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The Study of Ni Corrosion in Dependence of Time

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The aim of the present study is to investigate Ni corrosion behavior in solutions containing 0.25 M citrates at various pHs as a function of the immersion time. The corrosion tests consisted of electrochemical impedance spectroscopy (EIS), and chronopotentiometric and chronocoulometric measurements. The registration of the electrochemical data was started after pre-treatment of Ni electrode at potentials ranged – 0.7 V to – 0.5 V (NHE) during 300 s. Parameters of the corrosion process were determined upon the analysis of obtained impedance spectra that were interpreted in frame of equivalent circuit containing constant phase element is connected parallel to transfer resistance (related to corrosion resistance), then all these elements in series are connected to the solution resistance.

The open circuit potentials (OCP) of Ni are settling within 1000 s and changes of OCP are obtained from – 0.7 V to (– 0.1 ÷ 0.1) V. The values of the transfer resistance also depend on time: in acidic media almost constant values are settled within 500 s, whereas in alkaline media the steady and relatively fast increasing of corrosion resistance is observed. That might be explained by the developing passivity of the surface. The thickness of passive films were evaluated as about 100 – 300 layers of NiO or $Ni(OH)_2$ formed on the surface in the alkaline media.

Keywords: nickel, corrosion, citrates, electrochemical impedance spectroscopy (EIS).

INTRODUCTION

Ni-W alloys have been employed for the manufacturing of microstructured tools (e.g. heat microexchangers) with excellent mechanical properties, premium hardness, reasonable structure and surface properties. The citrate-ammonia solutions are widely used for electrodeposition of tungsten alloys with iron group metals comprising nickel [1 – 4]. The major limiting factor for the adaptability of conventional plating baths to deep recess plating is the variance in hydrodynamic conditions. Some problems might be solved by applying pulse current deposition, because in this case the morphology of surfaces improves sufficiently. The bath composition allows to obtain Ni-W electrodeposits with reasonable properties in pulse current mode was developed [5]. This solution contains citrates, ammonia and carbonates, and electrodeposition of Ni-W alloys in deep recesses could be performed successfully in pulse current mode (ON 10 s, OFF 30 s) in citrate-ammonia baths at (60 – 70) °C using Ni anodes. The process of electrodeposition and filling up of recesses lasts up to (30 – 48) h. It is important to obtain coatings having uniform composition through the entire length. The citrate-ammonia surrounding is aggressive for nickel *a priori*, and concentration of Ni(II) in the bath is changed due to corrosion of Ni anodes at least during pause. The increase of Ni(II) concentration causes the decreasing of W amount in alloys [5]. Therefore, the attention on the corrosion of Ni in the similar media was paid by us recently [6]. As continuation of this work, the aim of the present study is to investigate Ni corrosion behavior in solutions containing 0.25 M citrates as a function of time and pH.

EXPERIMENTAL PROCEDURE

The corrosion tests consisted of electrochemical impedance spectroscopy (EIS), chronopotentiometric and chronocoulometric measurements. The EIS spectra were obtained in the frequency range: 8 kHz to 0.10 Hz. The investigations were carried out by AUTOLAB system with the GPES and FRA software. The registration of EIS and chronopotentiometric or chronocoulometric data was started after pre-treatment of Ni electrode by applying potentials ranged – 0.7 V to – 0.5 V (NHE) within 300 s immediately after electrode was immersed. The hydrogen starts to evolve after the said potential was applied, and the oxide film was sufficiently removed during this procedure.

The electrochemical impedance spectroscopy (EIS) being non-destructive method is extensively utilizing in corrosion study. The physical behavior of the corrosion system can be simulated and quantified with equivalent circuit to gain insight into the important processes in the corrosion system. The obtained EIS data were construed in the frame of equivalent circuit that is convenient in corrosion science. This one consists on the uncompensated solution resistance R_0, constant phase element (CPE), and charge transfer resistance R_p as shown in Fig. 1.

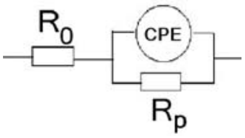

Fig. 1. Equivalent circuit utilized for EIS interpretation

The working electrode was made from Ni wire (99.9 % of Ni, Ø2 mm) produced by Aldrich Chemical Company, Inc. Before measurements, the surface of Ni was mechanically polished, rinsed in distilled water and transferred quickly to the electrolytic cell containing fresh solution. The counter electrode was platinum. The

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reference electrode was saturated Ag/Ag/Cl, KCl electrode. Electrode potentials are reported against the normal hydrogen electrode (NHE).

RESULTS AND DISCUSSIONS

The value of open circuit potential (OCP) is a parameter determined by the rates of cathodic reaction and anodic reaction of a corroding device. In the studying case, the cathodic reaction is hydrogen evolution reaction, and the anodic reaction is the active electrolytic dissolution of metal. At the open circuit potential, the rates of these reactions are equal. The rates of both reactions depend on the corrosion media, chemical composition of electrode material. Furthermore, the hydrogen evolution reaction depends on the state of surface. The study of corrosion behavior was performed in solutions containing 0.25 M of citrates as in baths used for the Ni-W alloys electrodeposition in pulse current mode. The desired values of pH were maintained by adding NaOH or H_2SO_4. The variation of the OCP for Ni in the studied solutions is shown in Fig. 2. The fastest changes and settling of the OCP are obtaining in H_2SO_4 and in citrate at pH 10.35, whereas in other solutions the settling of OCP lasts approx. 15 – 20 minutes. Interestingly, OCP at pH 5.41 and 7.75 are the same as in H_2SO_4 solution (pH 1.69).

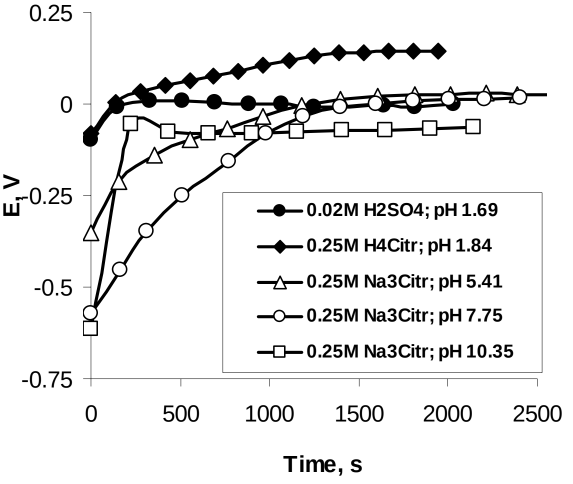


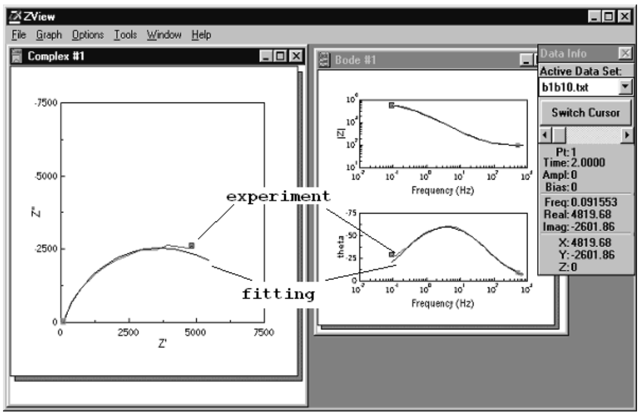
Fig. 2. OCP of Ni in various solutions

Addition information about corrosion behavior of Ni was received by means of EIS. The typical Nyquist and Bode plots as well as an example of fitting to equivalent circuit presented in Fig. 1 are shown in Fig. 3. The depressing of the semicircle is supposed due to surface roughness or caused by heterogeneity of the surface. In this case the impedance of non-ideal capacitor in complex plane can be expressed as:

$$Z = -\frac{j}{(wQ)^n}$$

where w is frequency; Q is equal to capacity; n – factor representing non-ideality ($n = 1$ for ideal capacitor).

The values of n obtained in the studied solutions are in the regular range: $n = 0.73 – 0.83$ (for Ni in solutions of citrates), and $n \sim 0.9 – 0.95$ in H_2SO_4. Also, the values of Q obtained for Ni in H_2SO_4 are typical as for the double electric layer capacity, e.g. up to 100 $\mu F\,cm^{-2}$, whereas in citrates solution Q values are sufficiently higher: 200 – 450 $\mu F\,cm^{-2}$. Such Q values probably indicate the formation of some inorganic film on the Ni surface during corrosion process. In this case, the EIS could be simulated by adding adsorption impedance to Randles circuit that is equivalent to decreasing the values of n.



Active Data Set: b1b10.txt
Pt: 1
Time: 2.0000
Ampl: 0
Bias: 0
Freq: 0.091553
Real: 4819.68
Imag: -2601.86
X: 4819.68
Y: -2601.86
Z: 0

Fig. 3. Examples of fitting experimental EIS to equivalent circuit shown in Fig. 1 (Nyquist and Bode plots) for Ni in citric acid at pH 1.84 after 107 seconds the electrode was immersed

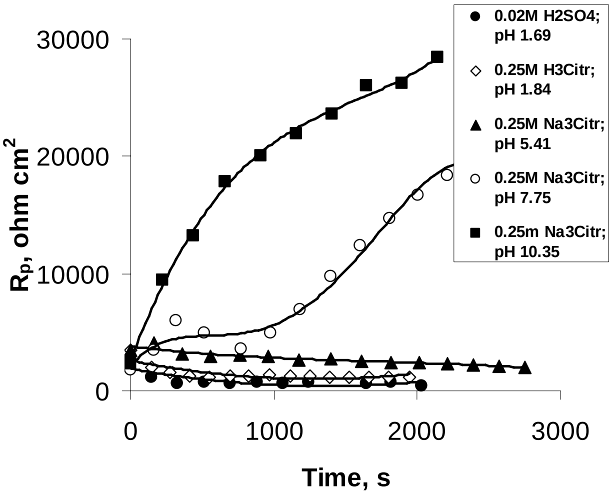


Fig. 4. R_p as a function of time obtained for Ni in the various solutions

In corrosion study the charge transfer resistance R_p is identifying with corrosion resistance which is inversely related to corrosion rate. The R_p as a function of time after Ni was immersed into solution is shown in Fig. 4. As it can be seen, the obtained R_p values for Ni in acidic solutions are significantly less than (and corrosion rate could be higher) that obtained in alkaline solutions. Moreover, in alkaline solutions the fast increase in values of R_p is evident after 5 – 15 minutes of the Ni electrode immersion, whereas in the acidic media the values of R_p change weakly with time. The R_p values sudden increase when OCP becomes relatively positive in alkaline media, i.e. approx. -0.05 V $\div$ 0.0 V (see Fig. 5). Such sufficient increase of R_p values at certain potentials might indicate the formation of passive film onto Ni surfaces.

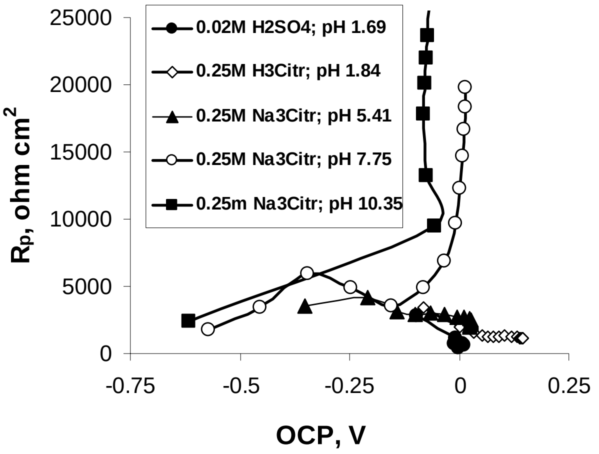


Fig. 5. The correlation between R_p and OCP of Ni in the various solutions

Chronocoulometric measurements were performed after potential drop from – 0.7 V to settled OCP value for Ni in various solutions. The quantity of electricity passing during potential drop from – 0,7 V to the previously determined values of OCP (see Fig. 1) shows a trend to decrease the amount of anodic current and quantity passing after potential drop (see Fig. 6). Interestingly, that in alkaline solutions the fast grow in R_p values could be caused by the relatively small amount of Q_a, i.e. approx. 5 mC cm^{-2}. Such values correspond to the 2 – 5·10^{-8} mol cm^{-2} amount need to form the passive film, and such values are closed to the about 100 – 300 layers of NiO or Ni(OH)$_2$ formed on the surface.

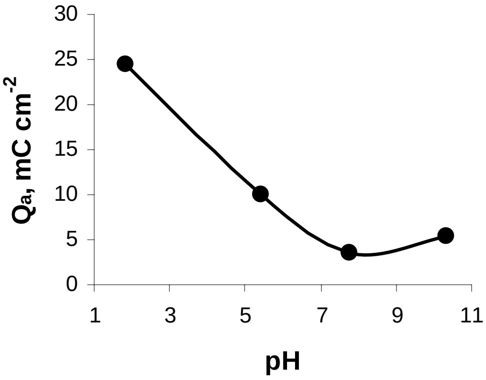


Fig. 6. The quantities of anodic current (Q_a) as a function of pH of 0.25 M citrate solutions obtained after potentials of Ni were dropped from – 0.7 V to the settled values of OCP

CONCLUSIONS

1. The fastest changes of the open circuit potential (OCP) and settling of the OCP are observed in H_2SO_4 and in citrate at pH 10.35, whereas in other solutions the settling of OCP lasts approx. 15 – 20 minutes. Interestingly, OCP at pH 5.41 and 7.75 are the same as in H_2SO_4 solution (pH 1.69). The OCP in the presence of citrates are more negative than that is observed in solutions does not containing complexing agents.
2. In alkaline solutions the strong increase in values of R_p is evident whereas in acidic media the weak decrease in values of R_p is observed. The biggest increase of R_p is observed at the potentials close to the OCP. The growing of R_p in time, dependency on pH could be caused by rising passivity of Ni in citrates media, especially in alkaline solutions.
3. Based on the chronocoulometric data the thickness of passive films were evaluated as about 100 – 300 layers of NiO or Ni(OH)$_2$ formed on the surface in alkaline media.

Acknowledgments

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