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ANODIC DISSOLUTION OF TITANIUM IN SULFURIC ACID BROMIDE SOLUTIONS

Abstract. Titanium is inert in many different oxidizing environments, prone to passivation. The metal is chemically insoluble in acids, resistant to corrosion and environmental impacts. In the present work, the dissolution behavior of titanium electrode in the sulfuric acid bromide solution under anodic polarization was shown for the first time and laws of the process were determined. The effects of the anode current density (200-1200 A/m²), potassium bromide solution (1.0-5.0 M) and sulfuric acid concentration (0.5-2.5 M), solution temperature (25-80 °C) and electrolysis duration (0.5-2 hours) on the current output of titanium dissolution were considered. With an increase in the current density at the anodic polarized titanium electrode from 200 A/m² to 600 A/m², the current output (CO) of titanium dissolution increases, and at higher current densities, a decrease in CO of titanium dissolution is observed due to the appearance of an oxide coating on titanium surface. The influence of the Br⁻ ion concentration and the sulfuric acid concentration was studied separately with the aim of systematically studying the effect of the electrolyte nature on the dissolution of titanium. With an increase of the bromide ions concentration, poorly soluble bromide compounds are formed, which leads to a decrease in the CO of the anodic dissolution of titanium. An increase in the concentration of sulfuric acid, i.e. the concentration of hydrogen ions contributes to the dissolution of titanium, the CO of the anodic dissolution of titanium increases. A 1.5 times increase in the CO of titanium was observed upon acidification of an aqueous electrolyte containing Br⁻ ions with 0.5 M sulfuric acid and an increase in the concentration of bromide ions. However, with an increase in the concentration of sulfuric acid in the bromide solution, the CO of the anodic dissolution of titanium increased significantly and reached 70%. The CO of titanium dissolution has a maximum value in a 2.5 M solution of sulfuric acid and in a 1.0 M solution of potassium bromide. The reaction order of the electrode process during electrolysis with sulfuric acid was calculated and it was shown that the reaction proceeds under diffuse conditions. An increase in the duration of electrolysis leads to concentration polarization due to the accumulation of electrolysis products on the electrode surface and slows down the electrochemical dissolution of titanium. The CO of the dissolution of the titanium electrode abnormally decreases with increasing temperature of the electrolyte. The influence of the basic electrochemical parameters on the dissolution of the titanium anode was studied and the optimal conditions for its dissolution were established. It was found that under optimal electrolysis conditions, the current output of dissolution of titanium has a value of more than 70%.

Key words: titanium, electrolysis, current output, anodic dissolution, potassium bromide, sulfuric acid.

In comparison with pure chemical methods, electrochemical methods allow to obtain high quality products in a simple and inexpensive way. In addition, it contributes to the development of new methods for the study and protection of corrosion processes in metals [1]. Also electrochemical methods will give an opportunity to investigate the electrochemical dissolution behavior of Ti alloys in aqueous solutions and explain the unique phenomena during its dissolution [2].

The specific properties of titanium and its alloys, such as lightness and corrosion resistance, have been widely used in all fields from aviation to nuclear production. Titanium is a thermodynamically active metal, but the oxide shell, which is always on its surface, allows this metal to have a stable corrosion resistance [3, 4].
Obtaining compounds of high melting temperature soluble and sparingly soluble metals by the electrochemical methods is one of the topical issues of today [5 - 7].

It is well-known from literature data that titanium electrode in sulfate, chloride, neutral and acid solutions does not dissolve in the anodic polarization. Titanium oxide (TiO_2) appears on the surface of anode polarized titanium electrodes and the current passage through the electrochemical circuit stops [8]. In the studies of A.B. Bayeshov and other scientists, the intensive dissolution of titanium electrode by forming salts in the sulfate, chloride, fluoride acid solutions when polarized with 50 Hz alternating current was shown [9 - 11]. The study investigated electrochemical properties of titanium electrode polarized with industrial alternating current in the media containing fluoride ions and in the phosphorus, hydrochloric, sulfuric acid media and provided optimal conditions for titanium electrode dissolution. The study result determined titanium electrode dissolution with high current output in various acidic environments containing fluoride ions. As a result, it was shown the possibility to obtain titanium salts [12, 13].

In our previous studies, titanium oxidation current was recorded by cyclic polarization curves and an intensive dissolution of titanium electrodes polarized by industrial alternating current of 50 Hz frequency in bromide acidic media was shown [14, 15].

The literature review results showed that the electrochemical properties of titanium electrode in bromide aqueous media were not fully studied [16 - 22].

In the present work, for the first time, we present the study results of the anodic dissolution laws of titanium electrode polarized by the direct current. The effect of the main parameters (current density, solution temperature and electrolyte concentration) on electrochemical dissolution process of titanium electrodes was considered.

Figure 1 describes the current density effect on current output of titanium electrode dissolution polarized by anodic current in sulfuric acid bromide solution. From the study results, it is possible to see an increase of the current output of titanium electrode dissolution from 31% to 55% when the current density was increased in the range from 200 to 1200 A/m², while a slight decrease up to 47% can be observed beginning from 600 A/m². The decrease in the current output of titanium dissolution at a current density of 800-1200 A/m² is due to the formation of oxidized layer on the titanium surface during high current density and the occurrence of the passivation process or additional reactions.

\[ [\text{KBr}] = 1 \text{ M}, [\text{H}_2\text{SO}_4] = 0.5 \text{ M}, t=0.5 \text{ h}. \]

Figure 1 - The current density effect in the titanium electrode on the current output of titanium dissolution polarized by anodic current

The effect of potassium bromide concentration on the dissolution properties of direct current (DC) polarized titanium in bromide aqueous solutions was studied in neutral medium without the presence of acid (Figure 2). The studies result showed that, as the potassium bromide concentration was increased in the range of 1.0-5.0 M, the current output of titanium electrode dissolution decreases from 38% to 10%. This phenomenon is due to a solubility decrease of the titanium bromide formed on the titanium surface.
The following figure shows titanium electrodes used in electrolysis (Figure 3). It is possible to observe the complete insolubility of the cathode polarized electrode and the active dissolution of the anode polarized titanium electrode.

In the following study, the current output of titanium was investigated in the presence of sulfuric acid since the current output of titanium dissolution in bromide aqueous solutions had low value (Figure 4). When the sulfuric acid concentration is increased up to 0.5-2.0 M, the current output value of the titanium dissolution gradually increases from 26.7% to 48%. This phenomenon is due to the interaction of sulfate ions with titanium ions and its creation of a favorable condition for the formation of titanium soluble salt.
It should be noted that the electrolyte color is white-yellow and it forms white loose tissues in the range of 0.5-1.0 M sulfuric acid concentration, while in the range of 1.5-2.5 M the electrolyte color changes to blue purple and a blue colored thick layer appears (Figure 5). The appearance of the white tissue is due to the discharge of hydrogen ions in the cathode and the increase of the electrolyte pH and the hydrolysis of titanium ions, and blue-purple colour shows the formation of titanium (III) sulfate.

The potassium bromide concentration effect was investigated in the solution in which the potassium bromide solution was oxidized with 0.5 M sulfuric acid since the current output of the anode current polarized titanium electrode does not exceed 48% in the sulfuric acid media (Figure 6a). The more the potassium bromide concentration is increased, the less a decrease in current output is observed.

![Figure 5 - Electrolytes that are changed in color as a result of electrolysis: (a) – at the initial stage, (b) – the change by the end of reaction](image)

Initially, 1.0 M potassium bromide and 0.5 M sulfuric acid oxidized bromide ions contributed to better titanium dissolution (CO - 53%), and the weak solubility of the electrolyte due to the increase of the potassium bromide concentration can be explained by the formation of bromide compounds and the passivation of titanium electrode surface.

At this point, as the potassium bromide concentration effect (Figure 6a) was considered, the current output value of titanium dissolution was reduced to a straight line, but it should be noted that in comparison with it the total current output increases 1.5 times.

Figure 6(b) shows the sulfuric acid concentration effect on current output of anode current polarized titanium electrode dissolution in electrolyte containing 1.0 M potassium bromide.

![Figure 6 - Potassium bromide (a) and Sulfuric acid (b) concentration effect on current output of titanium electrode dissolution polarized by anode current](image)

As the hydrogen ions concentration in the solution is increased, a gradual increase of the current output value of titanium dissolution is observed. The increase of the sulfate ions concentration creates a favorable condition for the titanium dissolution. According to this dependence result (Table 1) the reaction rate for bromide ions calculated which was equal to 0.5.
The calculations were made in accordance to the table 1 and the reaction rate was calculated according to the following formula:

\[
h = \frac{n \sum x \cdot y - \sum x \cdot \sum y}{n \sum x^2 - (\sum x)^2} = \frac{5 \cdot (1,65) - (0,57 \cdot 13,858)}{5 \cdot 0,157 - (0,367)^2} = 0,5
\]

This, in turn, indicates that the reaction takes place in a diffusion environment.

The following figure shows the electrolysis duration effect on the current output of titanium electrode dissolution (Fig. 7). As the electrolysis duration increases, the current output decreases; it can be explained by the occurrence of concentration polarization due to the accumulation of electrolysis products on the electrode surface as the electrolysis time increases.

![Figure 7](image)

\[i=600 \text{ A/m}^2, [\text{KBr}]=1,0 \text{ M}, [\text{H}_2\text{SO}_4]=0,5 \text{ M}\]

Figure 7 - The electrolysis duration effect on the current output of titanium electrode dissolution polarized by anodic current

The electrolyte temperature effect on the current output of DC polarized titanium electrode dissolution was considered (Figure 8). When the electrolyte temperature increased, a decrease of the current output from 55.4% to 27.6% was defined. The explanation of this anomalous phenomenon requires additional studies.

![Figure 8](image)

\[i=600 \text{ A/m}^2, [\text{KBr}]=1,0 \text{ M}, [\text{H}_2\text{SO}_4]=0,5 \text{ M}, \tau=0,5 \text{ h}\]

Figure 8 - The electrolyte temperature effect on the current output of titanium electrode dissolution polarized by anodic current
In conclusion, the electrochemical properties of the anode current polarized titanium in the acid bromide solution were investigated for the first time. The increase of the bromide ions concentration leads to a decrease in the current output of titanium anode dissolution, while the increase of the sulfuric acid concentration in the titanium anode dissolution increases the current output of titanium anode dissolution. In optimum conditions, it was shown that the current output of titanium dissolution was above 70%.

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АНОДНОЕ РАСТВОРЕНИЕ ТИТАНА В СЕРНОКИСЛЫХ БРОМИДНЫХ РАСТВОРАХ

Аннотация. Титан отличается инертностью во многих окислительных средах, склонен к пассивации. Металл химически нерастворим в кислотах, устойчив к коррозии и воздействиям окружающей среды. В настоящее время в связи с широкой областью применения раство́рение титан а с получением различных его соединений является очень актуальным. В данной работе впервые показана возможность раство́рения титанового электрода при анодной поляризации в сернокислых бромидных водных растворах и определены закономерности процесса. Рассмотрено влияние плотности анодного тока (200-1200 A/m²), концентрации раствора бромида калия (1,0–5,0 М) и серной кислоты (0,5–2,5 М), температуры раствора (25–80 С),
продолжительности электролиза (0,5–2 часа) на выход по току анодного раствораения титанового электрода. При повышении плотности тока на анондное-поларизованном титановом электролите от 200 А/м² до 600 А/м², выход по току (ВТ) раствораения титана повышается, а при более высоких плотностях тока наблюдалось снижение выхода по току раствораения титана из-за появления оксидного покрытия на поверхности титана. Влияние концентрации иона Бр в концентрации серной кислоты исследовалось отдельно с целью систематического изучения влияния природы электролита на растворение титана. Показано, что с увеличением концентрации бромид-ионов образуются плохо растворимые бромидные соединения, что приводит к уменьшению выхода по току анодного раствораения титана. Установлено, что увеличение концентрации серной кислоты, т.е. концентрации ионов водорода способствует растворению титана, выход по току анодного раствораения титана увеличивается. Увеличение выхода по току титана в 1,5 раза наблюдалось при подкислении водного электролита, содержащего ионы Бр 0,5 М серной кислотой и повышении концентрации бромид-ионов. Однако с увеличением концентрации серной кислоты в растворе брома выход по току анодного раствораения титана значительно увеличился и достиг 70%. Выход по току раствораения титана имеет максимальное значение в 2,5 М растворе серной кислоты и в 1,0 М растворе брома калия. Рассчитан порядок реакции электролитного процесса при электролизе по серной кислоте и показано, что реакция протекает с диморфизм режиме.

Показано, что увеличение продолжительности электролиза приводит к концентрационной поляризации из-за накопления продуктов электролиза на поверхности электрода и замедляет электрохимическое растворение титана. Было обнаружено, что с повышением температуры электролита выход по току раствораения титанового электрода аномально снижается. Изучено влияние основных электрохимических параметров на растворение титанового анода и установлены оптимальные условия его раствораения. Было установлено, что при оптимальных условиях электролиза выход по току раствораения титана имеет значение более 70%.

Ключевые слова: титан, электролиз, выход по току, анодное растворение, бромид калия, серная кислота.

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