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THERMODYNAMIC ANALYSIS OF Ti, As-CONTAINING SYSTEMS BASED ON E-pH DIAGRAMS AND PARTIAL PRESSURES

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The removal of arsenic from the technological circulation of metallurgical enterprises is a technologically necessary process, leading from year to year to the formation of new volumes of arsenic-containing objects. One of the forms of extracting arsenic from the production stage is arsenates of various metals, which are difficult and poorly soluble compounds. This approach also does not solve environmental issues in general. Thus, titanium arsenates under storage and burial conditions are subject to hydrolysis, which leads to gradual pollution and poisoning of the environment with arsenic-containing compounds. The practical value of titanium and its compounds in economic activities forces us to look for ways to rationally use arsenic-containing titanium compounds.

The article is the first to carry out a thermodynamic analysis of the behavior of arsenic and titanium based on potential-pH diagrams and partial pressures. The course and directions of chemical reactions in titanium- and arsenic-containing systems, the conditions for the stability of their constituent phases, the thermodynamic parameters of the behavior of the participating components, their compounds, the range of their stability, and the redox processes of the formation of chemical products have been studied.

The regions of existence of titanium arsenate are determined, and chemical and electrode reactions for the production of titanium arsenate from titanium and arsenic compounds are considered. The results of the work confirm both the effectiveness of using titanium compounds to remove arsenic from solutions in the form of poorly soluble manganese arsenate, and the possibility of regenerating titanium in the form of oxides and bases.

Keywords: thermodynamic systems, diagrams, arsenic compounds, titanium compounds, titanium arsenate.

E-pH МЕН ПАРЦИАЛДЫ ҚАСЫМДАР ДИАГРАММАЛАРЫ НЕГІЗІНДЕ Ti, As - ҚҰРАМДЫ ЖҮЙЕЛЕРДІҢ ТЕРМОДИНАМИКАЛЫҚ ТАЛДАУЛЫ

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Металлургиялық кәсіпорындардың технологиялық айналымнан мышьякты шығару бұл өндірістік қажетті процесс болып табылады. Бірақ бұл шара жылдан жылға құрамында мышьяк бар объектілердің жаңа көлемдерінің қалыптасуына әкеледі. Өндіріс сатысынан мышьяк алудың бір түрі нашар және нашар еритін қосылыстар болып табылатын әртүрлі металдардың арсенаттары болып табылады. Бұл тәсіл де жалпы экологиялық мәселелерді шешпейді. Осылайша, титан арсенаттары сақтау және көму жағдайында гидролизге ұшырайды, бұл қоршаған ортаны құрамында мышьяк бар қосылыстармен біртіндеп ластануына әкеледі. Титанның және оның қосылыстарының шаруашылық қызметтегі практикалық маңызы бізді құрамында мышьяк бар титан қосылыстарын ұтымды пайдалану жолдарын іздеуге мәжбүр етеді.

Мақалада потенциал-pH диаграммалары мен парциалды қысымдар негізінде мышьяк пен титанның мінез-құлқына термодинамикалық талдау жасалған бірінші мақала. Құрамында титан және мышьяк бар жүйелердегі химиялық реакциялардың жүруі мен бағыттары, олардың құрамдас фазаларының тұрақтылығының шарттары, қатысушы компоненттердің, олардың қосылыстарының әрекетінің термодинамикалық параметрлері, олардың тұрақтылық диапазоны және тотығу-тотықсыздану процестері. химиялық өнімдердің түзілуі зерттелді.

Титан арсенатының тіршілік ету аймақтары анықталып, титан және мышьяк қосылыстарынан титан арсенатын алудың химиялық және электродтық реакциялары қарастырылады. Жұмыстың нәтижелері нашар еритін марганец арсенаты түріндегі ерітінділерден мышьякты жою үшін титан қосылыстарын қолданудың тиімділігін де, титанды оксидтер мен негіздер түріндегі регенерациялау мүмкіндігін де растайды.

Түйінді сөздер: термодинамикалық жүйелер, диаграммалар, мышьяк қосылыстары, титан қосылыстары, титан арсенаты.

ТЕРМОДИНАМИЧЕСКИЙ АНАЛИЗ Ti, As - СОДЕРЖАЩИХ СИСТЕМ НА ОСНОВЕ ДИАГРАММ E-pH И ПАРЦИАЛЬНЫХ ДАВЛЕНИЙ

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Вывод мышьяка из технологического оборота металлургических предприятий это технологически необходимый процесс, ведущий из года в год к образованию новых объемов мышьяксодержащих объектов. Одной из форм извлечения мышьяка из производственного передела являются арсенаты различных металлов, представляющие собой трудно- и малорастворимые соединения. Такой подход также не решает в целом экологические вопросы. Так арсенаты титана в условиях хранения и захоронения подвержены процессу гидролиза, что ведет к постепенному загрязнению и отравлению окружающей среды мышьяксодержащими соединениями. Практическая ценность титана и его соединений в хозяйственной деятельности заставляет искать пути рационального использования мышьяксодержащих соединений титана.

В статье впервые проведен термодинамический анализ поведения мышьяка и титана на основе диаграмм потенциал-pH и парциальных давлений. Исследованы протекание и направления химических реакций в титан- и мышьяксодержащих системах, условия стабильности составляющих их фаз, термодинамические параметры поведения участвующих компонентов, их соединений, области их устойчивости, окислительно-восстановительные процессы образования химических продуктов.

Определены области существования арсената титана, рассмотрены химические и электродные реакции получения арсената титана из соединений титана и мышьяка. Результаты работы подтверждают как эффективность использования соединений титана для вывода мышьяка из растворов в виде малорастворимого арсената марганца, так и возможность регенерации титана в виде окислов и оснований.

Ключевые слова: термодинамические системы, диаграммы, соединения мышьяка, соединения титана, арсенат титана.

Introduction. Metallurgical enterprises, including producers of non-ferrous metals, are the main sources of environmental pollution with toxic substances. Thus, arsenic in the exhaust gases and wastewater of these enterprises violates environmental stability.

The problem of protecting the environment from industrial pollution in non-ferrous metallurgy is especially acute for copper enterprises, where significant amounts of arsenic are transferred into process gases and waste solutions during the production process. Disposing of arsenic in the form of sparingly soluble compounds does not solve the environmental problem. Due to the accumulation of huge quantities of arsenic-containing waste in dumps and tailings ponds, the issue of their processing into popular products is becoming increasingly important. The scope of application of arsenic-containing compounds is wide and covers such areas as chemotherapy, agriculture, production of alloys, catalysts, dyes and paints, cement and concrete, coating technologies for metals and alloys, wood preservation, synthesis of various compounds and polymers, corrosion protection, semiconductors and other areas [1-2].

Thus, to reduce industrial emissions and reduce the migration of arsenic from tailings, it is necessary to expand the range of arsenic-based products. This requires the development of effective integrated technologies for processing waste arsenic-containing waste into target products. Titanium compounds remain effective arsenic sorbents [3-4] and, if case of their regeneration, their use for purifying solutions from arsenic will be technically advantageous.

Materials and methods. In order to substantiate the physicochemical laws of the process of hydrolytic deposition of arsenic from a copper electrolyte by titanium-containing compounds and its further behavior under equilibrium conditions, a thermodynamic analysis of the Ti-As-H_2O system was carried out by calculating and constructing an E-pH diagram and a partial pressure diagram of the system Ti-O_2-SO_2 -As_2. This technique determines the conditions for the occurrence of chemical reactions in titanium- and arsenic-containing systems, the stability of their constituent phases, the thermodynamics of the possible behavior of the participating components, their compounds, the region of their stability, the chemical nature of the oxidation and reduction products.

When calculating E-pH diagrams, general methods recommended in works [5, 6] were used. The values of $G^0{}_{298}$ were taken from reference data [7-9].

The calculation and construction of partial pressure diagrams is based on well-known methods [5, 10, 11] and generally accepted reference data [7-9].

Results and discussion. For the first time, we calculated and constructed the E-pH diagram of the Ti-As-H_2O system under standard conditions (25ºC and 1 atm total pressure) taking into the particular E-pH diagrams of the As-H_2O and Ti-H_2O systems (Figure 1). Calculations determined for the first time the value of the isobaric-isothermal potential equal to -593,38 kcal/mol for titanium arsenate ($Ti_3(AsO_4)_2$).

All line numbers on the E-pH diagram of the Ti-As-H_2O system strictly correspond to the numbers of the chemical equations given in Table 1.

Analysis of the diagram shows that metallic titanium, Ti^{2+}, Ti^3+, $Ti(OH)_3$ coexist in a reducing atmosphere of titanium compounds and ions. It has been established that in the oxidative region within the pH range of 0-2,19, the main form of arsenic is undissociated H_3AsO_4. The existence of the anionic form of H_2AsO^{4-} corresponds to a pH range from 2,19 to 6,79, $HAsO_4{}^{2-}$ ion - pH values from 6,79 to 11,51, $AsO_4{}^{3-}$ anion - pH values> 11,51. Arsenous acid (H_3AsO_3) is stable in an acidic reducing environment, but with increasing pH it is replaced by $H_2AsO_3{}^-$, $HAsO_3{}^{2-}$, and $AsO_3{}^{3-}$ ions. When the potential values change, arsenous acid is oxidized, resulting in products of H_3AsO_4, $H_2AsO_4{}^-$ or $HAsO_4{}^{2-}$ ions. Under certain conditions, $H_2AsO_3{}^-$ can be oxidized to $HAsO_4{}^{2-}$ and $AsO_4{}^{3-.}$

In the area of water TiO_2, TiO_3, Ti^{3+} are present. TiO_2, TiO_3, $TiO_2{}^{3+}$ are stable in an oxidizing environment.

By interacting with arsine, titanium hydroxide ($Ti(OH)_3$) can form titanium arsenate in a reducing environment.

In an oxidizing environment, arsenic acid and its derivatives also form titanium arsenate with TiO_2 oxide.

Thus, titanium arsenate is stable in a wide pH range from 2 to 14.

The volumetric diagram of partial pressures of the Ti-O_2-SO_2-As_2 system was constructed by us for the first time and is presented in Figure 2. The line numbers on the partial pressure diagram of the Ti-O_2-SO_2-As_2 system correspond to the numbers of the chemical equations presented in Table 2.

At a low partial pressure of oxygen, metallic titanium and titanium oxide (II) interact with gaseous arsenic to form titanium arsenate $Ti_3(AsO_4)_2$, with an increase in the partial pressure of oxygen, and also in the aqueous region, titanium arsenate forms titanium oxide (II). With an increase in the partial pressure of oxygen, the region of existence of titanium arsenate increases by the interaction of gaseous arsenic with titanium (II) oxide TiO_2 and titanium (IV) oxide TiO_2.

Titanium (IV) oxide (TiO_2) is most stable in the reducing region, but it can also exist together with water and some of it goes into an oxidizing environment. Titanium (II) oxide (TiO) is stable in aqueous and oxidizing environments.

Titanium oxides and titanium metal interact with SO_2 gas to form titanium sulfate $Ti(SO_4)_2$. This titanium sulfate is highly stable in both the reducing and aqueous and oxidizing regions and occupies a large area of existence.

Analysis of the partial pressure diagram shows that in the studied system Ti-O_2-SO_2-As_2, titanium arsenate is a stable compound.

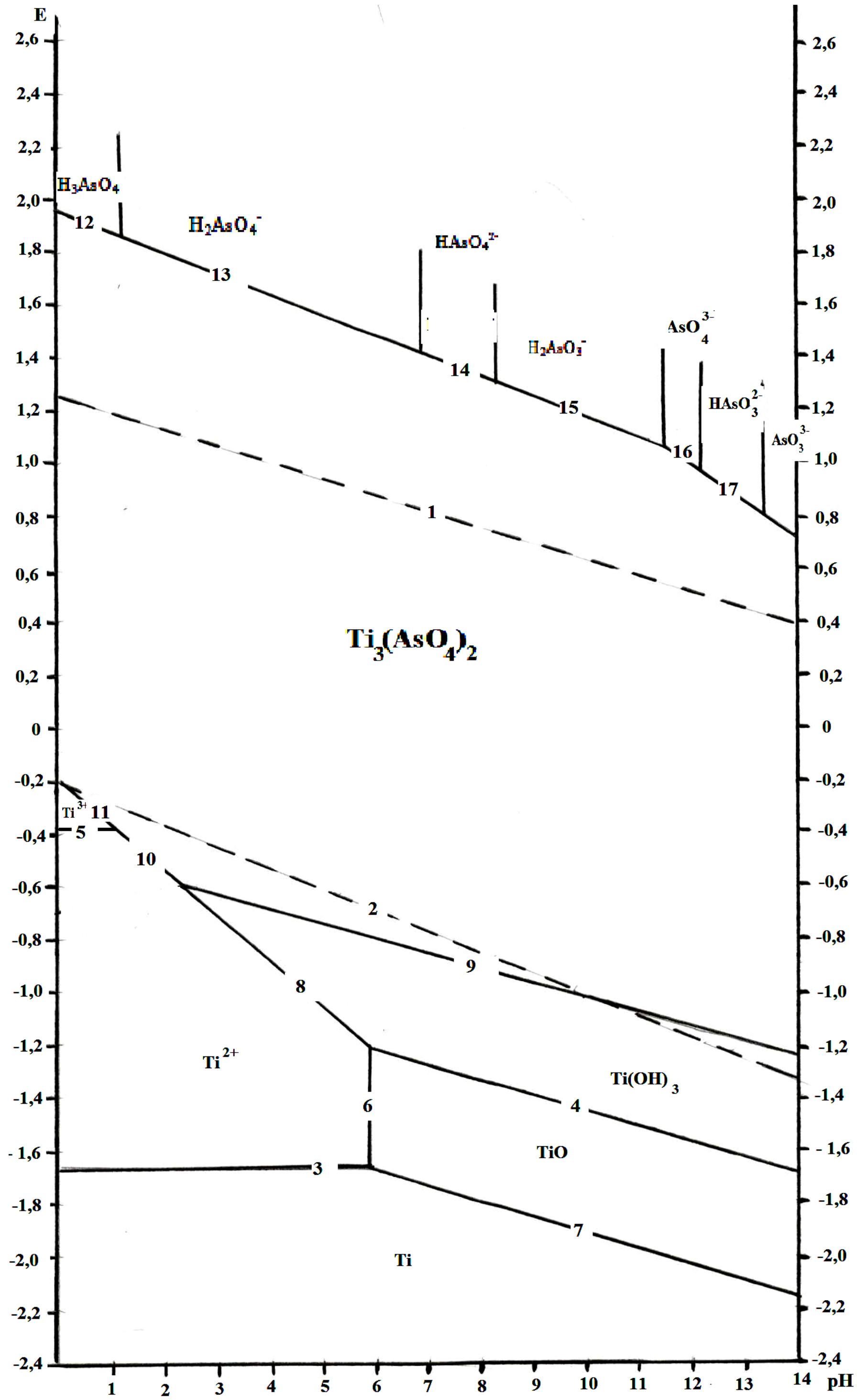

Fig. 1- E-pH diagram of the Ti-As-H_2O system

Table 1 - Reaction equations for the E-pH diagram of the Ti-As-H_2O system

Reaction №	Chemical reaction	Electrode reaction
1	2H2O(ж) = O2(г) + 4H+(ж) + 4e	E = 1,23-0,059 pH
2	H2(г) = 2H+(ж) + 2e	E = -0,059/2 lgH2 – 0,059pH
3	Ti(т) = Ti 2+(ж) + 2e	E = -1,630 + + 0,0295lg[Ti2+]
4	TiO(т) + 2H2O(ж) = Ti (OH)3(т) + H+(ж) + e	E = -0,849 – 0,0591 pH
5	Ti2+(ж) = Ti3+(ж) + e	E = -0,368
6	Ti2+ (ж) + H2O(ж) = TiO(т) + 2H+	lg [Ti2+] = 10,91 – 2pH
7	Ti(т) + H2O(ж) = TiO(т) + 2H+(ж) + 2e	E = -1,306 – 0,0591 pH
8	Ti2+(ж) + 3H2O(ж) = Ti(OH)3(т) + 3H+(ж) + e	E = -0,248 – 0,1773pH – -0,0591 lg [Ti2+]
9	3Ti(OH)3(т) +2AsH3 (г) =Ti3(AsO4)2 (т) +H2O(ж) + +13H+(ж) +13e	E = -0,79 - 0,059 pH
10	3Ti2+(ж) + 2AsH3(г) + 8H2O(ж) =Ti3(AsO4)2(т) + +22H+ (ж) +16e	E = -0,21 - 0,08 pH
11	3Ti3+(ж) + 2AsH3(г) + 8H2O (ж) = Ti3(AsO4)2(т) + +16H+(ж) +7e	E = 0,09 - 0,1349 pH
12	Ti3(AsO4)2(т) + 6H2O(ж) =3TiO2(т) +2H3AsO4(ж) + + 6H+(ж) + 6e	E = 2,36 - 0,059 pH
13	Ti3(AsO4)2(т) +6H2O(ж) =3TiO2(т) +2H2AsO4- (ж) + +8H+(ж) +6e	E = 2,37 - 0,078 pH
14	Ti3(AsO4)2(т) +6H2O(ж) =3TiO2(т) +2HAsO42-(ж) + +10H+(ж) +6e	E = 2,51 - 0,098 pH
15	Ti3(AsO4)2 (т) +4H2O(ж) =3TiO2(т) + 2H2AsO3-+ +4H+(ж) +2e	E = 6,38 - 0,059 pH
16	Ti3(AsO4)2(т)+ 6H2O(ж)= 3TiO2(т) +2AsO43- (ж)+ +12H+(ж) +6e	E = 2,74 - 0,188 pH
17	Ti3(AsO4)2(т) + 4H2O(ж) =3TiO2(т) +2HAsO32-(ж)+ +6H+(ж) +2e	E = 2,57 - 0,059 pH
18	Ti3(AsO4)2(т) + 4H2O(ж) = 3TiO2(т) +2AsO33-(ж) + +8H+ (ж) +2e	E = 2,67 - 0,08 pH
19	H3AsO4 (ж) = H2AsO4- (ж) + H+(ж)	lg[H2AsO4-] = 2,2 – pH; pH = 1,2
20	H2AsO4-(ж) = H2AsO42-(ж) + H+(ж)	lgKp=–pH; pH=6,99
21	H3AsO3(ж) = H2AsO3-(ж) + H(ж) +	lg[H2AsO3-]= 9,25 – pH; pH = 8,25
22	HAsO42(ж) - = AsO43-(ж) + H+(ж)	lgKp=– pH; pH=11,5

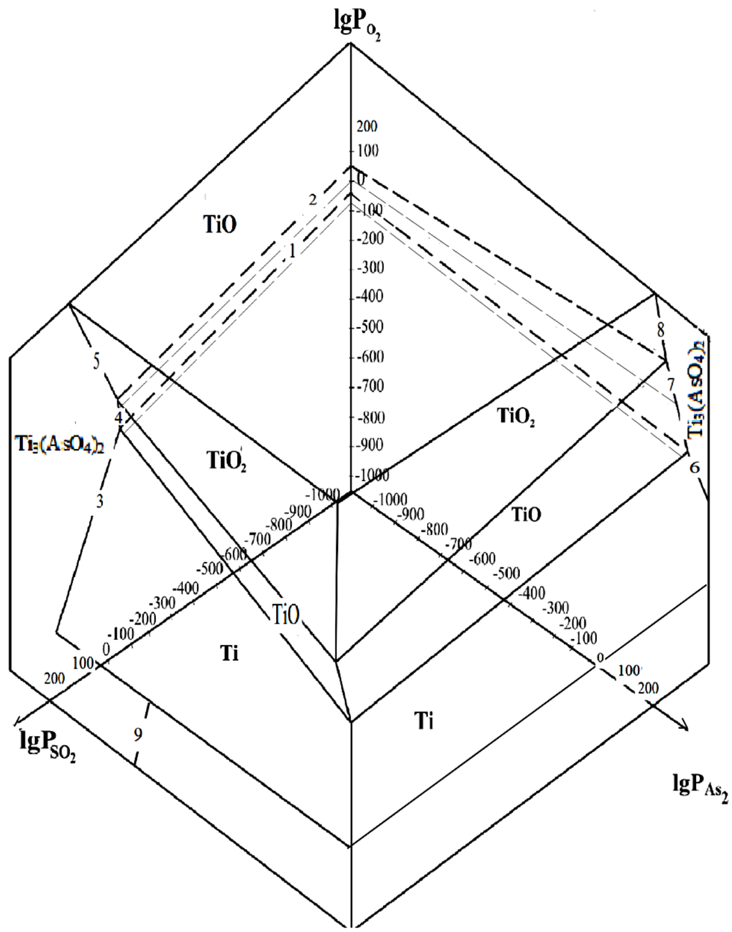

Fig. 2 - Diagram of partial pressures of the system Ti-O_2-SO_2-As_2

Table 2 - Reaction equations for the partial pressure diagram of the system Ti-O_2-SO_2-As_2

Reaction №	Reaction equation	ΔGº, kcal/mol	$lg^{P_{O_2}}$	$lg^{P_{S_2}}$	$lg^{P_{AS_2}}$
1	Ti+O2=TiO2	-79,82	-58,52	-	-
2	TiO2=Ti+0,5O2	-37,07	-54,34	-	-
3	Ti+2SO2+2O2=Ti(SO4)2	-1701,99	-623,89	-623,85	-
4	TiO2+2SO2+O2= Ti(SO4)2	-1614	-1183	-591	-
5	TiO+2SO2+1,5O2= Ti(SO4)2	-1992	-973	-730	-
6	3Ti+As2+4O2= Ti3(SO4)2	-557,44	-102	-	-408,68
7	3TiO + As2 +2,5O2=Ti3(AsO4)2,	-618,69	-181,43	-	-453,58
8	3TiO 2+ As2 +O2=Ti3(AsO4)2,	-389,86	-285,82	-	-285,82
9	3Ti(SO4)2 + As2 =Ti3(AsO4)2 + +6SO2 +2O2	4476,65	-	547	-3282

Conclusions. Based on the analysis of E-pH diagrams and partial pressures of systems involving arsenic and titanium, it was established that titanium arsenate is a stable compound with a wide range of existence, including the stability range of water, hydrogen, and oxygen. This confirms the effectiveness of the process of extracting arsenic from copper-containing acidic solutions using titanium compounds (up to 95%). Thermodynamic analysis of a titanium- and arsenic-containing system provides the basis for experimental work on the regeneration of arsenic deposits in order to obtain titanium oxides.

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