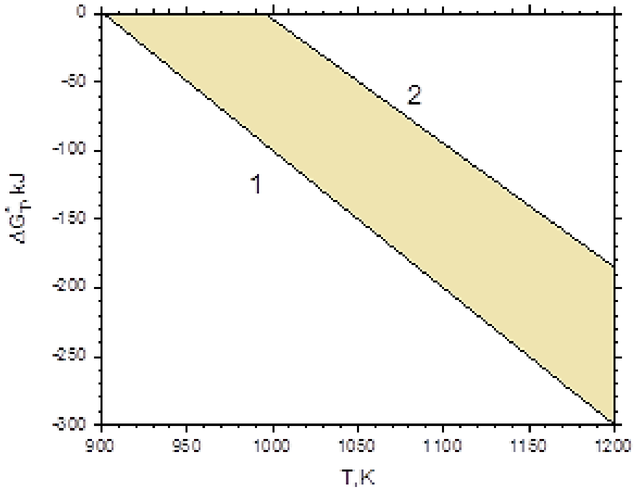

Fig. 1. Temperature dependences of the Gibbs energy of the reaction (1): 1- in the flow mode of the gas mixture (non-equilibrium state, Eq. 2); 2-equilibrium state (Eq. 3).

Fig.1 shows the temperature dependences of the Gibbs free energies of the reaction (1) for both the equilibrium state (line 2, calculation by equation 3) and the non-equilibrium state (line 1, calculation by equation 2). In the reactor, where methane and hydrogen are continuously supplied, the gaseous reaction products are removed, so for the Gibbs free energy we can write:

$$\Delta G^*_T/RT = \left(\Delta G_T - \Delta G^0_T\right)/RT = \textstyle\sum_i^n lnP_i^{\nu_i} \qquad (4)$$

where ΔG^*_T in (4) is a measure of the system deviation from the equilibrium state. In terms of the equilibrium standard state, the total vapor pressure $P_i^{\nu_i}$ is equal to 1 atm. In a non-equilibrium state where gaseous products are removed, this value decreases. In particular, in the reaction (1) in the non-equilibrium state, the quantity $\mathrm{P}^3_{CO_2}\mathrm{P}^6_{\mathrm{H_2O}}/\mathrm{P}^2_{\mathrm{CH_4}}\mathrm{P}^2_{H_2}$ varies from 0.1 (dependence 1 in Fig. 1) to 1 atm. (dependence

2 in Fig. 1). From Fig. 1 it follows that the reaction 1 in the equilibrium state is directed towards the products starting from 1000 K, and under total pressure of 0.1 atm — starting from 900 K.

To identify the nature of dependence on the deviation from the equilibrium state, 3D modeling of the dependence ΔG_T^* (Eq. 4) on the total ratio of partial pressures in the flow-through mode of reducing iron and vanadium with a mixture of methane and hydrogen (Fig. 2) was carried out. For 3D modeling of the ΔG_T^*, an analytical method was used and tested in [11-13].

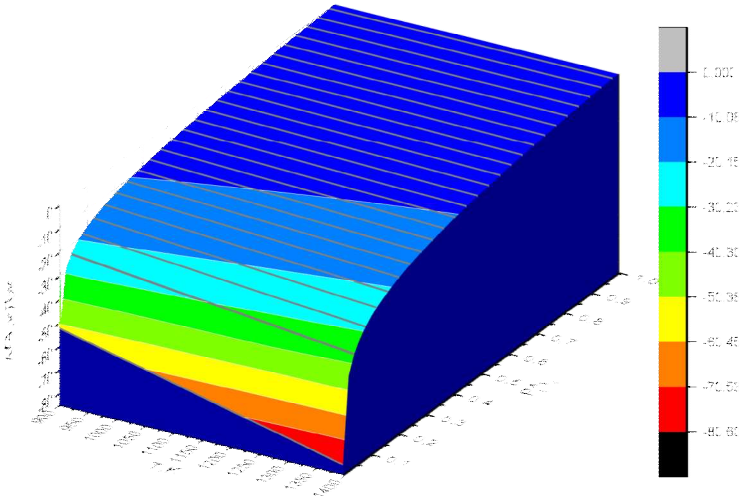

Fig. 2. 3D model of dependence ΔG_T^* (Eq. 4) on the total ratio of partial pressures in the flow mode of methane and hydrogen mixture in the reaction of iron reduction and vanadium oxidation.

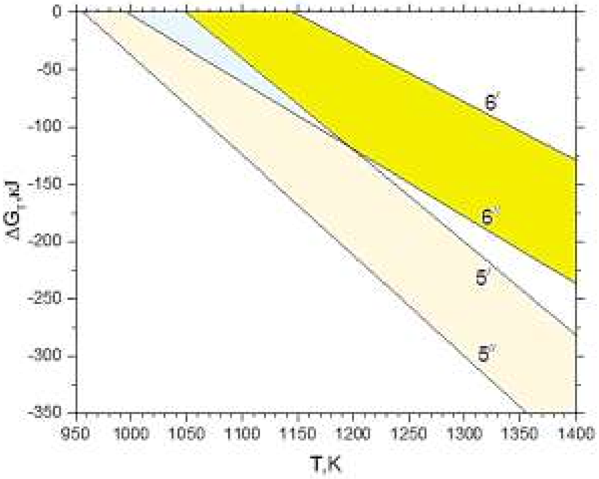

Fig. 3. Temperature dependences of the Gibbs free energies of reactions (5 and 6) at temperature in the equilibrium state (lines $5^{/}$, $6^{/}$, calculation by Eq.3) and non-equilibrium state (lines $5^{//}$, $6^{//}$, calculation by Eq. 2).

In the work [8], for the oxidation of vanadium oxide (3) to vanadium (5) and the reduction of magnetite, only methane was used:

$$4Fe_3O_4(s)+V_2O_3(s)+CH_4(g)+Na_2CO_3(s,l)=$$

$$12FeO(s)+2NaVO_3(s,l)+2CO(g)+2H_2O(g) \qquad (5)$$

$$Fe_3O_4(s)+V_2O_3(s)+CH_4(g)+Na_2CO_3(l)=$$
$$3Fe(s)+2NaVO_3(l)+2CO(g)+2H_2O(g) \quad (6)$$

Temperature dependences of the Gibbs free energy for these reactions are shown in Fig. 3.

From Fig. 1 and 3 it follows that reactions 1, 5, 6 proceed at lower temperatures where gas products of the reaction are removed, and the reactions proceed under non-equilibrium thermodynamic conditions. At the lowest temperature at 900 K, the reaction (1) begins. This is due to the fact that the redox gas phase in addition to methane still contains hydrogen.

Conclusion

In order to determine the equilibrium and non-equilibrium thermodynamic conditions of direct reduction of magnetite to free iron and oxidation of V^{3+} to V^{5+} in granules of vanadist titanomagnetite concentrates with the participation of natural gas, it is necessary to allow for free energies of the formation of solid solutions based on magnetite and the vapor pressure of the components in the flow system when methane is continuously supplied and gaseous reaction products are removed. The 3D model (Fig. 2) of the free energy of the system deviation from the equilibrium state depending on the total ratio of partial pressures in the flow mode of iron reduction and vanadium oxidation shows that the greatest effect of reducing the temperature of redox reactions is observed under low vapor pressure of the reaction products.

Based on the performed thermodynamic analysis, the temperature range 950-970 K was chosen for the implementation of reaction (1,6) in a flow-through mode when a mixture of methane and hydrogen is continuously supplied, and gaseous reaction products are removed. The selected temperature conditions allowed us to successfully solve the problem of obtaining iron and sodium vanadate.

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TƏRKİBİNDƏ VANADİUM OLAN TİTANMAQNETİT KONSENTRATLARININ OKSİDLƏŞMƏ-REDUKSİYA REAKSİYALARININ QEYRİ-TARAZLIQ TERMODİNAMİKASI

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Təbii qaz və hydrogen qarışığından istifadə edərək soda əlavəsi olan vanadium tərkibli titanomaqnetit konsentratlarının qranullarındakı magnetitin sərbəst dəmirə reduksiyasının və vanadiumun (III)-dən vanadium (V) qədər oksidləşməsinin qeyri-tarazlıq və tarazlıq termodinamik şərtləri müəyyən edilmişdir. Redoks reaksiyalarının Gibbs sərbəst enerjisinin temperaturdan asılılığını müəyyən etmək üçün Temkin-Şvartsman tənliyi magnetit əsaslı əvəzedici bərk məhlulların əmələgəlməsinin Gibbs sərbəst enerjisini və axın sistemindəki komponentlərin buxar təzyiqini nəzərə alaraq modifikasiya edilmişdir. Proses zamanı metan və hydrogen qarışığı fasiləsiz olaraq sistemə daxil edilir və qaz reaksiya məhsulları sistemdən çıxarılır. Tarazlıq və qeyri-tarazlıq şəraitində gedən reaksiyaların Gibbs sərbəst enerjilərinin fərqinin 3D modelləşdirilməsi aparılmışdır. Sistemin tarazlıq vəziyyətindən kənara çıxmasının sərbəst enerjisi əsasında, redoks reaksiyalarının temperaturunun azaldılması reaksiya məhsullarının təzyiq parametrinin çox kiçik qiymətləri bölgəsində müşahidə olunur. Termodinamik analiz nəticəsində metal dəmir və natrium vanadatı almaq üçün 950-970K temperature interval seçilmişdir.

Açar sözlər: *termodinamika, tarazlıq və qeyri-tarazlıq reaksiyaları, titanomaqnetit, dəmir, vanadium.*

НЕРАВНОВЕСНАЯ ТЕРМОДИНАМИКА ОКИСЛИТЕЛЬНО-ВОСТАНОВИТЕЛЬНЫХ РЕАКЦИЙ ВАНАДИЙСОДЕРЖАЩИХ ТИТАНОМАГНЕТИТОВЫХ КОНЦЕНТРАТОВ

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Определены неравновесные и равновесные термодинамические условия прямого восстановления магнетита до свободного железа и окисления ванадия (3) до ванадия (5) в гранулах ванадийсодержащих титаномагнетитовых концентратов, офлюсованных содой, с использованием смеси природного газа и водорода. Для определения температурных зависимостей свободной энергии Гиббса окислительно-восстановительных реакций было модифицировано уравнение Темкина-Шварцмана с учетом свободной энергии Гиббса образования твердых растворов замещения на основе магнетита и давления паров компонентов в проточной системе, когда смесь метана и водорода непрерывно подается, а газообразные продукты реакции удаляются. Проведено 3D моделирование разности свободных энергий Гиббса реакций, протекающих в равновесных и неравновесных условиях. На основании свободной энергии отклонения системы от равновесного состояния было выявлено, что наибольший эффект снижения температуры окислительно-восстановительных реакций наблюдается в области низких значений давления продуктов реакции. В результате термодинамического анализа был выбран температурный интервал 950-970 К для получения металлического железа и ванадата натрия.

***Ключевые слова**: термодинамика, равновесные и неравновесные реакции, титаномагнетит, железо, ванадий.*