Studies on the Electroless Nickel Plating with NaBH_4 as a Reducing Agent XI. Application of Computer Analysis for the Evaluation of Corrosion Resistance of Electroless Ni-B Deposits

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Computer analysis using Newton-Raphson method was proposed for the evaluation of corrosion resistance of electroless nickel deposits. The polarization curves of the Ni-B deposits in 0.5 M H_2SO_4 solution were analyzed by (1) the proposed computer method as well as (2) the intercept method, using Tafel line, (3) the Stern-Geary method and (4) Oldham's method. Dependence of the corrosion resistance of the Ni-B deposits on the concentration of sodium borohydride or thallous nitrate in the electroless nickel plating bath was investigated. It was found that the proposed computer analysis offers better means of evaluating the corrosion resistance of the Ni-B deposits. The corrosion current estimated by the computer analysis was fairly in good agreement with the values obtained by chemical analysis and also by electrochemical methods. The corrosion resistance of the Ni-B deposits decreased with an increase in NaBH_4 concentration in the bath, but it increased with an increase in TlNO_3 concentration.

1 Introduction

In the past decade, computer technologies have advanced at an almost unbelievable rate, so that they are now readily available to various problems in the branch of corrosion study^{1,2)}. Mansfeld has shown that instantaneous corrosion rates and Tafel slopes (b_a and b_c) could be obtained simultaneously from polarization curves in the non-Tafel region in the vicinity of the corrosion potential by means of a curve fitting method³⁾. This method has the advantage that the corrosion system is disturbed only very little by the polarization measurement. However, this method is somewhat troublesome and the error in the determination of b_a and b_c was more than 5 mV, because the values were graphically determined to give the best fitting between the observed and theoretical curves, which were calculated for various combinations of b_a and b_c in steps of 5 mV. Mansfeld has also analyzed the same experimental data with the linear least squares method using a computer program to confirm the accuracy of the kinetic parameters in the corrosion reactions¹⁾.

In this paper, a new computer analysis using non-linear least squares method was applied for the evaluation of the corrosion rates of electroless Ni-B deposits. Corrosion rates of the electroless Ni-B deposits were different from each other depending on the types of electroless nickel baths employed and operating conditions. The dependence of the corrosion resistance of the Ni-B deposits on the concentration of sodium borohydride or thallous nitrate in an electroless nickel bath was investigated in 0.5 M H_2SO_4 solution. Polarization curves of the electroless Ni-B deposits were analyzed by (1) the proposed computer method as well as (2) the intercept method, (3) the Stern-Geary method and (4) Oldham's method⁴⁾. The corrosion rates evaluated by the electrochemical methods described above were compared with the values estimated by the chemical analysis.

2 Experimental

2.1 Preparation of test specimens

Two types of electroless nickel plating bath, as shown in Table 1, were employed to prepare the electroless Ni-B deposit on copper substrate. The Ni-B film prepared at 60 °C for 2 h was used as the test specimen in electrochemical measurement and also in chemical analysis.

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Table 1 Bath composition for electroless nickel deposition

Bath type	A	B-1	B-2
Nickel chloride	0.04M	0.04M	0.04M
Sodium tartrate	0.16M	0.16M	0.16M
Monoethanolamine	—	60cm ³ /dm ³	60cm ³ /dm ³
Ethylenediamine	4cm ³ /dm ³	—	—
Sodium hydroxide	1.0M	0.3M	0.3M
Thallous nitrate	—	0.1g/dm ³	Variable
Sodium borohydride	Variable	Variable	30mM

2.2 Determination of nickel and boron

The electroless Ni-B deposit was dissolved in 1 M HNO₃ solution for analyzing its composition. The dissolved nickel was determined by spectrophotometric method with formation of water-soluble dimethylglyoxime complex⁹⁾. After removal of the nickel ion by amalgamation by pre-electrolysis, the dissolved boron in the form of boric acid was titrated with sodium hydroxide in the presence of mannitol, using a pH meter⁹⁾. The nickel dissolved in 0.5 M H₂SO₄ solution during the immersion test was also determined by the same method as described above.

2.3 Electrochemical measurements

Anodic and cathodic polarization curves of the Ni-B electrode were obtained in deaerated 0.5 M H₂SO₄ solution which was purified by pre-electrolysis before use. Saturated calomel electrode was used as a reference electrode and platinum electrode as an auxiliary electrode, respectively. All measurements were made at 30°C with an H-type cell, in which catholyte and anolyte were separated by a fritted glass. The potential sweep was carried out at a rate of 50 mV/min with the aid of a potentiostat coupled with a function generator as described in the previous paper⁷⁾.

3 Results and Discussion

3.1 Fundamentals for computer analysis

If a potential (E), other than corrosion potential (E_{corr}), is applied to the corroding electrode by means of an auxiliary electrode, external current (I) will flow through the electrodes because the anodic and cathodic partial currents are no longer equal. The relationship between I and E is generally expressed as in the following equation, known as the Butler-Volmer

equation.

$$I = I_{\text{corr}} [\exp\{(E - E_{\text{corr}})/0.434 b_a\} - \exp\{(E_{\text{corr}} - E)/0.434 b_c\}] \quad (1)$$

The best values of the constants such as I_{corr} , A and C are assumed to minimize the value of the following equation.

$$S = \sum_{i=1}^n [I_{\text{corr}} [\exp(A \Delta E_i) - \exp(-C \Delta E_i)] - I_i]^2 \quad (2)$$

where $\Delta E_i = E_i - E_{\text{corr}}$, $A = 1/0.434 b_a$ and $C = 1/0.434 b_c$.

The minimum in eq. (2) is found by partial differentiation. Thus,

$$(\partial S / \partial I_{\text{corr}}) = 2 \sum_{i=1}^n [I_{\text{corr}} [\exp(A \Delta E_i) - \exp(-C \Delta E_i)] - I_i] [\exp(A \Delta E_i) + \exp(-C \Delta E_i)] = 0 \quad (3)$$

$$(\partial S / \partial A) = 2 \sum_{i=1}^n [I_{\text{corr}} [\exp(A \Delta E_i) - \exp(-C \Delta E_i)] - I_i] I_{\text{corr}} \Delta E_i \exp(A \Delta E_i) = 0 \quad (4)$$

$$(\partial S / \partial C) = -2 \sum_{i=1}^n [I_{\text{corr}} [\exp(A \Delta E_i) - \exp(-C \Delta E_i)] - I_i] I_{\text{corr}} \Delta E_i \exp(-C \Delta E_i) = 0 \quad (5)$$

An initial assumption is made for A_j and C_j and then the value of $I_{\text{corr}, j}$ is calculated from eq. (3). (Step I) The current values of A_j and C_j are numerically corrected by the Newton-Raphson method as follows⁸⁾.

$$A_{j+1} = A_j - (\partial S / \partial A)_{A=A_j} / (\partial^2 S / \partial A^2)_{A=A_j} \quad (6)$$

$$C_{j+1} = C_j - (\partial S / \partial C)_{C=C_j} / (\partial^2 S / \partial C^2)_{C=C_j} \quad (7)$$

New approximations of A_{j+1} and C_{j+1} can be derived from eqs. 6 and 7 by using the value of $I_{\text{corr}, j}$ determined in the step I. (Step II) The steps I and II are repeated until the S value becomes smaller than a specific value. For the computations, TOSBAC-5600 Model 120 computer system (at the computer center, Univ. of Osaka prefecture) was utilized. As the proposed method has no approximation in the treatment of eqs. 1 to 5, all potential regions in the polarization curves are available for the computation without any restriction in contrast to the linear least squares method. In this experiment, 25 sets of I_i - E_i data in the range of $| \Delta E_i | \leq 60$ mV were used for the calculation of I_{corr} . Typical polarization curves estimated by the proposed method were compared with the experimental curve as shown in

Fig. 1. The results indicated that the smaller S value gave the better agreement between the observed and calculated curves.

Fig. 1 Comparison of the polarization curves obtained by computer analysis with the experimental result

3.2 Corrosion resistance

3.2.1 Effect of sodium borohydride

As the corrosion rate of the electroless nickel deposits was different from each other depending on the types of baths employed and operating conditions, the effect of NaBH_4 concentration on the corrosion resistance of the Ni-B deposits was investigated for the two types of baths (A and B-1). Fundamental difference in the deposits obtained from the different types of baths was given below. The boron content in the Ni-B(A) deposits varied between 7 and

9.5 wt %, whereas that of the Ni-B (B-1) deposits between 3 and 5 wt %. Typical surface appearance of the deposits obtained from baths A and B-1 is shown in Fig. 2. The Ni-B(B-1) deposit gave a granular and rough surface in contrast to Ni-B(A). Such a granular growth of the deposit was the most remarkable feature of the bath containing thallos nitrate. The corrosion rate of the Ni-B(A) deposits, as shown in Fig. 3, was evaluated by the

Fig. 3 Dependence of the corrosion currents of electroless Ni-B (A) deposits on NaBH_4 concentration

proposed computer analysis as well as conventional electrochemical methods and chemical analysis. Though some scattering was observed in the corrosion currents estimated by the different methods, the results indicated that the Ni-B deposits from the bath with a high concentration of NaBH_4 (≥ 20 mM) gave poor corrosion resistance. The proposed computer analysis gave reliable results for the evaluation of corrosion resistance of the electroless nickel deposits. Corrosion behavior of the electroless Ni-B(B-1), shown in Fig. 4, was essentially the same as that of Ni-B(A) deposit. The corrosion rate of Ni-B(B-1) deposit increased with increase in NaBH_4 concentration. Higher concentration of NaBH_4 in the baths resulted in lesser corrosion resistance in both the cases of Ni-B (A) and Ni-B (B-1). However, the corrosion resistance of Ni-B (A) is generally superior to that of Ni-B(B-1).

Fig. 2 Surface appearance of the electroless nickel deposit obtained from baths A and B-1

Fig. 4 Dependence of the corrosion currents of electroless Ni-B (B-1) deposits on NaBH₄ concentration

3.2.2 Effect of thallous nitrate As described in the preceding section, thallous nitrate when used as a stabilizer in the bath gave the characteristic morphology. Metallographic observation of the deposit indicated that the grain size increased with increasing TlNO₃ concentration, whereas, the color of the nickel deposit changed from gray to milky white above the concentration of 0.2 g/dm³ TlNO₃. Dependence of the corrosion resistance of a series of the Ni-B deposits on the concentration of TlNO₃, shown in Fig. 5, was determined by the proposed computer methods as well as chemical and electrochemical methods. The computer analysis was fairly in agreement with the results obtained from other methods. The corrosion rate was maximum at the concentration of 0.1 g/dm³ TlNO₃ and decreased abruptly with further increase in the concentration of TlNO₃. Under these conditions, the content of thallium incorporated in the Ni-B deposit was found to be proportional to the concentration of thallous ions in the bath. The improvement in the Ni-B deposits, therefore, seemed to be attributable to the increase in the thallium

Fig. 5 Dependence of the corrosion currents of electroless Ni-B (B-2) deposits on TlNO₃ concentration

content in the deposit, by which changes in morphology and also chemical nature of the deposit are pronounced.

4 Conclusions

Computer analysis using Newton-Raphson method has been proposed for the evaluation of the corrosion current of Ni-B deposit. The computer program used in this work is characterized by the least squares interpolation for non-linear model. The results of the conventional electrochemical methods and also chemical analysis of the deposit strongly indicate that the proposed computer method can be successfully applied to the evaluation of corrosion resistance of the Ni-B deposits. It was found that the increase in NaBH₄ concentration in the bath gives rise to less protective film of Ni-B(A) and Ni-B(B-1) deposits. The corrosion resistance of the Ni-B(B-1) deposits obtained from the bath containing 0.1 g/dm³ TlNO₃ is generally poor compared with the Ni-B(A). However, an increase in TlNO₃ concentration in the bath gives corrosion protective Ni-B film.

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