A STUDY ON THE KINETICS OF THE ELECTRODEPOSITION OF Ni, Co AND Ni-Co ALLOY IN CITRATE ELECTROLYTE
PART 1. THE KINETIC STUDY
OF THE INDEPENDENT ELECTRODEPOSITION OF Ni AND Co
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ABSTRACT

The electrodeposition of Ni and Co was studied by electrochemical techniques in varying compositions of slightly acidic citrate electrolyte. Cyclic voltammetry and current transient measurements were used to characterize the initial stages of nucleation, growth mechanism and electrodeposition of Ni and Co. The voltammetry analysis showed that the electrodeposition of both Ni and Co occurs under diffusion-kinetic control associated with a typical nucleation process. The deposition of Ni is in one act of charge transfer with exchange of two electrons, the deposition of Co is a two-stage process of reduction of free cobalt ions to cobalt, and reduction of complex ions type CoCit- to cobalt. The application of the method of chronoammetry proved that for cobalt the mechanism of nucleation is spontaneous, with three-dimensional nucleation and nuclei growth, while for nickel the slower progressive mechanism of nucleation is typical. The differences in the deposition mechanisms of the two metals is a possible explanation for their anomalous co-deposition in the electrolyte examined.

Keywords: electrodeposition kinetic, initial stages of nucleation, cyclic chronovoltammetry, chronoamperometry, nuclei growth.

INTRODUCTION

Over the past two decades there has been a growing interest in the applications of electrodeposited coatings of metals from the iron group (Ni, Co, and Fe) and their alloys for their unique magnetic, physical, mechanical, and thermophysical properties[1, 2].

The electrodeposition of Ni-Co alloys is classified as anomalous co-deposition which means that the less noble metal (Co) is preferentially deposited [10]. The disclosure of the reasons for anomalous co-deposition of Ni and Co in different electrolytes in many cases demands a combined application of several independent electrochemical methods and their diagnostic criteria [3, 5 - 10].

The electrochemical methods for preparation of metallic coatings and especially of the alloys are very attractive because of the high degree of control over the properties of the coatings while varying the experimental conditions [1 - 4]. To achieve this, a detailed knowledge on the mechanism of deposition of the metals both individually and in alloy is needed.

There are not enough data for the kinetics of independent deposition of Ni and Co in slightly acidic citrate electrolyte. The deposition kinetics of nanostructured Ni coating in sulphate electrolyte in presence of various organic additives was studied [5, 6] as well as in the typical Watts-bath [2, 7]. There are data for the kinetics of electrodeposition of Co in sulphate solutions [8, 9]. While the cyclic chronovoltammetry can give anotion
about the overall mechanism and kinetics of the occurring electrode processes [12], the chronoamperometric method [11] provides information about the initial stages of nucleation and the rate of nuclei growth, which can be used when searching the reasons for the anomalous co-deposition of the two metals in an alloy [5]. In this method the potential changes gradually from the equilibrium potential to potentials at which the metal begins depositing at a noticeable speed. Under these conditions, it is possible to compare the characteristics current-time (I - t) for potentials at which the main reaction does not occur, with potentials at which three-dimensional nuclei are formed and grow on an extrinsic substrate. The nucleation of the metal phase and the increase of the number of nuclei is usually illustrated with a few maxima in the I - t curves. The characteristic maxima indicate the mechanism of nucleation and the detention or the slow increase of the current up to a certain value suggest a three-dimensional growth of the nuclei [11].

The present study is aimed to obtaining some data about the general mechanism of independent deposition of Ni and Co in slightly acidic citrate electrolyte, as well as to obtain information about the initial stages of independent deposition of Ni and Co through application of the methods of cyclic voltammetry, chronoamperometry and chronopotentiometry.

EXPERIMENTAL

All electrochemical experiments were carried out in a thermostatic three-electrode cell without stirring. The working electrode was a copper disc with surface area 1 cm² and the platinum plate anode was about 30 times larger. All potentials were referred to the saturated calomel electrode (SCE). The solutions were prepared solving reagents of chemically pure substances in double-distilled water. The composition of the working electrolytes is shown in Table 1. The slightly acidic citrate electrolytes were brought to pH = 5.5 through addition of relevant quantities of sodium hydroxide and citric acid and all experiments were carried out at temperature of 20°C.

All experiments were carried out using computer controlled potentiostan type Wenking (Germany). The cyclic voltammograms were recorded in potential area from 0.2 V to -1.9 V (SCE) at scanning rate from 30 to 120 mV s⁻¹. The potentiostatic I - t dependencies and the galvanostatic E - t dependencies were recorded by rate equal to 1 s cm⁻¹ with respect to time.

RESULTS AND DISCUSSION

The method of cyclic voltammetry is used to define the area of potentials for reduction and to characterize the processes of deposition of Ni and Co. The characteristic voltammograms for deposition of Ni and Co recorded with scanning rates from 30 to 120 mV s⁻¹ in solutions 3 and 6, i.e. with concentration of Ni and Co 0,3 gmol dm⁻³ are shown in Fig. 1 a, b.

There is a long initial polarization observed in the curves for independent deposition of Ni (Fig.1a) followed by a plateau of boundary current for Co (Fig.1b), whose value increases with the increase of the rate of potential scanning. With the increase of the rate of scanning, the plateau decreases and almost disappears at the highest value (Fig. 1a, curve 4). The kinetic of deposition of Ni corresponds to a combined control with predominantly activation nature of the polarization. The absence of anode branch is the proof for this finding. The plateau of boundary current is due to reaching the diffusion limitations at higher cathode potentials.

This conclusion corresponds to the data for the influence of the concentration of Ni on the course of the cathode polarization curves (Fig. 2a) from which it fol-
allows that the plateau of boundary current is more typical for the lower concentrations of Ni where obviously the diffusion limitations are achieved sooner.

The deposition curves of Co (Fig. 1b) unlike those of Ni (Fig. 1a), have a pronounced cathode peak which increases with the increasing of potential scanning rate and the concentration of cobalt in the solution (Fig. 2b). The value of the peak current shifts to more cathodic potentials with the increase of the rate of scanning. There is not an identified oxidation peak in the working window of potentials when the curves turn scanning in anode direction. Thus the cyclic dependencies for deposition of Co evidences for the predominant diffusion limitations during its actual deposition (from -1.18 V to 1.30 V).

The chronovoltammetric examination also showed that the intersection of the cathode and anode branches of the curves is observed on the cathode sections that correspond to the potentials of nucleation: this is the area before the observed peaks, respectively plateaus for Ni. The voltammograms are analyzed based on Nicholson-Shain dependencies [12] and the developed diagnostic criteria of the method [13]. In Fig. 3a-d the dependencies \( \frac{1}{2} i_p - v^{1/2} \) (Fig. 3a), \( i_p/(v^{1/2}) - v \) (Fig. 3b), \( (E_p-E_{p/2}) - v^{1/2} \) (Fig. 3c), and \( E_p - \log v \) (Fig. 3d) obtained from the chronovoltammograms are shown that satisfy the following equations [5, 12]:

\[
\frac{1}{2} i_p = -0.496nFCE_{\infty}\left(\frac{nF}{RT}\right)^{1/2} D^{1/2}v^{1/2}
\]

(1)

\[
E_p = K_1 \frac{2.3RT}{2anF} \log v
\]

(2)

The linear character of dependencies \( i_p - v^{1/2} \) (Fig. 3a),
and particularly the increase of the current in the peak with \( v^{1/2} \), evidence that the deposition of Ni, Co is a diffusion controlled process. The application of the following diagnostic criteria specifies the degree of diffusion control and the interference on other stages in each case. Thus the practically weak dependence of \( i_p/(v^{1/2}) \) on \( v \) (Fig. 3b) in the deposition of Ni, as well as the absence of anode branch in the cyclic voltammograms for Ni (Fig. 1a) and the shift of the potential in the peak/semi-peak in cathode direction (Fig. 3c, curve 1) prove the quasi-reversible nature (diffusion-activation control) of the deposition of Ni [13]. The dependencies in Fig. 3c also indicate that the control for deposition of Co is different from those of Ni. It corresponds to diffusion-controlled process with interference on the chemical stage preceding the reaction of discharge [13] that could possibly be the dissociation of the adsorbed citrate complexes of Co. The shift of the potential in the peak towards more negative values (Fig. 3c, curve 2) is a proof supporting the above suggestion.

In order to further clarify the mechanism of independent deposition and co-deposition of Ni and Co, the chronoammetric analysis was applied [11]. The typical time-current dependencies in compositions 3 and 6 in potentiostatic conditions are shown in Fig. 4a,b in a wide range of potentials applied from \(-0.850 \text{ V}\) to \(-1.35 \text{ V}\). The same figure shows the processing of the curves in \( I - t^{-1/2} \) coordinates (Fig. 4a*,b*) and \( \ln I - t^{-3/2} \) coordinates (Fig. 5a,b) and this serves for the purpose of proving the growth mechanism of the nuclei formed, i.e. spontaneous in the first case and progressive in the second one.

It was found that there is neither deposition of the two metals nor any reactions associated with the background electrolyte at potentials more positive than \(-0.600 \text{ V}\) and only charging the capacity of the double electric layer occurs. There is a well defined and recognizable maximum of current observed in the course of the chronoammograms recorded in electrolyte 1 for deposition of Ni (Fig. 4a), which is followed by an abrupt drop and subsequent retention, as the current follows the Cottrell equation that is valid in the case of diffusion control.
It can be said that this course proves the reduction of nickel ions occurring in one stage with transfer of two electrons under the reactions:

\[ \text{Ni}^{2+} + 2e^- \leftrightarrow \text{Ni} \]

\[ \text{NiCit}^- + 2e^- \leftrightarrow \text{Ni}^+ + \text{Cit}^{3-} \]

The deposition of Ni initiates at potentials above -0.950 V with the simultaneous evolution of hydrogen upon the reaction:

\[ 2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{H}_2 + 2\text{OH}^- \]

which are evidenced by the time-current dependencies recorded additionally only in the background electrolyte. The course of the chronoammograms recorded in electrolyte 6 for deposition of Co (Fig. 6b) is quite typical. In the case of Co, there are two subsequent peaks of the current in the potential area from -1.0 V to 1.2 V, instead of one peak. The first one, i.e. for smaller values of time, is sharper and the decrease of current follows the Cotrell’s equation \[ [14] \]. The second peak in the curves of Co evidences for a process of occurrence of both active nucleation and nuclei growth in conditions of diffusion limitations. The dependencies in Fig. 6b indicate that the deposition of Co occurs through a two-stage electron transfer as it has already been found for other electrolytes \[ [8] \]. The first peak corresponds to reduction of the nearest free cobalt ions under the reaction:

\[ \text{Co}^{2+} + \text{e}^- \leftrightarrow \text{Co}^{+} \]

which is followed by a fast process of reduction of the monovalent ions to cobalt:

\[ \text{Co}^+ + \text{e}^- \leftrightarrow \text{Co} \]

As a result of depletion of the electroactive form (Co\(^{2+}\)) in the layer near to the electrode, the current decreases with time. The process is entirely diffusion controlled. With time the diffusing complex ions of cobalt (CoCit) reach slower the electrode. Their delayed reduction is also associated with purely chemical processes that precede the reduction itself, and namely dissociation of the adsorbed complexes, for which the criteria of cyclic chronovoltammetry applied above indicated. Upon reaching higher cathode values of potential, the reduction of the citrate complexes to cobalt takes place:

\[ \text{CoCit}^- + 2\text{e}^- \leftrightarrow \text{Co} + \text{Cit}^{3-} \]

The decrease of current with time as a result of depletion of the complex ions of cobalt is smoother and is explained with the simultaneous growth mechanism of the nuclei formed. The suggestion that complex ions of Ni and Co are involved is supported by the previous investigations proving their shape and stability \[ [15] \] that are also comparable with those in \[ [16, 17] \]. It was found that in slightly acidic citrate electrolyte (pH = 5.5), nickel and cobalt present both as free metal ions (Ni\(^{2+}\) and Co\(^{2+}\)) and complex citrate ions mainly of the type NiCit and CoCit mainly with stability constants \( \text{lgK}_{\text{st}}(\text{Ni}) = 5.379 \) and \( \text{lgK}_{\text{st}}(\text{Co}) = 4.38 \).

The general conclusion suggested by the chronoammetric analysis is that the behavior of the curves in Fig. 5(a, b) evidences for a typical process of nucleation with three-dimensional growth of the nuclei at predominantly diffusion control on the part of the electroactive forms \[ [11] \]. The critical time for nucleation, i.e. the time in which the current decreases, decreases with the increase of the cathode potential applied.

The method of chronoammetry provides clear diagnostic criteria to recognize the mechanism of nucleation. According to the theory developed by Scharifker-Hills \[ [11] \], there are two boundary cases of nucleation with a diffusion controlled growth. At a high rate of nucleation all nuclei are formed spontaneously and the dependence time-current is described by:

\[
\begin{align*}
\text{i}(t) &= \frac{zFD^{1/2}c}{(\pi t)^{1/2}} \left[1 - \exp\left(-\frac{N\pi kD}{2}ight)\right]
\end{align*}
\]

\[ (3) \]

where \( k = 8\pi C_o\ \text{M}/\rho; D \) is diffusion coefficient; \( C_o \) is volumetric concentration of \( \text{Ni}^{2+} \) or \( \text{Co}^{2+} \); M is molar mass; \( \rho \) is density of the metal; \( N_o \) is the number of spots for nucleation. In this case the chronoammograms are linearized in coordinates \( I - t^{-1/2} \).

In the second case, i.e. at lower rate of nucleation,ock the nuclei are formed continuously within the entire time window before reaching the area of overlapping with the diffusion limitation around the growing nuclei, we can speak about progressive (continuous) nucleation. In this case, the chronoammograms are linearized in coordinates \( I - t^{-3/2} \). The course of the current for progressive three-dimensional growth mechanism is described by the following equation:

\[
\begin{align*}
\text{i}(t) &= \frac{zFD^{1/2}c}{(\pi t)^{1/2}} \left[1 - \exp\left(-a\pi N_o k^+ D \text{Dr}^2 / 2\right)\right]
\end{align*}
\]

\[ (4) \]
where \( k' = \frac{4}{3}(8\pi C_o \infty M/\rho)^{1/2} \).

The chronoammograms of Ni are linearized to a higher degree in coordinates \( I - t^{-3/2} \) (Fig. 5a), which is indicative for a mechanism of progressive (continuous) nucleation. Unlike Ni, in the case of Co we can observe a better linearization of the chronoammograms. 

**Fig. 4.** Chronoammetric dependencies (a, b) and their derivative dependencies \( i_c - t^{-1/2} \) (a*, b*) in solutions 3 for Ni (a, a*), 6 for Co (b, b*).

**Fig. 5.** Dependencies \( i_c - t^{-1/2} \) (a*-c*), (a) - in solutions 3 (0.3M Ni), (b) - in solution 6 (0.3M Co).
in coordinates $I - t^{-1/2}$ (Fig. 4b*), which evidences for a mechanism of spontaneous nucleation that is super imposed onto the general diffusion controlled process of deposition of Co.

It is possible that the mentioned difference in the mechanisms of nuclei growth is due to the two-stage transfer of charge in the case of Co since the first stage has already localized the needed spots for crystal growth on the surface. The higher speed of nucleation in the case of Co through the mechanism of spontaneous nucleation can be a possible reason for its identified preferential (anomalous) deposition together with Ni. It also follows from the curves in Figs. 4 and 5 that with the increase of the potential applied the slope of dependencies $I - t^{-1/2}$ and $I - t^{-3/2}$ increases for both metals, which corresponds to the increase of the rate of nucleation.

The determination of the transition time as a function of current can provide additional information about the mechanism of interaction [14]. The course of the cathode potentiograms for Ni and Co is shown in Fig. 6a,b for solutions 3 (0,3M Ni) and 6 (0,3M Co), correspondingly.

The curves in Fig. 6a indicate that the cathode potentials for deposition of Ni shift smoothly to more negative potentials. In the case of Co (Fig. 6b), in the intermediate area of cathode potentials applied the dependencies $E - t$ follow the equation of Karagulanov [14], which means that the transition time is achieved decreasing with the increase of the current density. Thus the conclusion is proved that although being combined, the control of the process of Co deposition is diffusion to a higher extent than that of Ni. It is also proved that the mechanism of nucleation and nuclei growth of Co is faster than that of Ni.

CONCLUSIONS

The comparison of the dates from three electroanalytical methods shows the difference of the deposition kinetics and of the mechanisms of nucleation and crystal growth for Ni and Co in citrate electrolyte. The deposition of Ni occurs in one act of charge transfer with exchange of two electrons, and in the case of Co the deposition is a two-stage process of reduction of free cobalt ions to cobalt, and reduction of complex ions type CoCit- to cobalt. In the case of Co, there is a mechanism of spontaneous nucleation and three-dimensional growth, while in the case of Ni it comes to slower process of progressive (continuous) nucleation. The differences in the deposition mechanisms of the two metals is a possible explanation for their anomalous co-deposition in the electrolyte examined.

REFERENCES

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