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G.N. Zhylysbayeva[1], A.B. Baeshov[2], E.Zh. Tuleshova[1]

[1]Kh.A. Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan;
[2]D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan
(E-mail: elmira.tuleshova@ayu.edu.kz),

Electrochemical behavior of zirconium

In recent years, alternating current has been widely used in various fields of chemical and electrochemical technology. When a symmetric alternating current passes through an electrochemical cell, in principle there should be no visible changes, since the product restored to the cathode half-period should be oxidized back to the anodic half-period. However, depending on the conditions of electrolysis, electrode material, etc. a purposeful course of the electrochemical process is possible. From the point of view of developing methods for the production of pure metal and its various compounds widely used in modern industry, a study on the electrochemical behavior of zirconium is of theoretical and practical interest. The paper shows the distinctive peculiarities of electrochemical processes occurring on a zirconium electrode during electrolysis by an industrial alternating current. Optimal conditions for zirconium dissolution were determined when studying the influence of current density on zirconium and titanium electrodes, the concentration and temperature of the electrolyte, the duration of electrolysis and the frequency of alternating current. The elimination of the passivation process of the zirconium electrode and the increase of the rate of the metal dissolution were shown while the polarization of zirconium by an alternating current in combination with a titanium electrode.

Keywords: electrolysis, zirconium, industrial alternating current, current density, a frequency of alternating current.

Introduction

At present, the electrochemical behavior of metals under alternating current polarization is comprehensively investigated. However, there is no information on obtaining salt of refractory metals, such as zirconium in the literature. As can be seen from preliminary studies, one of the most promising methods for the preparation of zirconium compounds is the dissolution of metallic zirconium wastes by electrochemical means when polarized by alternating current in aqueous solutions.

Electrochemical properties of refractory metals have their own characteristics. Their anodic ionization proceeds by forming a nonmetallic solid phase. In the anodic polarization of refractory metals such as titanium, zirconium, tungsten passes in a passive, transpasive state, or some become metal-ion through the formation of a surface film when the anodic potential in the electrolyte increases [1–6].

Such properties of these metals are due to the electronic and external structure of atoms.

Studies of recent years on the study of electrode processes under the influence of alternating current have shown that under certain conditions some electrochemical reactions proceed with a sufficiently high rate with the formation of the target products [7]. In this regard, a comprehensive study of the electrochemical behavior of zirconium under polarization by alternating current of 50 Hz is perspective.

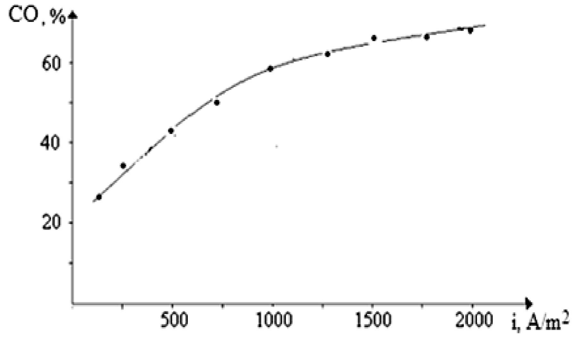
Experimental

The aim of this work was to study the electrochemical behavior of zirconium under polarization by alternating current in nitric acid solution, the effect of various electrolysis parameters and obtaining its salt — zirconium nitrate.

The studies were carried out in a 50 ml glass electrochemical cell; the electrode spaces were not separated. Zirconium plate of 2.5×2.5 size and a titanium wire (grade VT-01) were used as electrodes. The source of the sinusoidal alternating current was power supply V-24 (in simplified form, it is a step-down transformer with a smooth voltage regulation), which had AC terminals. Before the experiment, the electrodes were thoroughly cleaned and rinsed with distilled water. It should be noted that after electrolysis the loss of electrode mass was determined and the current output (CO) of zirconium was calculated for the anode half-period.

The effect of various parameters on the electrolysis process, in particular, the current density at electrodes, the concentration and temperature of electrolyte and the frequency of the current were studied.

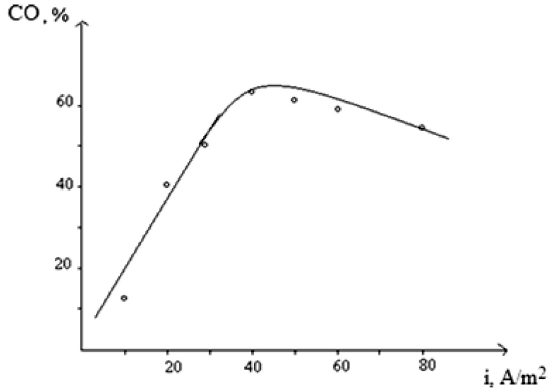
The influence of the current density on the zirconium electrode in the interval of 100–2000 A/m^2 was studied. As the results of the study showed, the current output increases from 26 % to 65 % with increasing current density (Fig. 1).



$C_{\mathrm{HNO_3}}$= 0.5M; τ = 0.5 hour; t = 20 ºC; υ = 50 Hz

Figure 1. Effect of current density on the zirconium electrode on the current output of zirconium dissolution in nitric acid solution

When investigating the effect of the alternating current density on a titanium electrode on the current output (CO) of zirconium dissolution in the range of 10–80 kA/m^2 in nitric acid solution 0.5M at a current density on a zirconium electrode of 2000 A/m^2, the dependence has a curve form passing through the maximum (Fig. 2). The results of the experiments showed that when the current density on the titanium electrode is increased up to 40 kA/m^2, the value of the CO of the zirconium dissolution increases, reaching 65 %. Since the current density is higher than 40 kA/m^2, the CO decreases, since it seems that more friable oxide films which have low semiconductor properties are formed at higher current densities on the titanium electrode. When zirconium is polarized by alternating current in the anodic half-period, zirconium ions (IV) are formed.



$C_{\mathrm{HNO_3}}$= 0.5M; τ = 0.5 hour; t = 20 ºC; υ = 50 Hz

Figure 2. Influence of the alternating current density on a titanium electrode on the current output of the zirconium dissolution in nitric acid solution

As is known, the use of alternating current accelerates the zirconium dissolution process. In the polarization of zirconium by alternating current in nitric acid solution, zirconium ions (IV) form salt by interacting with nitrate ions.

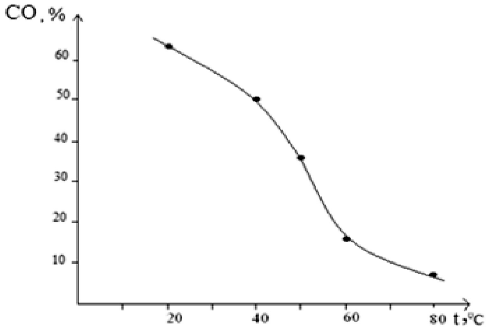
An increase of the concentration of nitric acid from 0.25 to 1.0M leads to an increase in the current output and a further increase of the concentration to 3.0M leads to a decrease in the current output of dissolution of the electrode under the study (see Table). The CO of the zirconium dissolution in nitric acid concentration of 5 mol/l is 41 %. An increase in the concentration of nitric acid leads to a decrease in electrical conductivity, which in turn reduces the CO. In addition, intense oxygen evolution is observed and the surface of the zirconium electrode is passivated with an increase of nitrate ions in the anode half-period.

Table

Influence of the nitric acid concentration on the current output of the zirconium dissolution
(i_{Zr} = 2000 А/м^2; i_{Ti} = 40кА/м^2; τ = 30 min; t =20 °C; υ = 50 Hz)

C, M	0.25	0.5	1.0	1.5	2.0	2.5	3.0
CO, %	37	63	82	78	74	72	70

The calculated reaction order is 1.24. It means that the reaction of the zirconium dissolution is first-order. The known regularities in the course of chemical reactions involve an increase in the rate of the reaction, however in our experiments it has been established that as the temperature rises (Fig. 3), a decrease in the current output on the dissolution of the zirconium electrode is observed. If the CO is 63 % at t = 20 ºC, then it is 10 % at 80 ºC. As the temperature rises, the mobility of ions decreases, which leads to a decrease in the current output. Optimal conditions for electrolysis: C_{HNO_3}= 0.5M, i_{Zr} = 2000 A/m^2; τ = 0.5 hour.

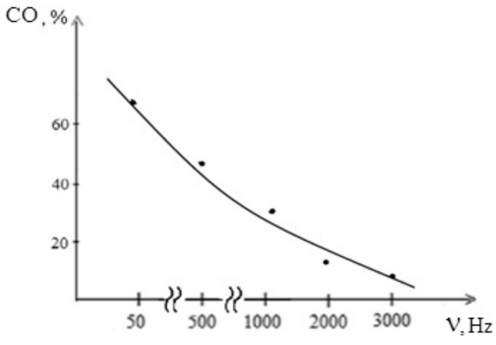


i_{Zr}= 2000 А/м^2; i_{Ti}=40 кА/м^2; τ = 0.5 hour; C_{HNO_3}= 0.5M; υ = 50 Hz

Figure 3. Influence of the electrolyte temperature on the current output of the zirconium dissolution in nitric acid solution

The dependence of the current output of the zirconium dissolution under the polarization by alternating current on the duration of electrolysis shows that with an increase in the time from 0.25 to 1.5 hours, the CO decreases. If the CO is 62 % at 0.25 h, then at 1.5 h it reaches 20 %. The decrease in the CO in prolonged experiments is due to the formation of an oxide on the surface of the electrode, resulting in partial screening of the electrode and inhibition of the dissolution process.

One of the main parameters of electrolysis is the frequency of alternating current. In this regard, the influence of the frequency of alternating current on the zirconium dissolution in nitric acid solution was studied (Fig. 4). It was found that the highest value of the CO on the zirconium dissolution is observed at a frequency of 50 Hz. An increase in the frequency of alternating current from 50 to 3000 Hz at a current density on zirconium electrode 2000 A / m^2 and titanium electrode kA/m^2 leads to a decrease in the current output of the zirconium dissolution from 64 % to 5 %.



i_{Zr}= 2000 А/м^2; i_{Ti}=40кА/м^2; τ = 0,5 hour; C_{HNO_3}= 0.5M; t =20 ºC

Figure 4. Influence of the alternating current frequency on the current output of the zirconium dissolution in nitric acid solution

Apparently, at a high current frequency, the required duration of the anode half-period is not ensured for the dissolution reaction to proceed. This decrease is also associated with a decrease in the magnitude of the average amplitude of the alternating current with increasing frequency, which leads to a decrease in the polarization of electrodes. At this point, hydrogen ions are involved in the electrode process. In the cathode half-period, hydrogen ions are reduced to an active atomic state and in the anodic half- period they are back oxidized to hydrogen ions.

Conclusions

Thus, for the first time, we have studied the electrochemical behavior of zirconium under polarization by alternating current. The effect of various parameters of the electrolysis of the current density, the concentration and temperature of the electrolyte, the duration of electrolysis and the frequency of the alternating current on the current output zirconium dissolution have been studied. Optimal conditions for the zirconium dissolution have been determined. It was established that zirconium nitrate is formed when zirconium is polarized by the alternating current, which allows to develop optimal methods for obtaining zirconium nitrate.

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Г.Н. Жылысбаева, А.Б. Баешов, Э.Ж. Тулешова

Цирконийдің электрохимиялық қасиеті

Соңғы жылдары айнымалы ток әртүрлі химиялық және электрохимиялық технология салаларында кеңінен қолдануда. Симметриялы айнымалы токты электрохимиялық ұяшықтан өткізген кезде негізінен ешқандай өзгерістер орын алмауы керек, себебі катодты жартылай периодта тотықсызданған өнім анодты жартылай периодта кері тотығуы тиіс. Алайда электролиз жағдайына электрод материалына және тағы басқа жағдайларға байланысты мақсатты электрхимиялық процесс жүруі мүмкін. Теориялық және практикалық тұрғыдан цирконийдің электрохимиялық қасиеттерін зерттеу қазіргі заманғы өнеркәсіпте кеңінен қолданатын таза металл және оның қосылыстарын алуда қызығушылық туындайды. Мақалада айнымалы токпен поляризацияланған цирконий электродында жүретін электрохимиялық үрдістердің ерекшеліктері көрсетілген. Цирконий және титан электродтарындағы ток тығыздығының, электролит концентрациясы мен температурасының, электролиз ұзақтығының және айнымалы ток жиілігінің әсерлерін зерттегенде айнымалы токпен поляризацияланған цирконийдің еруінің оңтайлы жағдайлары анықталды. Титан электродымен жұптасқанда цирконий электродында пассивтену процесі жойылып, металдың еру жылдамдығы артатындығы белгілі болды.

Кілт сөздер: электролиз, цирконий, өндірістік айнымалы ток, ток тығыздығы, айнымалы ток жиілігі, электрхимиялық процесс.

Г.Н. Жылысбаева, А.Б. Баешов, Э.Ж. Тулешова

Электрохимическое поведение циркония

В последние годы переменный ток находит все более широкое применение в различных областях химической и электрохимической технологии. При пропускании через электрохимическую ячейку симметричного переменного тока в принципе никаких видимых изменений произойти не должно, так как восстановленный в катодный полупериод продукт должен обратно окисляться в анодный полупериод. Однако, в зависимости от условий электролиза, материала электрода и т.д., возможно целенаправленное протекание электрохимического процесса. Исследование электрохимического поведения циркония представляет и теоретический, и практический интерес, с точки зрения разработки методов получения чистого металла и различных его соединений, широко применяемых в современной промышленности. В работе показаны отличительные особенности электрохимических процессов, протекающих на циркониевом электроде при электролизе промышленным переменным током. Определены оптимальные условия растворения циркония при исследовании влияния плотности тока на циркониевом и титановом электродах, концентрации и температуры электролита, продолжительности электролиза и частоты переменного тока. Показано, что при поляризации переменным током циркония в паре с титановым электродом устраняется процесс пассивации циркониевого электрода, и скорость растворения металла возрастает.

Ключевые слова: электролиз, цирконий, промышленный переменный ток, плотность тока, частота переменного тока, электрохимический процесс.

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