measurement and cell current method in which measure the current of the cell combined with platinum and aluminum specimen was measured.

2) The result obtained from the current-time curve was similar to that of the corrosion potential measurement in viscoplastic substance.

3) The result obtained from the corrosion potential or cell current were similar to that of the weight loss measurement. Then, the electrochemical methods such as the corrosion potential measurement are significant ways in corrosion test of viscoplastic substance.

4) The order of acceleration of cations of fluorides on corrosion of aluminum in viscoplastic substance was as follows; $\text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+}$, $\text{Ca}^{2+} > \text{blank} > \text{Zn}^{2+} > \text{Sn}^{2+}$.

5) The corrosion potential in addition of NaCl, NaBr or NaI had very small difference to that in case of no addition; while in case of addition of NaF the corrosion grew larger than that in case of no addition.

6) The penetration was proportional to the concentration of sodium fluoride in this experiment (the amount of additives was below 2.35×10^{-2} g eq. NaF/100 g viscoplastic substance), while the addition of inhibitor such as sodium silicate was satisfactory for the inhibition of these corrosion of aluminum.

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Boron and Chloride in Nickel Deposits

Taro SEKINE*, H. GESSER**, Zanolvia NOSYK** and Ed. JANZEN**

*Tokyo Institute of Technology, Okayama, Meguro-ku, Tokyo

**University of Manitoba, Winnipeg, Manitoba, Canada

The work described in this paper is concerned chiefly with attempts to explain how the contaminants enter into the nickel deposit, especially at low current density. With this point of view the determination of boron and chloride in nickel deposits prepared from Watt's type electrolyte or all chloride (sulfate free) electrolyte at various current densities was carried out. From the results, minimum amount of contamination was noticed at a current density of 1 amp/dm², and a distinct increase of its amount was observed at the lower current density of less than 1 amp/dm².

Introduction

The mechanism whereby the contamination of nickel deposit during the electro-plating is not yet understood. Three recent explanations which have been proposed to explain the inclusion of hydrogen and oxygen, and which can be extended to other contaminants in general, are (I) the inclusion of hydrous nickel oxide¹⁾; (II) the co-deposition of coordinated water or complex molecules or ions²⁾; (III) the adsorption of colloidal nickel hydroxide³⁾.

Although it has been shown⁴⁾ that a diborate of nickel hydroxide can be formed from basic solution of nickel containing boric acid, no evidence is available concerning the formation of a soluble complex between nickel ions and boric acid. A study was carried out on the possible migration of boric acid in electrolytic Hittorf cell to determine if complex formation may account for inclusion of boron in

nickel. Using a three compartments cell with nickel anode and nickel cathode, electrodeposition was allowed to proceed until noticeable deposition of nickel corresponded to about 20 to 80% of nickel included in the electrolyte. Analysis for boric acid, under these conditions, in the three compartments showed that boric acid did not migrate along with the nickel during the electrodeposition. Thus, mechanism (II), though adequate to account for the presence of hydrogen, oxygen and perhaps chloride in nickel, can not explain the presence of boron.

It was believed that if colloidal nickel hydroxide is adsorbed on the nickel deposit, it should also carry adsorbed boric acid and chloride into the deposit. With this in view, as it was described above, the determination of boron and chloride in nickel deposits prepared at various current densities was carried out.

Experimental

A Haring Cell constructed by lucite (methyl methacrylate resin) similar to that used by Winkler and coworkers⁵⁾ was used to measure cathode polarization and to obtain the nickel deposit for analysis.

Rectangular nickel plate (2.5 cm wide, 10 cm long and 0.1 cm thick) was prepared as the base structure of the cathode. After it was filled, it was treated by, first electro-plating to clean up its surface electrochemically at the desired current density until constant polarization was obtained (about 1 hr.). The cathode was then etched by the mixture of nitric acid and hydrochloric acid for few seconds, washed by water and allowed to dry before it was used for the following test to obtain the nickel deposit. The cathode was introduced into the electrolysis cell and fixed on its wall by paraffin wax. About 1 gram of the nickel deposit was formed on the cathode (effective cathode area was 10 cm² in general case) when nearly 1 Ahr. of current was passed at the desired current density. The deposit thus obtained was readily peeled from the cathode and subsequently analysed for boron or chloride.

Nickel was separated from boron or chloride by the electrolysis in a polyethylene cell having a mercury cathode⁶⁾ in very dilute sulfuric acid solution (10 cc of 0.024% sulfuric acid was used for each electrolysis).

Table 1 Boron in Nickel Deposit Prepared at Various Current Densities

Current density amp/dm ²	Boron in Nickel (A) Weight (B)		Polarization (A) Millivolts (B)	
0.25	—	0.0023	—	661
0.50	0.0012	0.0017	530	626
1.0	0.00037	0.00059	550	648
2.0	0.00023	0.00047	630	685
3.0	0.00028	0.00059	690	731
4.0	0.00032	0.00063	730	790
5.0	0.00049	0.00059	775	827
6.0	0.00028	0.00034	840	877
7.0	0.00024	0.00022	870	919

All Chloride Electrolyte (A): pH=3.8, temp.=25°C

Watt's Electrolyte(B): pH=5.0, temp.=25°C

Electrolyte(A): 237 gm/liter NiCl₂·6 H₂O, 30 gm/liter H₃BO₃

Electrolyte(B): 240 gm/liter NiSO₄·7 H₂O, 45 gm/liter NiCl₂·6H₂O, 30 gm/liter H₃BO₃

Table 2 Chloride in Nickel Deposit Prepared at Various Current Densities

Current density amp/dm ²	Chloride in Nickel (A) Weight (B)		Polarization (A) Millivolts (B)	
0.25	0.0042	0.0089	519	654
	—	0.0069		
0.50	0.0026	0.0051	552	670
	0.0024	—		
1.0	0.0012	0.0015	625	676
	—	0.0018		
2.0	0.0010	0.0022	637	733
	—	0.0028		
3.0	0.0017	0.0018	645	829
	0.0013	0.0022		
6.0	—	0.0016	740	987
	—	0.0019		

All Chloride Electrolyte(A): pH=3.1 to 3.5
temp.=25°C,

Watt's Electrolyte (B): pH=3.5 to 4.1
temp.=25°C

The solution containing boron and chloride was divided into two parts for the determination of these contaminants. After they were divided, each solution was carefully concentrated at low temperature (25–35°C) in teflon beaker. When a certain volume of these concentrated solution were ready, each solution was used for the determination of boron and chloride. Analysis of boron was then carried out by the spectrometric method⁷⁾ by means of carmine complex method in concentrated solution. Chloride was

Fig. 1 Amount of contaminants at various current densities

mechanical disk-rotating switch driven by motor, and the rate of rotation was measured by stroboscope.

Results and Discussion

The results for boron content and chloride content in the deposit obtained by ordinary direct current are recorded in Table 1 and 2, respectively, and they are plotted in Fig. 1 where they are compared with Brenner's¹⁾ result showing the oxygen content of nickel plated from Watts' type electrolyte.

Fig. 2 The rate of contamination at various current densities

also analysed in duplicate by the Conway's micro-diffusion method⁸⁾. The chemicals used were all guaranteed reagent to prepare the electrolyte. 237 gm. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 30gm. of H_3BO_3 were dissolved into 1 liter of distilled water as all chloride electrolyte, and 240 gm. of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 45 gm. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 30 gm. of H_3BO_3 were dissolved into 1 liter of distilled water as Watt's type electrolyte, and their pH were 2.1 and 2.9 at 25°C when they were newly prepared.

After a week of standing, the pH value of the electrolyte was controlled by $\text{Ni}(\text{OH})_2$ to obtain the desired value as it was shown in the following table.

Intermittent current which has the interrupted period from 1/60 to 1/4 sec was obtained by

Fig. 3 Applied intermittent current

An increase in temperature from 25°C to 50°C at 5 Amp/dm² (in Electrolyte A) showed a slight (about 10%) increase in the boron content of the nickel deposit. However, any distinct effect of temperature could not be found from these results, and the change of the amount of boron is approximately only within the accuracy of boron analysis.

From these results shown in Table 1, Table 2 and Fig. 1 it would seem that all contaminants in the deposit showed an increase at low current density. The consistent difference in chloride content of nickel obtained from these two different kinds of electrolyte used is parallel to that obtained for boron and it indicates that the rate controlling step for inclusion of chloride is not necessarily concentration but pH which is more important in influencing inclusion or absorption.

This can be explained by assuming that at low current density the impurities enter the deposit at an approximately constant rate. Hence the product of (% impurity) and (current density) ought to be a constant or a plot of $1/(\% \text{ impurity})$ vs. (current density) should be a straight line passing through the origin. Such a plot is shown in Fig. 2. It is evident that this relation is not followed at the current density above 2 amp/dm^2 where another mechanism of contamination such as (I) or (III) become predominant.

Table 3 Chloride in Nickel Deposit Prepared by Intermittent Current at Various Current Densities

Intermittent sec c/s	Period	0.25 amp/dm ²	0.5 amp/dm ²	1.0 amp/dm ²	2.0 amp/dm ²	3.0 amp/dm ²
1/4	2	0.0012	0.0002	0.0010	0.0013	0.0020
1/8	4	0.0027	0.0010	0.0018	0.0013	0.0023
1/15	7.5	—	—	0.0025	0.0015	0.0020
1/17	8.5	0.0041	0.0025	—	—	—
1/60	30	0.0059	—	0.0021	—	0.0021
ordinary DC		0.0079	0.0051	0.0017	0.0025	0.0020

Electrolyte (240 gm/liter $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 45 gm/liter $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 30 gm/liter H_3BO_3): pH=3.5 to 4.9; Temperature=25°C

To further make sure of this relation, it was proposed to deposit at 0.25 to 3 amp/dm^2 with intermittent current as shown in Fig. 3 where x represents the magnitude of the current density flowing for time y , and z represents the off or waiting time.

The results are condensed in Table 3, and are plotted in Fig. 4 along with previously obtained results by ordinary direct current for comparison. In these experiments the time y was chosen as same as time z .

Fig. 4 Amount of chloride in nickel by applying of intermittent current at various current densities

Fig. 5 The rate of contamination by applying of intermittent current

From these results it seems that at higher current density more than 2 amp/dm^2 , the effect of intermittence of the current was not evident in each case, but in rather lower current density, less than 0.5 amp/dm^2 , the contamination of deposit by chloride was obviously decreased when intermittent current was supplied.

Then, to clarify the relation among amount of contamination, current density and intermittent period, $1/(\% \text{ chloride})$ vs. current density was plotted in each intermittent period as shown in Fig. 5. The plot shows a straight line passing through the origin till 1 and 0.5 amp/dm^2 at ordinary direct current and intermittent current respectively, and the gradient of these lines were steeper when the

Fig. 6 Influence of intermittent period on the amount of chloride in nickel

of contamination by such an impurity into the nickel deposits during the electro-plating at low current density.

It was observed that a distinct increase of the amount of impurity occurred at lower current density of less than 1 amp/dm² when an ordinary direct current was supplied. This can be explained by assuming that the impurities enter the deposit at an approximately constant rate at low current density.

Furthermore, from the results obtained by using the intermittent current, it is suggested that when the current is stopped the impurity leaves the newly deposited nickel layer for the electrolyte at another constant rate after it was introduced into the deposit at a constant rate associated by the electro-deposition of nickel when a current is passed.

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