Bulgarian Chemical Communications, Volume 47, Number 2 (pp. 678 – 683) 2015

Electrodeposition of Ni-Co alloy on chemically oxidized Al

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Received September 19, 2013, Revised March 25, 2015

The kinetics of deposition of Co, Ni, and Ni-Co from low-acid citrate electrolyte on Cu and on chemically oxidized Al is compared. It is found that the formation of Ni-Co alloy on the Al cathode is hampered to a greater extent in comparison with the Cu electrode. In both cases (Cu and Al electrodes) "anomalous" co-deposition of Co and Ni is registered especially in an electrolyte with higher content of Ni. In case of deposition on Al cathode in stationary potentiostatic mode (cpm), the content of Co in the Ni-Co alloy is by 10 wt% higher than that in case of deposition of Ni-Co on Cu cathode. The Ni-Co alloy deposited on Al may be characterized as island-style coating, with spheroidal shape of the crystals (10-17 μm). The application of pulse potential mode (ppm) of deposition on the Al cathode leads to increased structural homogeneity and higher extent of filling the surface with crystals of Ni-Co alloy. The effect of the application of pulse potential mode, however, is strongly reduced when the extent of pulse filling at a given frequency is reduced.

Keywords: electrodeposition, chemically oxidized aluminum, pulse mode

INTRODUCTION

The interest in the industrial use of aluminum and aluminum alloys is related to the combination of factors such as low cost, light weight and good corrosion resistance [1]. A particularly important feature when using aluminum in aqueous solutions is the formation of oxide film on its surface that leads to passivation. The preparation of aluminum based micrometric and sub-micrometric materials is in the focus of a number of scientific research papers [2,3,6,7].

The application of metallic micro- and nano-particles on aluminum substantially changes its physical properties and behavior due to the increased unfolded surface area that determines its application in such important areas as catalysis [4]. An important issue is the "prevention" of nano-particles from agglomeration into larger structures [5]. Electrochemical methods are widely applied for preparation of micro- and nanostructured materials on oxidized aluminum [6,7]. The oxidation of aluminum itself can be carried out by either chemical or electrochemical means. The electrochemical method is preferred in the technology for manufacture of the so called "nanoneedles" that are formed in purposely created pores of predetermined size in aluminum foil [7]. This method is known as “electrochemical templating” and is used for preparation of nanoneedles of Ag [8], Au [9], Cd [10] and even conductive polymers [11,12]. There is also evidence for application of non-electrochemical methods, e.g. pulsed laser deposition, for preparation of such materials [13].

This paper summarizes the results of the examination of the deposition kinetics of Co, Ni, and Ni-Co and the morphology of Ni-Co alloy from low-acid citrate electrolyte on Cu and on chemically oxidized Al in constant and in pulse potential mode.

EXPERIMENTAL

Oxidation of aluminum

The chosen procedure for preparation of the Al samples for galvanization involves chemical oxidation. The rectangular Al samples have dimensions 4 cm × 1.5 cm and thickness of 0.5 mm. Prior to galvanization, the samples undergo the following sequence of operations:

(1) Chemical (alkaline) degreasing for 5-10 min in a solution composed of 30 g/l $Na_3PO_4.12\ H_2O$; 30 g/l Na_2CO_3; and 30 g/l Na_2SiO_3 at a temperature of 60-70°C.

(2) Washing in warm water (t= 50-60°C) and cold water for 1-2 min.

(3) Chemical etching in 100 g/l NaOH for 0.5-1 min at t = 50-60°C followed by washing according to (2).

(4) Lightening in 0.6 M HNO_3 for 20-30 sec at t = 18-25°C and washing according to (2).

(5) Chemical oxidation for 5-7 min in a solution of 20 g/l Na_2CO_3, 15 g/l $Na_2Cr_2O_7$, and 2.5 g/l NaOH, (t = 80-100°C), followed by washing according to (2).

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(6) Immersion for 4-5 min in a hydrochloric acid solution of 0,05 M Pd (t = 40-50°C) to improve the conductivity of the oxidized surface, followed by washing according to (2).

After carrying out the above sequence of operations, the Al samples are ready for use as electrodes, as well as for taking of the polarization dependencies, and for deposition of Ni-Co alloys on their surface.

Experimental conditions

A conventional three-electrode cell (with total volume of 150 dm^3) provided with platinum foil counter electrode and saturated calomel electrode (SCE) as comparative electrode was used. All potentials were quoted with respect to SCE (E_{SCE} = 0.241 V). The kinetics of deposition is examined using electrodes of chemically oxidized aluminum or pure copper foil. The copper electrode is disc-shaped, with surface area of 1 cm^2 soldered in epoxy resin. The preparation of the copper cathodes involves etching in a special solution, washing in distilled water, and drying.

The examination is carried out in low-acid citrate electrolyte solutions with two ratios of the concentrations of Ni (as $NiSO_4 2H_2O$) and Co (as $CoSO_4 7H_2O$): Ni/Co=3 (electrolyte I), and Ni/Co=1 (electrolyte II). The concentration of Ni is constant (0.3 M) and the background additives are 0.485 M H_3BO_3 and 0.2 M $Na_3C_6H_5O_7.H_2O\,(Na_3citrate)$. The pH=5.5 of the electrolyte is controlled through addition of NaOH or citric acid.

The deposition kinetics of Ni-Co alloys is examined in constant potential mode using a Wenking electrochemical analysis system (Germany) at a scanning rate v=30 mV s^{-1}. The pulse electrodeposition of the coatings was carried out using rectangular potentiostatic pulses generated by a pulse generator connected to the input of a potentiostat especially designed for the purpose. In turn, the potentiostat is connected to the three-electrode cell. The average values of potential $\bar{E}$ and current $\bar{I}$ were measured using a digital voltmeter with high input resistance and ammeter, respectively, and the amplitude values of the potential E_p were measured using an oscilloscope. The relation between the value of average polarization ($\Delta\bar{E}$) and that of amplitude polarization (ΔE_p) in potentiostatic rectangular pulse conditions is $\Delta\bar{E} = \theta.\Delta E_p$, where $\theta = \frac{\tau_p}{\tau_p + \tau_z}$ is pulse filling, τ_p is pulse time, and τ_z is interval between the pulses. At a pulse frequency of 500 Hz ($f = \frac{1}{T}$, Hz where $T = \tau_p + \tau_z$), and pulse fillings θ in the range from 0.2 to 0.5, the dependencies $\Delta\bar{E} - I_{av}$ and $\Delta E_p - I_{av}$ were calculated.

The morphology and the elemental content were examined using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively, on a JEOL JEM 2100 instrument (Bulgarian Academy of Science, Institute of Optical Materials and Technologies).

RESULTS AND DISCUSSION

Kinetics of deposition of Co, Ni and Ni-Co

In order to verify the possibility for co-deposition of Ni and Co in alloy, their individual polarization dependencies were compared with the dependencies of their co-deposition in electrolyte I (Fig.1 a,b) and electrolyte II (Fig.2 a,b).

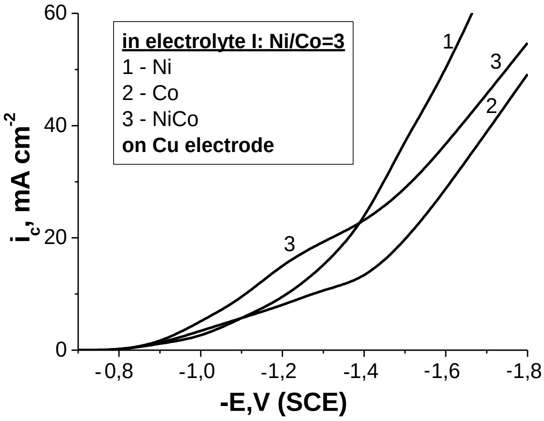


Fig. 1 a. Juxtaposition of the polarization dependencies of self-deposition in constant potential mode of: Ni (1); Co (2) and Ni-Co (3) on copper in electrolyte I (v=30 mV s^{-1}).

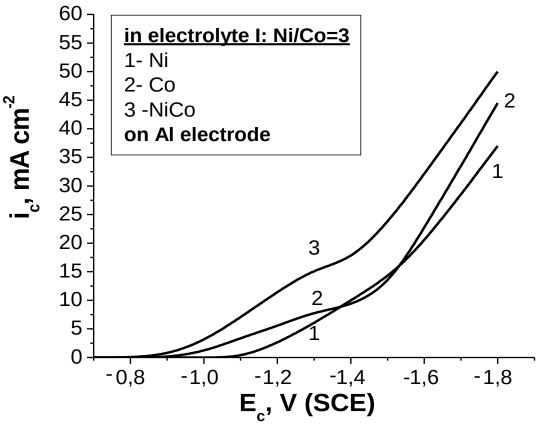


Fig. 1 b. Juxtaposition of the polarization dependencies of self-deposition in constant potential mode of oxidized aluminum in electrolyte I (v=30 mV s ^{1}).

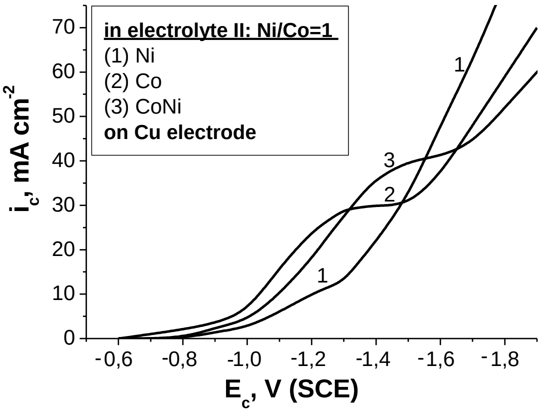


Fig. 2 a. Juxtaposition of the polarization dependencies of self-deposition in constant potential mode of Ni (1); Co (2) and Ni-Co (3) on copper in electrolyte II (v=30 mV s^{-1}).

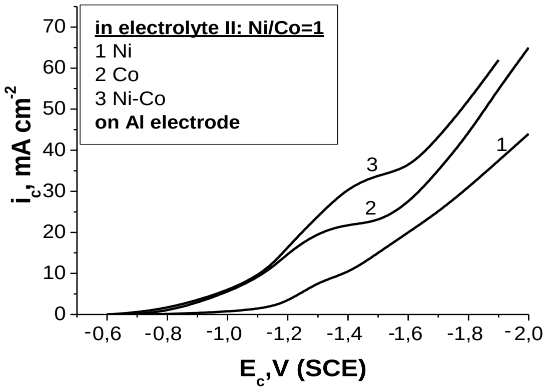


Fig. 2 b. Juxtaposition of the polarization dependencies of self-deposition in constant potential mode of Ni (1); Co (2) and Ni-Co (3) on oxidized aluminum in electrolyte II (v=30 mV s^{-1}).

As is seen from Figs. 1 and 2, the course of the polarization dependencies in the deposition on oxidized aluminum cathode is identical with that on copper cathode but the current is much lower and the deposition always takes place at much higher polarization in the first case (on Al cathode). These regularities are reported by other researchers too, regardless of the method of oxidation [9].

As it is seen from the juxtaposition made, a much closer proximity of the curves of self-deposition of Ni and Co in the case of electrolyte I (Ni/Co=3) is observed (Fig.1 a,b), especially on Cu cathode. The co-deposition of the two metals in alloy is also possible in the case of oxidized Al cathode (Figs.1 b and 2 b) but the extent of approximation of their deposition potentials is lower. These results give reasons to suggest that the alloy formation on Al cathode will be inhibited to a higher extent in comparison with the case on Cu cathode. It follows from Figs. 1 and 2 that "anomalous" co-deposition takes place on both cathode metals in electrolyte II (Fig.2 a, b), and only on the Al cathode in electrolyte I (Fig.1 b), which is typical for the metals from the iron group [14]. The "anomalous" co-deposition consists in preferential deposition of Co prior to Ni, in spite of the more positive standard electrode potential of Ni compared to Co (E^o= -0.22 V and E^o= -0.27 V *vs* NHE, respectively). The possible explanation of this phenomenon is the formation of oxides on the cathode [15] or adsorption and chemical processes associated with the complexes of the two metals (Co and Ni) [16].

Properties of the Ni-Co coatings

Chemical content

In Fig. 3 the data for the chemical content of Ni-Co coatings deposited on Cu cathode (curves 1, 2) or on oxidized Al cathode (curves 1*, 2*) in electrolyte I (curves 1, 1*) and electrolyte II (curves 2,2*) are juxtaposed. As is seen from the results obtained on the Cu cathode, as the potential increases from -1.1 V to -1.5 V, the Co content in the alloy decreases by about 10 wt % in both electrolyte I and electrolyte II (Fig.3, curves 1 and 2).

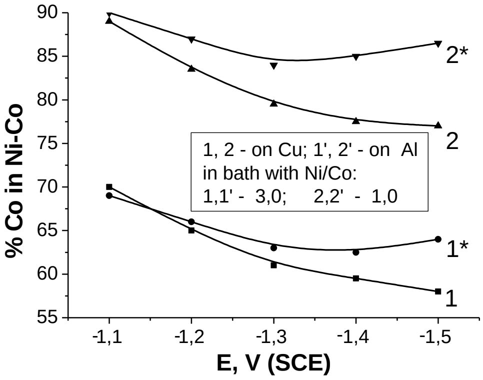


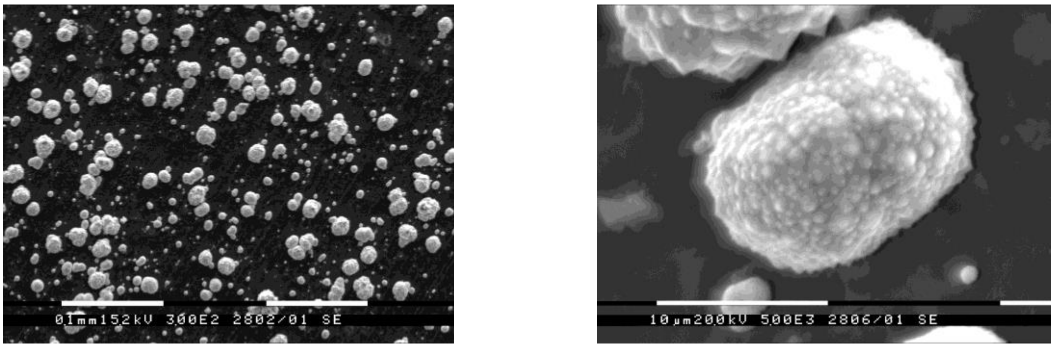
Fig. 3. Chemical content of Ni-Co coatings depending on the cathode potential on copper (1, 2) and on oxidized aluminum (1*, 2*) in electrolyte I (1, 1*) and electrolyte II (2, 2*) in constant potential mode.

However, in the case of oxidized aluminum cathode, the content of Co varies within 5 wt% with the variation of potential applied (Fig.3, curves 1* and 2*), as the dependencies run through a less pronounced minimum. The dependencies obtained can be explained with the different extent of approximation of deposition potentials. It was mentioned above that this extent is higher in the case of copper cathode. Therefore, when shifting from more positive to more negative potentials, the increase of Ni percentage in the Ni-Co alloy is much more easily achieved. In the case of oxidized Al, the same variation of potential from -1.1 V to -1.5 V results in a slight variation of Ni percentage.

With the increase of Co content in the solution, i.e. decrease of the ratio Ni/Co=3 (electrolyte I) to Ni/Co=1 (electrolyte II), its content in the alloy obviously increases (Fig. 3). In electrolyte I the content of Co is about 62 wt% on the copper cathode and about 69 wt% on the aluminum cathode; in electrolyte II the content of Co is about 80 wt% on the copper cathode and about 88 wt% on the aluminum cathode.

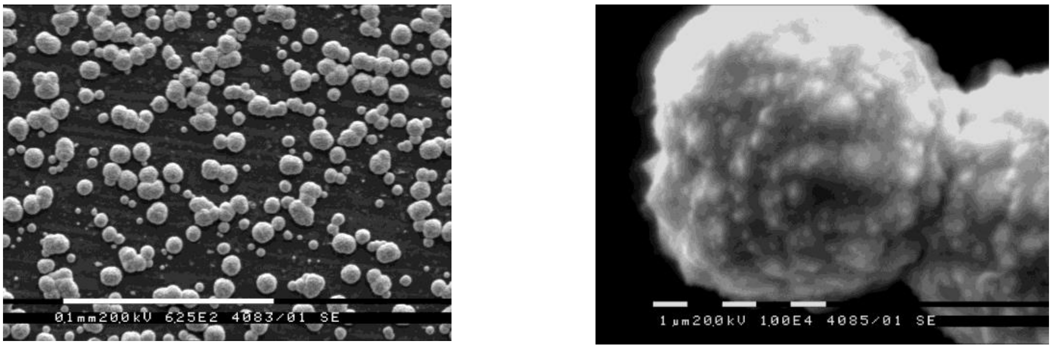
Morphology of the Ni-Co alloy

The scanning electron microscopy (SEM) images of Ni-Co alloy deposited on oxidized Al cathodes in both constant and pulse potential modes are shown in Fig. 4 (a) and (b,c) for two values of pulse filling, θ = 0.5 (b) and θ = 0.2 (c), and frequency f=500 Hz. The SEM images in two magnifications are juxtaposed. As is seen, the Ni-Co alloy deposited on oxidized Al substrate at two current modes do not have the character of a coating that fills the surface. The coating obtained is island-type coating and the average size of the crystals of the Ni-Co alloy formed varies from 5 µm to 17 µm (Fig. 5).



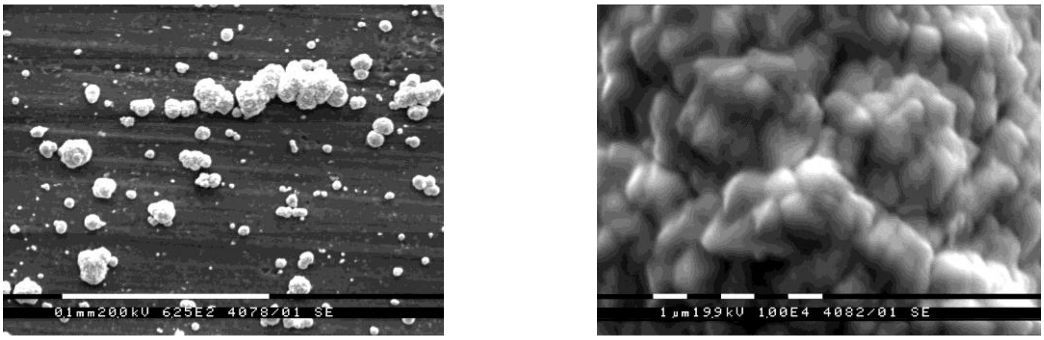
50µm …… 5 µm

(a) c.p.m. E=-1,350 V(92% Co-8%Ni)



50 µm 5 µm

(b) $\overline{E} = -1{,}350V$; f=500 Hz, θ=0,5; (82%Co-18%Ni)



50 µm 5 µm

(c) $\overline{E} = -0{,}780V$; f=500 Hz, θ=0,2; (89,7%Co-10,3%Ni)

Fig. 4. SEM images and data for the chemical content of Ni-Co alloys deposited on oxidized Al in electrolyte II in constant potential mode (a), pulse potential mode at frequency 500 Hz at pulse filling θ=0.5 (b) and θ=0.2 (c) (E, resp. $\overline{E} = -1{,}350\,V$ (SCE).

The SEM images evidence that the application of pulse potential mode with frequency of 500 Hz and pulse filling θ=0.5 (Fig.4 b) leads to higher structural homogeneity of the alloy deposited on the surface of the Al cathode.

The density of filling the surface with spherical crystals increases in pulse mode compared to stationary mode (Fig. 4 a). At lower pulse filling θ=0.2 (Fig.4 c), the formed crystals have rather irregular than spherical shape. The data from the chemical analysis of the alloys (Fig.4 a-c, under the photos) indicate that regardless of the more unfavorable conditions proven for co-deposition of the two metals on oxidized aluminum cathode compared to copper cathode (Fig. 2), in pulse mode, and especially at high pulse filling (Fig.4 b), the content of Ni in the alloy is18 wt%.

The explanation for the high content of Ni is that when applying rectangular potential pulsesto a certain average polarization $\overline{\Delta E}$ there is a much higher corresponding amplitude polarization $\Delta E_p = \overline{\Delta E}/\theta$: for example, when θ=0.5 the amplitude polarization is twice higher. Thus, during the pulses there is a possibility to shift from lower polarizations corresponding to preferential deposition of Co, to polarizations corresponding to preferential deposition of Ni. With the decrease of pulse filling that effect should increase. At shorter duration of the pulses (θ=0.2), the time for crystals generation and growth is negligible and during the longer pauses a certain blocking of the surface by products of adsorption and simultaneously emitted hydrogen gas is also possible. All the mentioned features make the above-described conditions less effective, not only for obtaining Ni-Co alloys enriched in Ni, but for the formation of morphologically uniform crystals too.

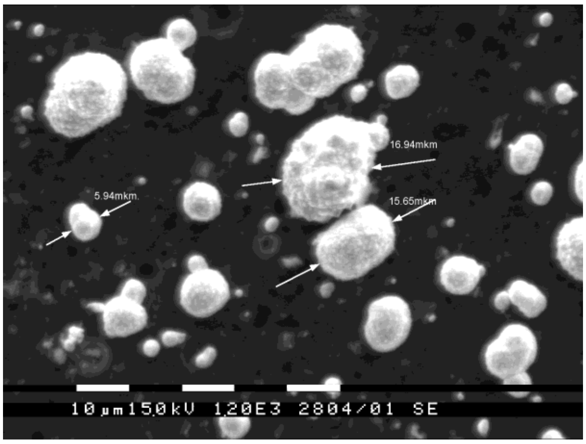


Fig. 5. SEM images of Ni-Co alloy from electrolyte II with designation of the size of crystals ($\bar{E} = -1{,}350\,V$; f=500 Hz; θ=0.5).

CONCLUSIONS

Based on the research carried out, we can conclude that the formation of Ni-Co alloy on aluminum cathode will be inhibited to a greater extent in comparison with that on copper cathode. On both Cu and Al cathodes “anomalous co-deposition” of Co and Ni is found, especially in an electrolyte with higher content of Ni. The Ni-Co alloy coating on aluminum can be characterized as island-style coating with spheroidal shape of the crystals (10-17 µm) and Ni content from 10 wt% to 18 wt% depending on the applied average potential and pulse filling at a ratio Ni/Co=1 (0.3 M Ni) in the electrolyte. The application of pulse potential mode (ppm) of deposition in an electrolyte of the same composition leads to increased structural homogeneity and higher extent of filling the surface with crystals of Ni-Co alloy.

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ЕЛЕКТРООТЛАГАНЕ НА Ni-Co СПЛАВ ВЪРХУ ХИМИЧЕСКИ ОКСИДИРАН Al

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Постъпила на 19 септември 2013 г.; Коригирана на 5 март 2015 г.

(Резюме)

Съпоставена е кинетиката на отлагане на Co, Ni, и Ni-Co из слабокисел цитратен електролит върху електроди от Cu и химически оксидиран Al. Установено е, че отлагането върху алуминиев електрод е затруднено в по-голяма степен в сравнение с това върху меден електрод. И върху двата електрода (Cu и Al) се установява съотлагане на Co и Ni от „аномален“ тип, като то е по-характерно в електролит с по-високо съдържание на Ni. При отлагане в стационарен потенциостатичен режим (cpm) върху електрод от алуминий съдържанието на кобалт в Ni-Co сплав е с около 10 % по-високо отколкото при отлагането му върху меден електрод. Ni-Co сплавно покритие върху алуминий може да бъде охарактеризирано като покритие от островен тип, кристалите на което са със сфероидна форма (10-17 μm). Прилагането на импулсен потенциостатичен режим (ppm) на отлагане върху алуминиев електрод води до нарастване на структурната еднородност и степента на запълване на повърхността с кристали от Ni-Co сплав. Ефектът от прилагането на импулсния режим силно отслабва с понижаване на степента на запълването на импулсите при дадена честота.