

Study of Gallium Plating of Metal Electrodes

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Received August 2013

ABSTRACT

Conditions of gallium plating of metal electrodes were studied in the paper. It was found that stability of gallium cover depends on the material and is increasing in the row: stainless steel 08X18H12T < Steel 1, Steel 2, Steel 3, Steel 45 < Ni < Cd < Cu. Phase composition of the electrode surface layer obtained after gallium plating was studied. It was found that gallium with nickel form $Ga_{36}Ni_{64}(Ga Ni_2)$ compound and gallium with copper form $CuGa_2$ compound. Different acids were used for electrode leaching: H_2SO_4 ; HNO_3 ; H_3PO_4 ; HCl. It was shown that only hydrochloric acid is suitable for gallium plating of the electrodes.

Keywords: Gallium Plating; Metal Electrodes; Hydrochloric Acid; Gallium Covering; Stainless Steel 08x18H12T; Steel 1; Steel 2; Steel 3; Steel 45; Nickel; Cadmium; Copper

1. Introduction

Gallium is widely used in opto-electronics, telecommunications, and aerospace industry. Great share of gallium is used for production of GaAs, integrated circuits for electronic industry. Importance of gallium for electronic industry of the world is great, whereas annual production in tons is pretty small [1-4].

The analysis of the world market tendencies of non-ferrous and rare metals indicates a rapid growth in demand for gallium, up until 2020. For this reason there is a need for substantial increase of its output. Currently, the main source of gallium is aluminium raw materials processed by the aluminium oxide plants, which simultaneously extract gallium [5-9].

Use of gallium plated cathodes in electrolysis of aluminate-gallate solutions showed high efficiency of them [10-12]. Therefore, determination of the conditions to get stable and uniform gallium covering on metal electrodes is an important practical task.

In electrolytic cells with solid revolving gallium plated cathode the surface of the cathode is damping with liquid gallium thus restoring the surface. The sites of the cathode where gallium covering is poor could not be moistening with liquid gallium.

When steel surface of the cathode in such sites in alkaline solution becomes uncovered galvanic pair Me-Ga is formed, where gallium is anode component. At these sites gallium covering could be destroyed mechanically by evolved hydrogen gas. Vigorous bubble-formation at such sites during gallium electrolysis promotes

strong sludge formation. The sludge on the electrode surface inhibits renovation of the sites during contact with liquid gallium and promotes expansion of the sites thus decreasing efficiency of gallium electrolysis on the cathode.

When uniformity of gallium covering on cathode surface is broken activity of the electrolysis cell is stopped, electrolyte is removed and the cathode is covered with gallium again. The process requires additional work time, additional amount of gallium and the acid.

Stable and uniform covering of the electrodes with gallium lets to increase efficiency of gallium electrolysis and facilitate maintenance of the electrolysis cell during exploitation.

Covering of electrode surfaces with liquid gallium or its compounds is described in papers [13-15].

2. Experimental Method

We studied dependency of gallium cover stability in alkaline solution from material of the electrode and composition of leaching solution using different inorganic acids.

The time from the beginning of exposure to the time when uniformity of gallium cover is broken and potential of the gallium plated electrode in alkaline solution drops sharply is considered as stability of gallium cover. Metal electrodes in the kind of 8 mm rods were used for the experiments.

Before gallium covering surface of the electrode was grinded, polished and degreased in the solution, g/dm^3 :

NaOH 20.0; Na₂CO₃ 25.0; Na₂SiO₃ 10.0. The treatment was made for 10 ÷ 30 min at 70°C ÷ 90°C until complete watering. The degreasing solution was washed out with hot water. To exclude oxidizing of the electrode it was put in 5% solution of hydrochloric acid.

Metal electrodes were covered with gallium via multiple submerging in liquid gallium with 20% hydrochloric acid solution over it at 70°C - 80°C [13]. The duration of gallium covering was 1 ÷ 2 min. Surplus of liquid gallium was removed from the electrode surface with a filter moistened with 5% hydrochloric acid solution.

Phase composition of solid-liquid interface was studied with X-ray diffractometer D8ADVANCE "Bruker" using filtered Co-K_α radiation.

Stationary potential was recorded with PGSTAT12 potentiostat. All potential values were measured referring to standard hydrogen electrode. Concentration of gallium in the solution was determined using chemical methods.

To determine stability of the gallium cover electrodes were put in the 100 ml Pyrex glass cell filled with alkaline solution at 50°C. Composition of the solution was similar to that for commercial electrolytic cells, *i.e.* Na₂O_{total} = 160 g/dm³. Each result was reproduced five times.

3. Results and Discussion

Pretreatment of the electrode surface is very important to get stable and uniform gallium cover.

Different inorganic acids, HCl, HNO₃, H₂SO₄ and H₃PO₄, with concentrations from 0.1% to 20%, were used for the pretreatment but gallium covering is possible only when hydrochloric acid solution was used.

Leaching of metal electrodes (Steel 3) with HNO₃, H₂SO₄ and H₃PO₄, solutions cause vigorous hydrogen bubble-formation on steel surface. The bubble-formation is increased greatly when gallium is put in contact with the surface.

Intensive gas formation on the surface of the electrode excludes the possibility of damping the surface with gallium. Besides, flow characteristics of gallium in solutions of the acids are reduced.

The value of gallium potential in the acid solution (**Table 1**) showed that in hydrochloric acid solution gallium surface is activated. Potential of liquid gallium is moving to electronegative direction when concentration of hydrochloric acid in the solution is higher.

In the other acids potential of liquid gallium is be-

coming electropositive, *i.e.* the surface is passivated. The passivation is most valuable in nitric acid solutions.

Stability of gallium covering was studied on the following electrodes: stainless steel 08X18H12T, Steel 1, Steel 2, Steel 3, Steel 45, nickel, cadmium and copper.

Thickness of gallium covering depends on gallium diffusion into the metal, temperature of electrode and gallium and the contact time. Chemical composition and structure depend on the equilibrium diagram of gallium and electrode material.

Initial compromise potentials of uncovered electrodes in alkaline solution (160 g/dm³ Na₂O_{total}) at 50°C are shown in **Table 2**.

After submerging of steel gallium plated electrodes in alkaline solution their stationary potential was 1,365 V (**Figure 1**). At the initial part A¹B¹ of the curve 1 one can see small positive shift of the potential because of dissolution of gallium chloride and gallium oxide. Gallium chloride is formed because of interaction of gallium with hydrochloric acid solution whereas gallium oxide is formed when gallium plated electrode is submerged in alkaline solution [16].

Change of gallium dissolution rate dC/dt from the surface of the metal electrode at this moment is reflected by A³B³ part of the curve (**Figure 2**, curve 3). Sharp decrease of the rate of the process is related to decreasing of gallium oxide amount on the surface of the gallium plated electrode. The increase of gallium dissolution rate at B³C³ part of the curve is related to de-passivation of the gallium plated electrode surface due to dissolution of the oxide film and the beginning of gallium layer uniformity breakage at point B³. After this potential of the

Table 1. Potential of gallium electrode in different acid solutions at 80°C.

Acid concentration, %	Potential, V			
	HCl	H ₂ SO ₄	HNO ₃	H ₃ PO ₄
0.1	-0,520	-0,56	-0,55	-0,530
0.5	-0,520	-0,56	-0,46	-0,525
1	-0,560	-0,54	-0,44	-0,522
3	-0,562	-0,52	-0,40	-0,520
5	-0,565	-0,51	-0,38	-0,500
10	-0,570	-0,50	-0,25	-0,485
20	-0,585	-0,49	-0,20	-0,450

Table 2. Initial compromise potentials in alkaline solution (160 g/dm³ Na₂O_{total}) at 50°C.

Electrode material	Stainless steel 08X18H12T	Steel 1	Steel 2	Steel 3	Steel 45	Ni	Cu	Cd	Ga
φ, V	-0,7	-0,8	-0,8	-0,8	-0,8	-0,55	-0,36	-0,85	-1,38

electrode is declining slightly, and curves 1 and 2 have almost horizontal parts (part C^1D^1 and C^2D^2).

Reduction of gallium dissolution rate at C^2D^2 part of the curve can be explained by sharp increase of gallium ion concentration at the electrode-solution interface. This is confirmed by minor decrease of electrode potential during the said time.

At electrode potential equal to $-1,295$ V (point D^1) surface of the electrode is covered with gallium monolayer, which is being dissolved in alkaline solution until metal core is fully uncovered.

Galvanic pairs promote active dissolution of the gallium. Potential of the electrode is moving fast to positive direction beginning from $-1,15$ ÷ $-1,17$ V and is reaching eventually compromise potential of passive steel electrode in alkaline solution $-0,126$ V.

Study of phase composition of gallium plated steel electrode surface layer showed that gallium and steel do not interact and the layer is formed only because of damping. This could be confirmed by the fact that potential curves of steel electrode and steel electrode with removed gallium cover via dissolution in alkaline media are coincide in time. The thickness of the gallium cover is $(1,5 \div 2) \cdot 10^{-2}$ mm.

Stability of the gallium cover and potential curves of gallium plated electrodes in time depending on the material of the electrodes are shown in **Table 3** and on **Figure 3**.

It is seen from **Figure 3** that stability of gallium cover on the electrodes made of different steel (Steel 1, Steel 2, Steel 3, Steel 45) is the same and is equal to 1.2 min after 2 minute gallium plating. The worst stability was found for the stainless steel (curve 5), because of insufficient activation of its surface in leaching solution before gallium plating.

Stability of gallium cover on nickel core is 4 min (curve 3), after gallium plating for $0,5 \div 1,0$ min. Nickel interacts with liquid gallium forming $Ga_{36}Ni_{64}(Ga Ni_2)$ compound on the interface.

The best stability of gallium cover (14 - 15 min) was found for copper core (**Figure 3**, curve 1), because of good damping of copper with gallium. The surface layer of the electrode is represented by Θ – phase of $CuGa_2$ compound. The layer is thin because X-ray diffractogram has intensive lines of pure copper.

Potential of gallium plated copper electrode in alkaline solution is decreased from $-1,43$ V to $-1,05$ V (potential of copper covered with $CuGa_2$) and not to $-0,36$ V (potential of copper).

Therefore, stability of gallium cover is mainly depends on the core material in the following sequence: stainless steel 08X18H12T < Steel 1, Steel 2, Steel 3, Steel 45 < Ni < Cd < Cu.

4. Conclusions

Conditions of gallium plating of metal electrodes were studied. It is shown that stability of gallium cover depends on the metal core and is increasing in the following

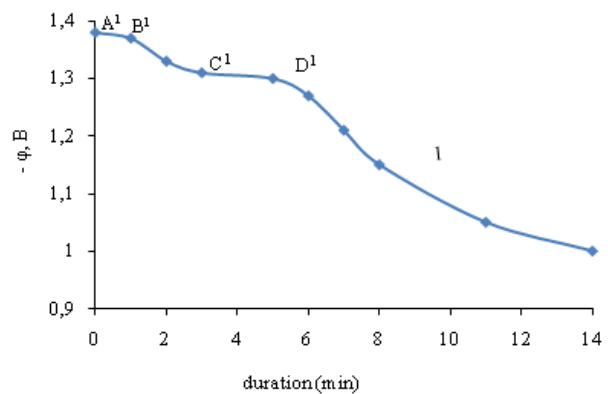


Figure 1. Dependency of gallium plated electrode potential from time of exposition in alkaline solution.

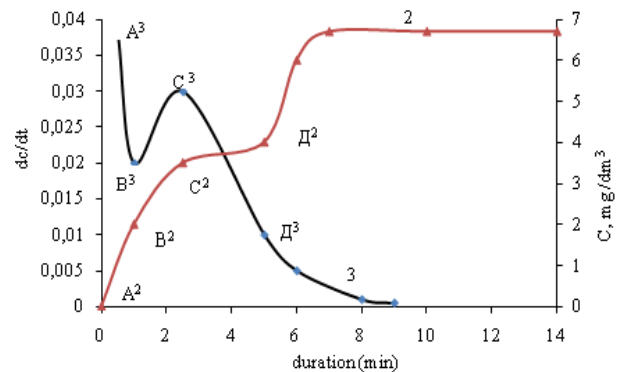


Figure 2. Dependency of gallium concentration in the solution (2) and rate of gallium dissolution (3) from time of gallium plated electrode exposition in alkaline solution.

Table 3. Stability of gallium cover depending on the electrode material.

Electrode	Material of electrode							
	Stainless steel 08X18H12T	Steel 1	Steel 2	Steel 3	Steel 45	Ni	Cd	Cu
Stability of the cover, min	0,3	1,2	1,2	1,2	1,2	4	11 ÷ 12	14 ÷ 15
Time of gallium plating, min.	4 - 5	2	2	2	2	1 ÷ 0,5	0,5	0,2 ÷ 0,5

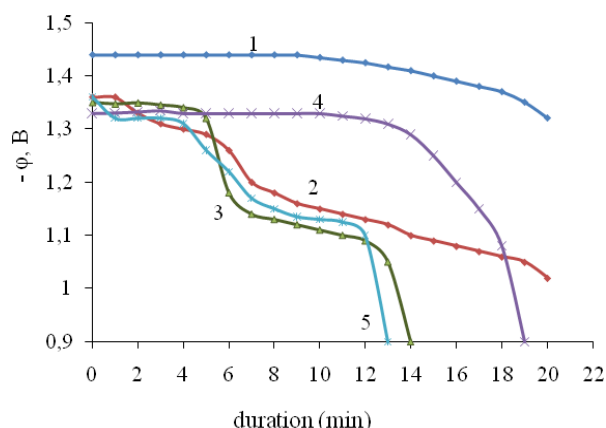


Figure 3. Dependencies of gallium plated electrode potentials from time for different electrode cores. Materials of the core: 1—copper; 2—Steel 1, Steel 2, Steel 3, Steel 45; 3—nickel; 4—cadmium; 5—stainless steel 08X18H12T.

raw: stainless steel 08X18H12T < Steel 1, Steel 2, Steel 3, Steel 45 < Ni < Cd < Cu. The best material for electrode is copper.

Phase composition of electrode surface layer obtained after gallium plating was studied. It was found that gallium with nickel form $Ga_{36}Ni_{64}(Ga Ni_2)$ compound and gallium with copper form $CuGa_2$ compound.

Different inorganic acids were used for leaching of electrode core surface before gallium plating. It was shown that only hydrochloric acid activates damping of the core with gallium

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