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EFFECT OF THE BROMIDE IONS ON THE TITANIUM ELECTRODE DISSOLUTION POLARIZED BY ALTERNATING CURRENT IN AQUEOUS SOLUTIONS

Abstract. The titanium electrode dissolution possibility polarized by industrial alternating current (AC) with 50 Hz frequency in potassium bromide aqueous solution acidified by sulfuric acid was shown for the first time and the process dissolving titanium were determined. The influence of alternating current density (200-1200 A/m^2), potassium bromide solution concentration (1.0-5.0 M) and sulfuric acid concentration (0.5-4.0 M), AC frequency (25-150 Hz), electrolyte temperature (25-80°C) and electrolysis duration (0.5-2 hours) on the current efficiency (CE) of the titanium dissolution were considered. It was observed extremely low CE (1.8%) of the titanium dissolution by polarization anodic direct current. When titanium was polarized by alternating current, the CE reached 60% at a current density of 200 A/m^2 in the titanium electrode, and as the current density was increased the CE of titanium dissolution was decreased. The titanium dissolution CE showed the maximum value in 0.5 M sulfuric acid and 1.0 M potassium bromide solution. The decrease of titanium electrode CE due to the increase of the electrolysis duration and the AC frequency effect was determined.
Keywords: titanium, alternating current, electrolysis, potassium bromide, sulfuric acid.

Today the application of industrial alternating current frequency of 50 Hz to the electrolysis processes in the field of applied electrochemistry contributes to the new scientific trends development. This method allows conducting electrochemical reactions in solutions, dissolving insoluble metals and activating these processes [1-4].

Titanium and its compounds are light, biologically harmless and resistant to corrosion and environmental impacts. Though this metal is one and a half times heavier than aluminum, two times lighter than iron, it is widely used for the production of aircraft engines, orthopedic implants, construction materials, submarines, electrode and pyrotechnics due to its six times stronger solidity [5-7]. Titanium dioxide has a great deal to contribute to the food industry as an additive labeled E171. Titanium (III) nitride is a unique compound in covering metal surfaces, also known as fake gold, which is resistant to the decays king's water and is much cheaper than gold [8].

Titanium is an element with high melting point that is not soluble in acids by chemical methods. Due to its wide use today, obtaining various compounds through its dissolution is of great importance [9].

Titanium dissolution in hydrochloric acid with fluoride ions and in phosphoric acid solution in the presence of industrial alternating current has been shown in scientific works [10-15]. However, the works do not specify the electrochemical properties of titanium electrode in the bromide aqueous media [16-20]. In this regard, the present work considered the electrochemical dissolution behavior of titanium electrode in bromide aqueous media. In addition, the influence of the main parameters (current density, electrolyte temperature and solution concentration, alternating current frequency, etc.) on electrochemical dissolution process of titanium electrode was investigated.

Results and discussion

The preliminary experiments results showed the insolubility of the two titanium plates in bromide aqueous solutions in the presence of direct current as their surface was covered by a layer of oxide film. However, when the two titanium electrodes were polarized with industrial alternating current, intensive dissolution of the metal was observed.

The current density effect on the titanium electrode dissolution in bromide aqueous solution was investigated (Table 1). The research results showed that the current efficiency reached 60% at a current density of 200 A/m^2 in the titanium electrode, but while the current density was increased the CE of titanium dissolution was decreased. This phenomenon can be explained with the oxide film formation on the titanium surface in the anodic half period of the alternating current at high current densities and these inherent oxide films could lead to passivation of electrode surface.

Table 1 - The influence of Current density on titanium electrodes polarized by alternating current on the CE of their dissolution

[KBr]=1,0 M, $[H_2SO_4]$=0,5 M, τ=0,5 h

i, A/m²	200	400	600	800	1000	1200
CE, %	60	41.6	28.2	22.4	18.3	14.7

The potassium bromide concentration effect in the absence of acid in the neutral medium was investigated to determine the titanium dissolution specificity in bromide aqueous solutions (see Table 2). The results showed the current efficiency decrease of the titanium electrode dissolution from 25% to 8% due to the increase of the potassium bromide concentration in the range of 1.0-5.0 M.

Table 2 - The effect of Potassium bromide concentration on the CE of titanium electrodes dissolution rate polarized by alternating current

i = 200 A/m^2, τ = 0.5 h

[KBr], M	1	2	3	4	5
CE, %	25	17.2	13.4	10	8

Due to the low current efficiency of titanium dissolution in bromide aqueous solutions, it was investigated the titanium dissolution specificity in the presence of sulfuric acid (Table 3). With the increasing sulfuric acid concentration from 0.5M to 2.0 M there was observed dynamically increase of titanium dissolution current efficiency value from 12% to 44%. Further increase of sulfuric acid concentration leads to the current efficiency decrease up to 16%. This phenomenon can be assumed that sulfate ions first interact with the film on the titanium surface and create a favourable condition for the titanium dissolution. Further, the increase of oxygen-containing sulfate ions concentration simplifies the oxide film formation on the titanium surface and allows its passivation.

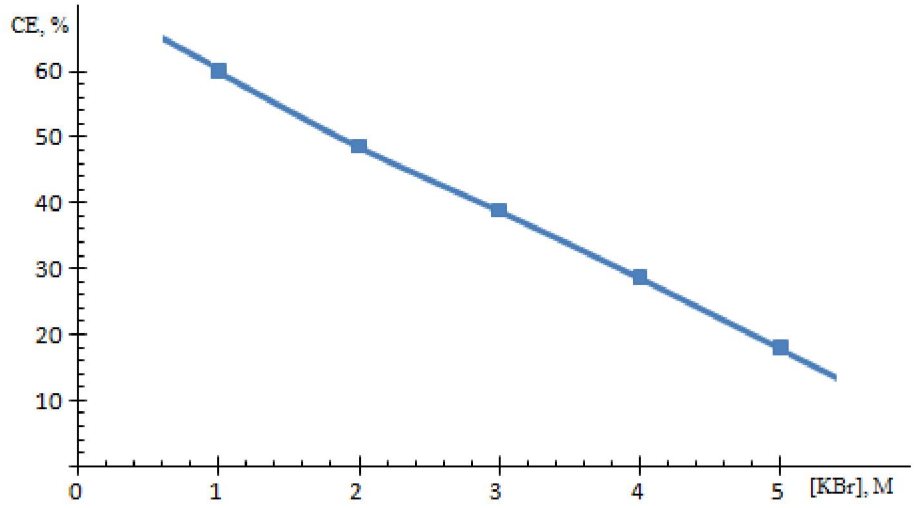
Table 3 - The effect of Sulfuric acid concentration on the CE of titanium electrodes dissolution rate polarized by alternating current

i = 200 A/m^2, τ = 0.5 h

[KBr], M	0.5	1	2	3	4
CE, %	12	24.5	44	29.6	16

As the current efficiency of alternating current polarized titanium electrode did not exceed 44% in sulfuric acid, the potassium bromide solution was acidified with sulfuric acid 0.5 M and the potassium bromide concentration effect on the solution was investigated (Figure 1). The more the potassium bromide concentration was increased, the less the current efficiency decreased. This phenomenon can be explained by the fact that initially when 1.0 M potassium bromide solution acidified with 0.5 M sulfuric acid, these acidified bromide ions created conditon for titanium dissolving, but futher increasing the potassium bromide concentration leads to the increase of bromide ions amount as a result of which the titanium passivation takes place. In this case, as the potassium bromide concentration effect (Table 2) is considered, a straight line decrease of the current efficiency value was observed. However, it should be noted that current efficiency increased by 2.5 times.

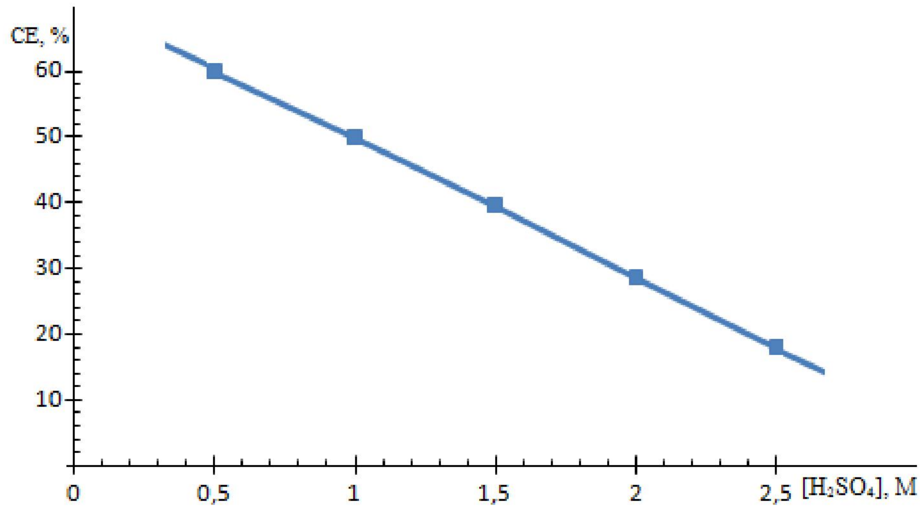
With a view to further increasing the titanium electrode current efficiency, the potassium bromide was acidified with sulfuric acid and the change in its concentration was investigated (Figure 2).



i = 200 A/m^2, [H_2SO_4] = 0.5 M, τ = 0.5 h

Figure 1 - The influence of Potassium bromide concentration on the CE of titanium electrodes dissolution polarized by alternating current

However, if an sharply fluctuate in a peak was observed in the sulfuric acid concentration, a straight line decrease in the titanium current efficiency took place when the potassium bromide solution was acidified with sulfuric acid solution and the sulfuric acid concentration was increased. The titanium electrode current efficiency decreased from 60% up to 18%.



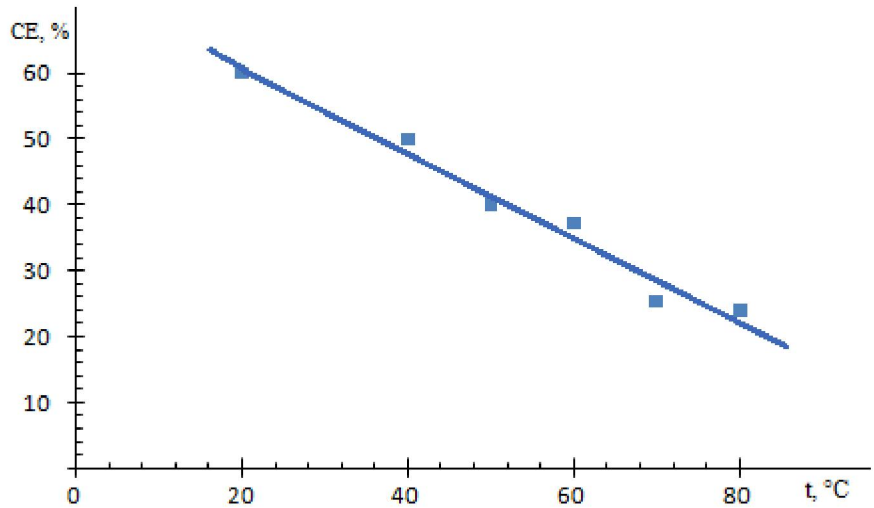
i = 200 A/m^2, [KBr] = 1.0 M, τ = 0.5 h

Figure 2 - The effect of Sulfuric acid concentration on the CE of titanium electrodes dissolution polarized by alternating current

The temperature effect on titanium electrode dissolution in bromide-acid aqueous solutions was considered (Figure 3). Studies have shown the current efficiency decrease of titanium electrode dissolution due to the temperature increase. According to the fundamental principles, the increase of solution temperature should cause the increase of chemical reactions rate. Explaining the abnormal decrease in the titanium electrode dissolution rate due to the temperature increase requires additional studies. It is possible to assume that as the solution temperature increases, the oxide film stability on the titanium surface increases.

The temperature effect on the current efficiency of alternating current polarized titanium electrode was investigated from 25°C up to 80°C. It should be noted that temperature increase lead to downward trend and the titanium current efficiency decreased from 60 to 24%.

Following figure 4 shows the electrolysis duration effect on the current efficiency of alternating current polarized titanium electrode. The current efficiency of titanium electrode decreased from 60% to 20% between 0.5-2.0 hours. As we have seen, as the electrolysis time was increased, the current efficiency firstly increased and then decreased. The bromide ions reacted with the oxide film on the titanium surface and created a complete titanium dissolution. As the time passed, the dissolved titanium slowed down by forming oxide film again on the electrode surface.

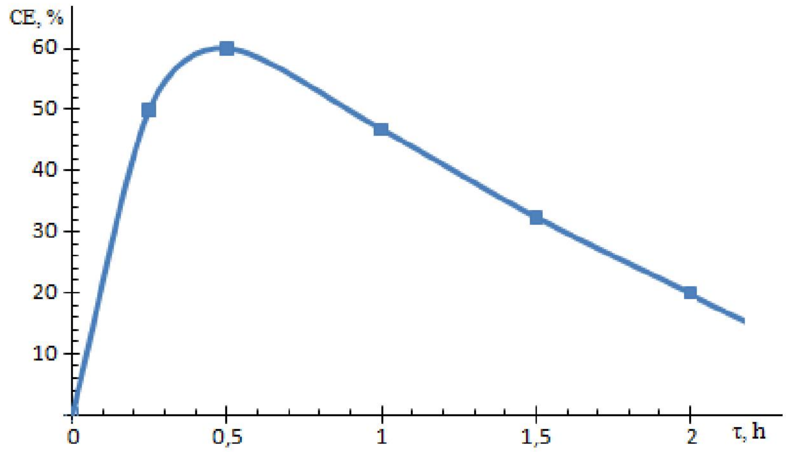


i = 200 A/m^2, [KBr] = 1.0 M, [H_2SO_4] = 0.5 M, τ = 0.5 h

Figure 3 - The influence of temperature in the CE of titanium electrodes dissolution polarized by alternating current

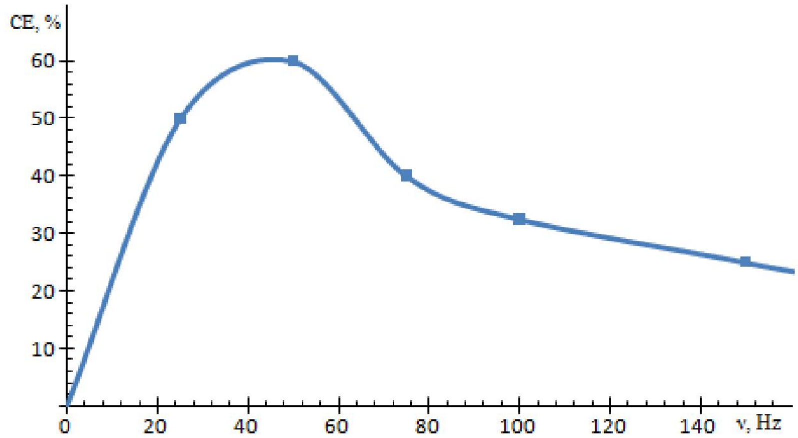
The current frequency effect on the titanium electrode dissolution in bromide-acid aqueous solutions is given in Figure 5. Experimental data have shown that as the current efficiency rate is increased from 25 to 150 Hz, the titanium dissolution current efficiency increases up to 50 Hz and then gradually decreases. This change can be assumed that the more the current frequency increases, the better rational condition is created for the oxygen shell formation on the surface of the alternating current polarized titanium electrode.

The titanium electrode dissolution in bromide-acid aqueous solutions showed a decrease in the current efficiency from 60% to 25% between 50 - 150 Hz.



i = 200 A/m^2, [KBr] = 1.0 M, [H_2SO_4] = 0.5 M

Figure 4 - The effect of electrolysis duration on the CE of titanium electrodes dissolution polarized by alternating current



i = 200 A/m^2, [KBr] = 1.0 M, [H_2SO_4] = 0.5 M, τ = 0.5 h

Figure 5 - The influence of current frequency on current efficiency
of titanium electrodes dissolution polarized by alternating current

In conclusion, titanium electrode dissolution polarized by alternating current in bromide aqueous solutions was shown for the first time. The various parameters influence on the titanium dissolution rate was investigated. It has been found that titanium dissolution current efficiency reached 60% in effective conditions of electrolysis. The results of this study allow dissolving the insoluble titanium electrode in bromide acid solutions and producing technologies for obtaining its various compounds.

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АЙНЫМАЛЫ ТОКПЕН ПОЛЯРИЗАЦИЯЛАНҒАН ТИТАН ЭЛЕКТРОДЫНЫҢ СУЛЫ ЕРІТІНДІЛЕРДЕ ЕРУІНЕ БРОМИД ИОНДАРЫНЫҢ ӘСЕРІ

Аннотация. Ұсынылып отырған жұмыста күкірт қышқылымен қышқылданған калий бромиді ерітіндісінде жиілігі 50 Гц өндірістік айнымалы токпен поляризацияланған титан электродының еритіндігі алғаш рет көрсетілді және еру заңдылықтары анықталды. Титанның еруінің ток бойынша шығымына айнымалы ток тығыздығының (200-1200 А/м^2), калий бромиді ерітіндісі концентрациясының (1,0-5,0 М), күкірт қышқылы концентрациясының (0,5-4,0 М), айнымалы ток жиілігінің (25-150 Гц), ерітінді температурасының (25-80°С), электролиз ұзақтығының (0,5-2 сағат) әсерлері қарастырылды. Тұрақты токпен поляризацияланғанда титанның өте төмен ток бойынша шығыммен еритіндігі байқалды (1,8%). Айнымалы токпен поляризацияланғанда титан электродындағы ток тығыздығы 200 А/м^2 кезінде ток бойынша шығым 60% тең болды да, ток тығыздығын жоғарылатқан сайын оның еруінің ТШ төмендегендігі анықталды. Титан еруінің ток бойынша шығымы 0,5 М күкірт қышқылы және 1,0 М калий бромиді ерітіндісінде максималды мәнді көрсетті. Электролиз ұзақтығының және айнымалы ток жиілігінің әсерін арттырған сайын титан электродының ток бойынша шығымы төмендейтіндігі анықталды.

Түйін сөздер: титан, айнымалы ток, электролиз, калий бромиді, күкірт қышқылы.

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ВЛИЯНИЕ БРОМИД-ИОНОВ НА РАСТВОРЕНИЕ ТИТАНОВЫХ ЭЛЕКТРОДОВ В ВОДНОМ РАСТВОРЕ ПРИ ПОЛЯРИЗАЦИИ ПЕРЕМЕННЫМ ТОКОМ

Аннотация. В данной работе впервые показана возможность растворения титана в сернокислых бромидных растворах при поляризации промышленным переменным током частотой 50 Гц и установлены протекания процесса закономерности растворения титана. Изучено влияние – плотности переменного тока (200-1200 А/м^2), концентрации раствора бромида калия (1,0-5,0 М), концентрации серной кислоты (0,5-4,0 М), частоты переменного тока (25-150 Гц), температуры раствора (25-80 °С) и продолжительности электролиза (0,5-2 часа) на выход по току (ВТ) растворения титана. При поляризации анодным постоянным током наблюдалась низкий ВТ растворения титана (1,8%). А при поляризации титана переменным током, при плотности тока 200 А/м^2 ВТ составил 60 %, а с увеличением плотности тока ВТ растворения титанового электрода уменьшается. Устанавлено, что в растворе, содержащем 1,0 М бромистого калия и 0,5 М серной кислоты наблюдается максимальное значение ВТ растворения титанового электрода. При увеличении продолжительности электролиза и частоты переменного тока ВТ растворения титана уменьшается.

Ключевые слова: титан, переменный ток, электролиз, бромид калия, серная кислота.

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