Eurasian Chemico-Technological Journal 16 (2014) 287-291

Corrosion of Indium in Chloride and Sulfate Electrolytes

G. Rakhymbay[1*], M.K. Nauryzbayev[1], B.D. Burkitbayeva[1],
A.M. Argimbaeva[1], A.P. Kurbatov[1], F. Vacandio[2]

[1]Al-Farabi Kazakh National University, 71 al-Faraby Ave., Almaty, Kazakhstan,
[2] Aix-Marseille University, CNRS, MADIREL UMR 7246, 13397 Marseille cedex 20, France

Abstract

When the electrochemical purification of rough indium is used as sulfate, and chloride electrolytes. Significant differences in the values of the stationary potential indium electrode in the above solutions weren't observed.

The corrosion behavior of rough indium in chloride and sulfate electrolytes with potentiodynamic method was studied. For determining the influence of the electrolyte composition obtained corrosive diagram for solution: sodium chloride; sodium chloride containing indium chloride (III); indium chloride (III); sulfuric acid; sulfuric acid containing sulfate indium (III). Experimental results allowed to determine the composition of the electrolyte, characterized by a high rate of dissolution of indium. It was found that dissolution of the indium occurs at high velocity in the indium-containing electrolytes and at higher temperatures. For electrolytes containing indium with pH = 4 was observed increase dissolution rate of indium anode with increasing temperature, indicating that the limitation of the process electrochemical stage and the beginning of the formation of indium hydroxide. Research results can be used in the electrochemical refining of rough indium.

Introduction

Indium, an element of Group IIIA, is an important strategic metal, widely used in high-tech industries.

Semiconductor and optoelectronic characteristics of indium, used in the manufacture of liquid crystal displays, semiconductors and infrared photodetectors. [1-5].

Practical application of indium requires its high purity [6]. One of the objectives during the development of electrochemical refining of indium is to study the process of dissolution of rough indium. In this regard, this paper investigates the corrosion behavior of indium anode. Anodic behavior of indium electrode was considered in studies researching corrosion inhibition of indium and its alloys, as well as the oxidation of indium tin oxide films in hydrochloric acid [7-9].

The mechanism of the corrosion behavior of multivalent metal according to work [10] has a stepwise character and is accompanied by the formation of unstable intermediate low valence compounds.

$$M \rightarrow M^{+} + e \tag{1}$$

$$M^{+} \rightarrow M^{n+} + (n-1)e \tag{2}$$

Electrochemical oxidation of metal is complicated by chemical reactions with components of the electrolyte (hydrogen and oxygen).

$$M^{+} + (n-1)O_x \rightarrow M^{n+} + (n-1)O_x^{-} \tag{3}$$

Chemical oxidation of low-valence metal ions does not require transfer of charge at the metal-solution interface, leading to an increase in the general corrosion rate as compared with that corresponding to the electrochemical mechanism.

Therefore, the mechanism of the corrosion behavior of the metal is electrochemically-chemical and has stepwise character.

Cathodic reaction can be represented by the reaction:

$$O_x + e \rightarrow O_x^{-} \tag{4}$$

---

* Corresponding author. E-mail: gulmirarahymbay@gmail.com

M^+ ions formed diffuse into the volume of solution with a velocity

$$\upsilon_3 = (\Delta/\delta)(M^+)_s \tag{5}$$

In the absence of an external polarization the sum of the rates of anodic reactions (1) and (2) becomes equal to the rate of the cathodic reaction (4).

Under static conditions, the rate of M^+ ions formation, corresponding to the rate of corrosion of metal, is the sum of the rate of electrochemical (υ_1), chemical (υ_2) stages and the rate of diffusion (υ_3).

$$\upsilon = \upsilon_1 + \upsilon_2 + \upsilon_3 \tag{6}$$

Investigation of the corrosion behavior of indium showed that its dissolution proceeds by the above described EC-mechanism. In acidic solutions, the dissolution of indium occurs stepwise by the formation of unstable intermediates - In^+ ions:

$$In \rightarrow In^+ + e \tag{7}$$

$$In^+ \rightarrow In^{3+} + 2e \tag{8}$$

In addition to oxidation reactions, reduction of hydrogen ions proceeds

$$In^+ + 2H^+ \rightarrow In^{3+} + H_2 \tag{9}$$

It was established that the presence of chloride ions in the acidic medium leads to an increase in rate of formation of higher oxidation state of indium (In^{3+}). This apparently explains a marked increase in the rate of corrosion of indium in acidic chloride containing solutions [10].

The proposed mechanism of corrosion of indium explains the electrochemical behavior of indium anode in our used electrolytes. Addition of indium salts to the electrolyte leads to greater increase of the oxidation indium rate, compared with chloride solutions. The results of this work can be used for the electrochemical refining of rough indium.

Experimental

Corrosion behavior of indium in this work was studied in solutions of the following composition:

Chloride medium
NaCl (pH = 1; 4; 10)
$InCl_3$ 0.1 M (pH = 4)
NaCl + 0.1 M $InCl_3$ (pH = 2; 4; 10)

Sulfate medium
H_2SO_4 (pH = 1)
$In_2(SO_4)_3 + H_2SO_4$ (pH = 1)

Changing the pH of the solutions was carried out by addition of HCl or NaOH for chloride electrolyte and H_2SO_4 for sulfate electrolyte. Reagents used were of purity 99.99%-99.999%. An electrochemical cell consisting of rough indium anode, a platinum cathode and silver/silver chloride reference electrode (0.222 B) was used to carry out the study. All voltages are calculated and presented with respect to the SHE. The anode is made of rough indium of following composition (%): In-99.98; Fe-0.0010; Cd-0.0010; Cu-0.0010; As-0.00010; Ni-0.00050; Sn-0.0010; Hg-0.0010; Pb-0.0010; Tl-0.0010; Zn-0.0030. Potential of the working electrode ranges from (-0.5) V to (-1.1) V. The working electrode was a rectangular indium rod molded into teflon (S = 0.9 cm^2) and disposed parallel to the cathode.

Indium electrode surface preparation was carried out mechanically using emery papers and rinse with distilled water before each measurement. According to ISO-6344, used emery papers corresponds to the P400 make. After completion of a series of experiments a platinum electrode was immersed in the solution of nitric acid.

Varying the following parameters was carried out during the experiment: current density, electrolyte composition, temperature and pH. When establishing the polarization curves, scan rate was 0.2 mV/s. In order to determine the stationary potential of indium electrode in different electrolytes, dependence of tested electrode potential on time was obtained. Potentiodynamic measurements were performed in different solutions to find the rate of corrosion of indium electrode, what made it possible to determine the dissolution current of indium and corrosion potential. Faraday's law was used to calculate the corrosion rate (Eq. 10)

$$\Delta e = \frac{j_{corr} t M}{nF\rho} = \frac{365 \cdot 24 \cdot 3600 \cdot 114{,}8}{3 \cdot 96500 \cdot 7{,}31} \cdot j_{corr} = 1710{,}73 \cdot j_{corr} (cm/year) \tag{10}$$

where j_{corr} is a corrosion current, t the time, M molar mass of indium, n the number of electrons involved, F Faraday's constant (≈ 96500 C/mol), ρ the density of indium.

Results and Discussion

Experiments on measurement of the potential of indium over time in different electrolyte systems were carried out to define the scope of the corrosion potential of indium electrode (Fig. 1). Corrosion potential value for indium in solutions of sodium chloride, indium chloride and sodium chloride solutions containing $InCl_3$, are in the range of (-440 mV) – (-550 mV) vs SHE. There is a strong shift of the stationary potential to the cathode region (-1000 mV) in the electrolyte consisting of sodium chloride and indium chloride at pH 11, which is explained by the formation of indium hydroxide precipitated on the electrode surface.

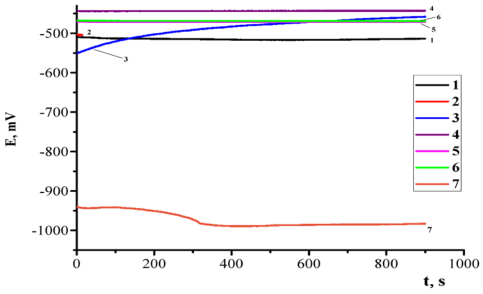

Fig. 1. Potential of indium electrode corrosion in chloride solutions, (1 – NaCl, pH =1; 2 – NaCl, pH = 4; 3 – NaCl, pH = 10; 4 – $InCl_3$, pH = 3; 5 – $InCl_3$ + NaCl, pH = 2; 6 – $InCl_3$ + NaCl, pH = 4; 7 – $InCl_3$ + NaCl, pH = 11).

The above experiments were also carried out in sulfate medium (Fig. 2). Replacing chloride electrolyte by sulphate hardly changes the stationary potential of indium electrode.

Shift of the stationary potential of indium electrode in electrolytes of different composition and pH can be calculated from the Nernst equation. The values obtained are consistent with the experimental results.

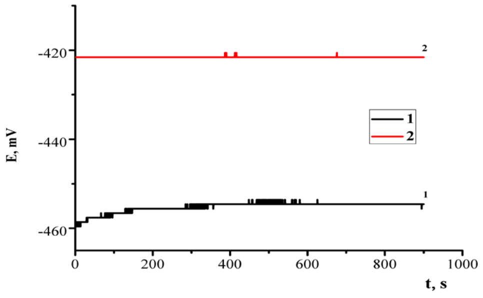

Fig. 2. Potential of indium electrode in sulfate solutions, (1 – H_2SO_4, pH = 1; 2 – H_2SO_4 + $In_2(SO_4)_3$, pH = 1).

To determine the rate of corrosion of indium electrode in selected electrolytes we used the potentiodynamic method (Figs. 3 and 4). Potentiodynamic method is most commonly used to study the corrosion of metals, and allows to observe the corrosion behavior of metall and determine the corrosion current density, which is proportional to the rate of metal corrosion, by extrapolation of the linear part of the Tafel slope to the value of the corrosion potential in the polarization curve. Corrosion currents that characterize the corrosion rate of indium electrode were determined from the experimental potentiodynamic measurement (Table 1). The dissolution rate of indium in chloride and sulfate electrolytes has a maximum value in sodium chloride solutions containing indium chloride, which causes a shift of the corrosion potential of indium to the anode region. At cathodic branch of the polarization curve for solutions containing In^{3+} ions the presence of the limited current is clearly obvious corresponding to the reduction of indium ions. In the absence of indium cathode branch currents are caused by protons reduction reaction.

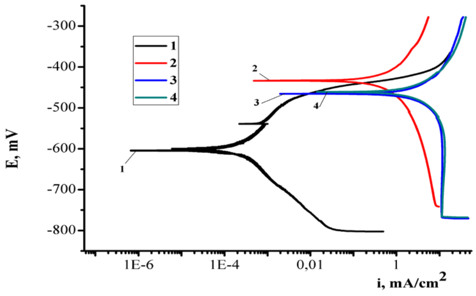

Fig. 3. Potentiodynamic polarization curves of indium electrode in chloride solutions, (1 – NaCl, pH = 4; 2 – $InCl_3$, pH = 3; 3 – $InCl_3$ + NaCl, pH = 2; 4 – $InCl_3$ + NaCl, pH = 4).

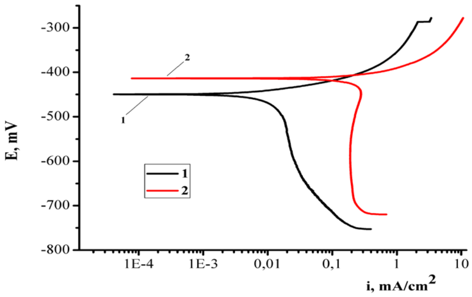

Fig. 4. Potentiodynamic polarization curves of indium electrode in solutions containing sulphate ions, (1 – H_2SO_4, pH = 1; 2 – H_2SO_4 + $In_2(SO_4)_3$, pH = 1).

Analysis of the experimental data shows the effect of indium ions in the background electrolyte on the corrosion processes. Increase in the dissolution currents of rough indium indicates a synergistic effect of indium ions presented in the background electrolyte.

Table 1
Results of potentiodynamic measurements

	Ba, mV	Bc, mV	I_{corr}, mA/cm^2	E_{corr}, mV vs. SHE	v_{corr} cm/year
NaCl, pH = 1	245.19	-390.6	$2.26 \cdot 10^{-2}$	-517.6	0.039
NaCl, pH = 4	328.3	-90	$2.02 \cdot 10^{-4}$	-607.6	$3.46 \cdot 10^{-4}$
$InCl_3$, pH = 4	369.4	-194.89	$7.25 \cdot 10^{-1}$	-427.6	1.24
$InCl_3$+NaCl, pH = 4	515.4	-1884	11	-457.6	18.82
$InCl_3$+NaCl, pH = 2	544.4	-2196	9.78	-457.6	16.73
H_2SO_4, pH = 1	253.7	-504	$1.31 \cdot 10^{-2}$	-447.6	0.024
$In_2(SO_4)_3$+H_2SO_4, pH = 1	261.2	707	$3 \cdot 10^{-1}$	-407.6	0.51

Synergistic effect is due to the following reactions:

$$In^0 \rightarrow In^+ + e^-$$

$$In^+ + In^{3+} \rightarrow 2In^{2+}$$

$$In^{2+} \rightarrow In^{3+} + e^-$$

As established in the paper [7], presence of chloride ions contribute to the formation of indium (III) and accelerates the dissolution of indium electrode. In this paper, the accelerating effect of indium (III) ions on the oxidation of rough indium was found.

The data indicate a greater rate of dissolution of indium in chloride medium in comparison with sulfuric acid. From this it follows that the use of chloride electrolyte during the electrochemical refining of rough indium preferable due to high dissolution rates indium electrode.

For comparison of the results obtained was plotted schedule of dependence the dissolution rate of indium electrode on solution composition (Fig. 5). The diagram shows that the dissolution rate of indium in the medium $InCl_3$ + NaCl at different pH values is not changed.

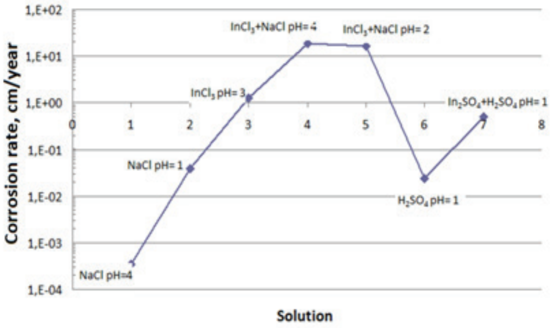

Fig. 5. Corrosion rate of indium electrode in various solutions at room temperature.

Anodic behavior of metals depends on the temperature of the environment in which it occurs dissolution. Therefore, investigated the effect of temperature on the dissolution of indium electrode at different pH (Figs. 6 and 7). Aggressive medium was dissolved NaCl, containing ions of indium (III). As seen from Figs. 6 and 7, a temperature increase leads to an increase in the corrosion current in most cases, which clearly indicates an increase of the corrosion rate of indium. However, at pH = 2 and 30-50 ºC decrease of corrosion currents was observed presumably associated with the passivation of the electrode surface. This is particularly evident from the run of the curve 4 in Fig. 6.

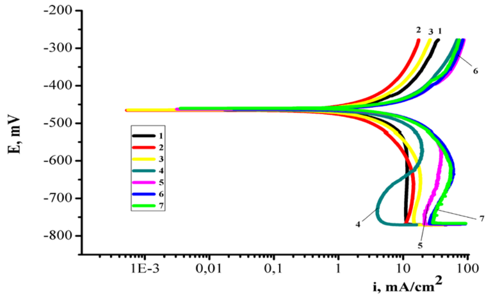

Fig. 6. Potentiodynamic polarization curves of indium electrode in chloride solution (pH = 2) at various temperatures (1 – 25 ºC; 2 – 30 ºC; 3 – 40 ºC; 4 – 50 ºC; 5 – 60 ºC; 6 – 70 ºC; 7 – 80 ºC).

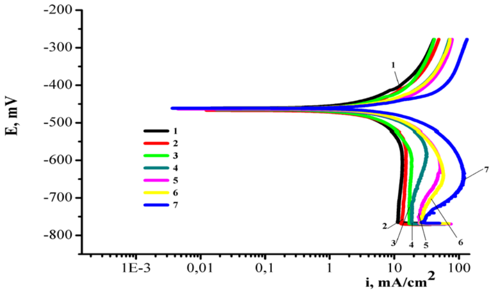

Fig. 7. Potentiodynamic polarization curves of indium electrode in chloride solution (pH = 4) at various temperatures (1 – 25 ºC; 2 – 30 ºC; 3 – 40 ºC; 4 – 50 ºC; 5 – 60 ºC; 6 – 70 ºC; 7 – 80 ºC).

Table 2

Results of potentiodynamic measurements of dissolution of indium at various temperatures in 0.1 M $InCl_3$ + 1 M NaCl

	T, °C	25	30	40	50	60	70	80
pH = 2	I_{corr}, mA/cm^2	9.78	5	7.6	75	14	11	10
	v_{corr} cm/year	16.731	8.554	13.002	12.8305	23.950	18.818	17.107
pH = 4	I_{corr}, mA/cm^2	11.9	13.3	14.9	23	32.8	27	55
	v_{corr}, cm/year	20.358	22.753	25.490	39.347	56.112	46.189	94.09

Corrosion currents and rate of indium electrode were newly calculated based on the experimental results and reported in Table 2.

For clarity, the above results can be represented graphically (Fig. 8). The obtained dependence shows that increasing the temperature accelerates the dissolution of indium in selected electrolytes. Corrosion rate of indium electrode at pH = 2 with increasing temperature remains unchanged. In the case of the electrolyte with lower concentration of hydrogen ions (pH = 4) not only the overall gain of indium electrode dissolution occurs, but much dependence on the temperature of the corrosion rate is also observed. When increasing the temperature from 25 °C to 80 °C, rate of anodic dissolution of indium increases 4.5 times. This effect suggests that the process is limited by the electrochemical step.

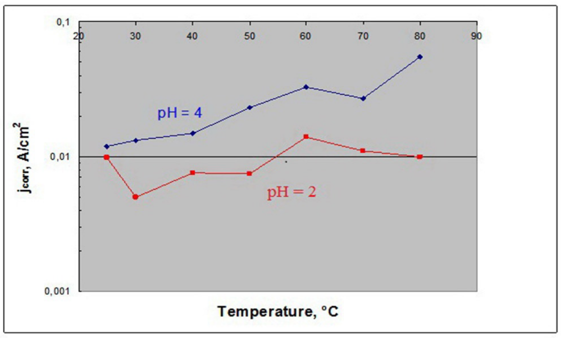

Fig. 8. Dependence of the corrosion current of indium electrode on temperature.

Conclusions

Thus, we study the influence of the electrolyte composition and temperature on the anodic dissolution of indium electrode. The maximum dissolution rate is observed in the solutions NaCl, containing $InCl_3$, due to synergetic action of ions of indium (III). Effect of temperature on the electrochemical dissolution of indium was studied in the range of 25-80 °C. Increasing temperature leads to an increase in dissolution rate of indium in solution at pH = 4. This shift is explained by the corrosion potential indium electrode in the cathode region, which facilitates the process of dissolution. The results obtained can be used in conducting the electrochemical refining of rough indium .

References

[1]. Wei-Lung Chou, Yen-Hsiang Huang, J. Hazard. Mater. 172 (2009) 46–53.

[2]. A.M. Alfantazi, R.R. Moskalyk, Processing of indium: a review. Minerals Engineering 16 (2003) 687–694.

[3]. M.G. Panthani, V. Akhavan, B. Goodfellow, J.P. Schmidtke, L. Dunn, A. Dodabalapur, P.F. Barbara, B.A. Korgel, J. Am. Chem. Soc. 130 (49) (2008) 16770–16777.

[4]. Ahmed Diab, Salah Abd El Wanees, American Journal of Physical Chemistry, 3 (3) (2014) 33–40.

[5]. Yonghwa Chung, Chi-Woo Lee. Journal of Electrochemical Science and Technology 3 (1) (2012) 1–13.

[6]. Zhou Zhi-hua, Mo Hong-bing, Zeng Dong-ming, Trans. Nonferrous Met. Soc. 14 (3) (2004) 637–640.

[7]. Abdel-Rahman El Sayed, Ali M. Shaker, HAny M. Abd El-Lateef, Corros. Sci. 52 (2010) 72–81.

[8]. Achim Walter Hassel, Matsuhide Aihara, Masahiro Seo, Electrochim. Acta, 45 (2000) 4673–4682.

[9]. G. Folcher, H. Cachet, M. Froment, J. Bruneaux. Thin Solid Films, 301 (1997) 242–248.

[10]. V.V. Losev and A.P. Pchelnikov, Electrochim. Acta, 18 (1973) 589–592.

Received 3 July 2014