obtained from eq. (2) at various $D$ are also shown in Fig. 6.

In Fig. 7, $D$ values obtained in this study are shown in the Arrhenius plot. Although $D$ values considerably fluctuated, these values were $10^4 \sim 10^5$ cm$^2$/sec and about $10^4$ times as large as those in the reaction between zirconium and nitrogen gas at about 1,000°C.$^{12}$ In this figure, $T$ is a surface temperature of the zirconium metal under the nitrogen plasma jet, and is listed in Table 1.

Table 1  Surface temperature of zirconium under the nitrogen plasma jet $T$ (°K)

<table>
<thead>
<tr>
<th>$N_2$ flow rate A</th>
<th>2 l/min</th>
<th>3 l/min</th>
<th>4 l/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3020</td>
<td>3150</td>
<td>3370</td>
</tr>
<tr>
<td>70</td>
<td>3250</td>
<td>3400</td>
<td>3520</td>
</tr>
<tr>
<td>80</td>
<td>3370</td>
<td>3570</td>
<td>3600</td>
</tr>
<tr>
<td>100</td>
<td>3670</td>
<td>3770</td>
<td>3920</td>
</tr>
<tr>
<td>110</td>
<td>3770</td>
<td>3970</td>
<td>4120</td>
</tr>
</tbody>
</table>

It is noted from Fig. 7 that the diffusion constant increased with increasing nitrogen flow rate and rising temperature.

As shown in Fig. 3, the region with high intensity of NK$_4$ line increased with increasing reaction time.

Some Observations of Initial Stage of Nickel Deposition

Tadashi YOSHIDA*, Itsuaki MATSUDA* and Shuichi FURUYA*

A small amount of nickel, deposited galvanostatically on platinum, was estimated by the anodic dissolution through triangular potential scanning. It was confirmed that the amount of deposited nickel, obtained by the graphical integration of dissolution diagram, was substantially reliable within the experimental condition. The two steps revealed by the galvanostatic charging trace for the deposition in NiSO$_4$ bath of low pH were discussed, and the transition time $\tau$ for the hydrogen evolution, observed from the above, supported the well known relation $i_e \tau^{1/2} = \text{const}$. The time dependence of nickel deposition and each current allotted to the deposition or to the evolution of hydrogen out of a small applied current were observed and discussed.

1 Introduction

The investigation of nickel deposition should be conducted with special regard to the parasitic evolution of hydrogen. Yeager, et al.$^{1}$, examined the Tafel lines for the nickel deposition and hydrogen evolution respectively in the steady state, where the current efficiency was determined by the chemical analysis. Arvia, et al$^{2}$, reported that the mechanism of nickel deposition in perchlorate or chloride bath differed little from that proposed by Bockris, et al$^{3}$, for the deposition of iron. According to Heusler, et al$^{4}$, the deposition mechanism was analogous to that proposed...
by them for the cobalt deposition\textsuperscript{13}.

In this paper, the initial stage of nickel deposition on platinum was investigated, where the minute amount of the deposited nickel was estimated by the graphical integration of its dissolution diagram.

2 Experimental

The solution were prepared from the reagents of chemical grade and triply distilled water, where the pH value of the bath was adjusted by 1.0 N H\textsubscript{2}SO\textsubscript{4}.

The test electrode was a platinum disk or wire with apparent surface area of 0.071 or 0.197 cm\textsuperscript{2}, and the section or the side wall of platinum wire of diameter about 3 or 1 mm was used respectively, where the insulation of needless surface was made with the Pyrex glass. The counter electrode was a platinum net or plate of large surface area.

The experiments were always conducted in the atmosphere of purified nitrogen and all the potentials were observed or described with reference to the saturated calomel electrode (S.C.E.).

Nickel was deposited on platinum from 1.0 M NiSO\textsubscript{4} at 30°C with galvanostatically single pulse circuits\textsuperscript{5} equipped with a mercury relay (NEC, MCA-1), and then the deposit was dissolved anodically in 1.0 N H\textsubscript{2}SO\textsubscript{4} at 30°C by the triangular potential scanning method, where a potentiostat (Hokuto Denko, PS500B) was driven by a linear scanning unit (Hokuto Denko, LS2D). A memoriscop (Iwasaki, MS-5103) or a highly sensitive X-Y recorder (Toa Denpa, XYR-1A) was employed for the observation.

3 Results

3.1 Potential vs. current curves of anodic dissolution of deposits

It was confirmed that the nickel deposited on the platinum electrode almost dissolved in 1.0 N H\textsubscript{2}SO\textsubscript{4} with a single anodic scanning, provided that electric charge corresponding to the deposit was so small as about 30–40 mcoul/cm\textsuperscript{2}. The above confirmation was made from the result that the cathodic trace after the first anodic scanning nearly accorded with that for the bare platinum electrode and the second cyclic trace was also in agreement approximately with that for the bare platinum electrode in the same condition. Consequently, the charge \( Q_d \) obtained by integrating the dissolution peak region of the dissolution diagram as shown in Fig. 3, is considered approximately to be a reliable value corresponding to the total nickel deposited before the anodic dissolution, while the charge \( Q_d \) (\( = i_e \times t \)) used for the deposition differs from \( Q_d \).

Examples of the potential vs. current curves for the anodic dissolution of the deposits in 1.0 N H\textsubscript{2}SO\textsubscript{4} are shown in Fig. 1, where the deposit was prepared galvanostatically with a current density (\( i_e \)) of 30 mA/cm\textsuperscript{2} in 1.0 M NiSO\textsubscript{4} of pH 3.0. And the deposit was cathodically pretreated at \(-0.4 \text{ V (S.C.E.)} \) for 30 sec in 1.0 N H\textsubscript{2}SO\textsubscript{4} before the anodic scanning.

\[ Q_d = (i_e \times t) \]

\[ a: 49 \text{ mcoul/cm}^2, \quad c: 20 \text{ mcoul/cm}^2 \]

\[ b: 34 \text{ mcoul/cm}^2, \quad d: 12 \text{ mcoul/cm}^2 \]

Fig. 1 Potential vs. current curves for dissolution of nickel deposit on platinum with scanning rate of 0.2 V/sec in 1.0 N H\textsubscript{2}SO\textsubscript{4} at 30°C. Deposition was prepared in 1.0 M NiSO\textsubscript{4} with \( i_e \) of 30 mA/cm\textsuperscript{2} at 30°C

Next, the result obtained for the case where the amount of the deposit is too small to cover the platinum substrate, is given in Fig. 2. The curve denoted by---, for the bare platinum electrode, is a typical result obtained by a single cyclic scanning from \(-0.25 \text{ V} \) after the cathodic pretreatment for 60 sec at \(-0.4 \text{ V} \) in 1.0 M H\textsubscript{2}SO\textsubscript{4}, where the obvious current is shown owing to oxidation of hydrogen evolved during the pretreatment. The curve denoted by----- is observed for bare platinum electrode by the repeated cyclic scanning between \(-0.25 \text{ V} \) and \(+1.2 \text{ V} \), where the well known peaks\textsuperscript{11,12} are found owing to adsorption or desorption of hydrogen and oxygen. Further, the solid curve is a typical result by a single scanning cycle for the electrode partially covered by nickel, where the peak \( P_N \) region is considered to be composed of the current due to nickel dissolution and that due to oxidation of hydrogen evolved during the pretreatment. In the case of the above or of the bare platinum, observed by a single scanning after the cathodic pretreatment, the cathodic parts are depressed compared with that for the bare platinum observed by the repeated scanning. These depression is considered
For nickel dissolution after cathodic polarization (−0.4 V, 30 sec), by single scanning.

---: For platinum after cathodic polarization (−0.4 V, 60 sec), by single scanning.

---: For platinum by repeated scanning (−0.25~+1.2 V)

Fig. 2 Potential scanning traces at 0.2 V/sec for dissolution of deposited nickel or for platinum in 1.0 \( \text{NH}_2\text{SO}_4 \), at 30°C, where nickel was deposited on platinum from 1.0 M \( \text{NiSO}_4 \), of pH 3.0, with \( i_\text{c} \) of 30 mA/cm\(^2\) under \( Q_\text{d} \) of 7.1 mCoul/cm\(^2\) to be caused by the hydrogen oxidation which may take place during the cathodic scanning.

For the anodic dissolution conducted in the hydrogen saturated solution of low pH value, it was found by some authors\(^{5,6}\) that the current efficiency for nickel dissolution was approximately 100% in the range observed. Therefore, it is assumed that the oxidation of hydrogen is able to take place almost exclusively on the bare platinum under a certain condition. The above assumption was verified by the result shown in Fig. 6 (4.3).

Meanwhile, the charge \( Q_\text{p} \) corresponding to the dissolved nickel was evaluated through the graphical integration as illustrated in Fig. 3. In the case of Fig. 3 (a), where \( Q_\text{p} \) is expected to be about 3 mCoul/cm\(^2\) and the deposit covers almost over the platinum substrate, the evaluation is valid under the assumption that the peak region is exclusively due to the dissolution of nickel. However, in the case similar to Fig. 2, where \( Q_\text{p} \) is so small as about 1 mCoul/cm\(^2\) that the substrate is covered partially with nickel, the peak region is considered to be due to both of nickel dissolution and hydrogen oxidation. Therefore, as shown in Fig. 3 (b), it is necessary to make approximate correction for the oxidation of hydrogen expected from the result by a single scanning for the platinum electrode.

**3.2 Dependence of \( Q_\text{p} \) on scanning rate**

The scanning rate (\( V_\text{s} \)) dependence of \( Q_\text{p} \) is plotted in Fig. 4 where the applied charge \( Q_\text{d} \) for the deposition was always 20 mCoul/cm\(^2\). The values of \( Q_\text{p} \) are approximately constant regardless of \( V_\text{s} \) within the condition observed. And so, it follows from the above that almost complete dissolution by a single scanning is expected independently of \( V_\text{s} \), under the condition for deposition. The charge \( Q_\text{p} \) is Coulombs corresponding to nickel dissolved in 1.0 \( \text{NH}_2\text{SO}_4 \), \( Q_\text{d} \) is Coulombs used for deposition.

\[
\begin{align*}
Q_\text{p} & : \text{Coulombs corresponding to nickel dissolved in 1.0 } \text{NH}_2\text{SO}_4 \\
Q_\text{d} & : \text{Coulombs used for deposition}
\end{align*}
\]

Condition for deposition.

Substrate: Pt, Solution: 1.0 M \( \text{NiSO}_4 \), pH 3.0, 30°C, \( i_\text{c} \): 30 mA/cm\(^2\), \( Q_\text{p} \): 20 mCoul/cm\(^2\)

Fig. 4 Dependence of \( Q_\text{p} \) on scanning rate.
condition as mentioned previously.

3.3 Galvanostatic charging trace for initial stage of deposition

Some examples of the galvanostatic charging trace are shown in Photo 1. The trace (a) was observed for platinum substrate in 1 M NiSO₄ of pH 1.6 with \( i_c \) of 30 mA/cm². In this case, the potential jumps at once with the switching on (A in the photo.), and then hydrogen evolution is considered to take place in the course of the first step. Further, the potential goes up rapidly owing to the concentration polarization of hydrogen ion until the inflection point (B in the photo.) appears. Subsequently, the trace ascends to an overshoot (C in the photo.) and then it descends slowly to its steady state. The range extending from the overshoot to the steady state is regarded as the second step. The above inflection point is considered to be an approximate transition point where the limiting current for the hydrogen evolution is nearly attainable. And so, the time necessary to attain the inflection point since the start of electrolysis (i.e. the time from A to B) is considered to be the transition time \( (\tau) \) for hydrogen evolution. It is found for the case (a) in Photo. that \( \tau \) is about 1.1 sec, while the time necessary to attain the second step is approximately 1.5 sec.

The trace (b) was obtained in the solution of pH 1.6 with \( i_c \) of 40 mA/cm², where \( \tau \) is about 0.5 sec which becomes short as compared with that for the case (a) with \( i_c \) of 30 mA/cm².

The trace (c) is the result observed in the solution of pH 3.0 with \( i_c \) of 30 mA/cm², where no step due to hydrogen evolution is visible, and the time needed to attain the second step is found to be 0.05~0.1 sec by the highly sensitive observation.

4 Discussion

4.1 Transition time for hydrogen evolution

The transition time \( (\tau) \) for the hydrogen evolution process was observed through the charging trace as shown in Photo. 1. It was found that \( \tau \) decreased as \( i_c \) increased, and the plots for \( i_c \times \tau^{1/2} \) vs. \( i_c \) are shown in Fig. 5. The value of \( i_c \times \tau^{1/2} \) is approximately constant regardless of \( i_c \) under a given pH. The well known equation⁹ is available, provided that the process becomes controlled by diffusion of the reactant.

\[
2 \times i_c \times \tau^{1/2} = n^{1/2} \times R \times C \times D^{1/2}
\]

where \( i_c \), \( \tau \), \( n \), \( C \) and \( D \) are current density \([\text{A/cm}^2]\), transition time \([\text{sec}]\), number of electron for the process, concentration of the reactant \([\text{mol/cm}^3]\) and diffusion coefficient of the reactant \([\text{cm}^2/\text{sec}]\) respectively.

The result in Fig. 5 is consistent with Eq. (1) where \( i_c \times \tau^{1/2} \) should be constant regardless of \( i_c \) under a certain pH. Further, it may be expected from Eq. (1) that the ratio of \( i_c \times \tau^{1/2} \) for pH 1.6 to that for pH 2.0 is 2.5 which differs little from the result of 2.49 obtained in Fig. 5, on the assumption of constant diffusion coefficient within the pH range observed. Moreover, it is found from the observed \( i_c \times \tau^{1/2} \) that

\[
\begin{align*}
(a) & : 1.0 \text{M NiSO}_4, \text{pH} 1.6, i_c = 30 \text{ mA/cm}^2 \\
(b) & : 1.0 \text{M NiSO}_4, \text{pH} 1.6, i_c = 40 \text{ mA/cm}^2 \\
(c) & : 1.0 \text{M NiSO}_4, \text{pH} 3.0, i_c = 30 \text{ mA/cm}^2
\end{align*}
\]

Photo 1 Galvanostatic charging traces for initial stage of nickel deposition accompanied with hydrogen evolution
values.

As stated previously, it is considered that $Q_p$ corresponds approximately to the net nickel deposited under the condition observed. In Fig. 6, $Q_p$ vs. $t$ relation for the bath of pH 3.9 gives approximately a straight line passing through the origin, therefore it seems that the nickel deposition commences at once with the start of electrolysis and the current assigned to the nickel deposition out of applied $i_e$ (30 mA/cm²) is kept nearly constant throughout the deposition time.

Next, for the bath of pH 3.0, the straight line passes the abscissa at about 0.1 sec. This result may be understood from the fact that the time from 0.05 to 0.1 sec was needed to attain the second step since the start of electrolysis, as described previously for Photo. 1 (c).

For the bath of pH 1.6, it seems that the plot is nonlinear and passes through the abscissa at about 1.5 sec, until when the current is used mainly for the hydrogen evolution as observed in Photo. 1 (a).

On the other hand, Fig. 7 shows a typical charging curve with very low $i_e$ of 0.5 mA/cm² in the bath of pH 2.8*1, where the time needed to attain the apparently steady potential is about 60 sec. Further, the variation of $Q_p$ with $t$ is plotted in Fig. 8 (a), where the nonlinear plot is shown. The slope $dQ_p/dt$ for the plot is considered to be the current $i_{H}$ used for the nickel deposition, and the current $i_{H}$ used for the hydrogen evolution is easily estimated from the relation of $i_e=i_{H}+i_{Ni}$. And the variation of $i_{Ni}$ and $i_{H}$ with $t$ is shown in Fig. 8 (b), where $i_{H}$ or $i_{Ni}$ varies with time even after the observation of apparent steady potential at about 60 sec on the charging curve in Fig. 7. In regard to the starting time of nickel deposition, some discrepancy between the times expected from Figs. 7 and 8 is considered to be caused by the difficulty due to too small $Q_p$ to be observed.

---

4.2 Amount of nickel deposit in relation to deposition time

The charge $Q_p$, found by the graphical integration of the dissolution diagram, is plotted to the deposition time $t$ in Fig. 6, where the nickel used for the dissolution was deposited from $1.0\ M\ NiSO_4$ with $i_e$ of 30 mA/cm² under several deposition times and pH values.

As stated previously, it is considered that $Q_p$ corresponds approximately to the net nickel deposited under the condition observed. In Fig. 6, $Q_p$ vs. $t$ relation for the bath of pH 3.9 gives approximately a straight line passing through the origin, therefore it seems that the nickel deposition commences at once with the start of electrolysis and the current assigned to the nickel deposition out of applied $i_e$ (30 mA/cm²) is kept nearly constant throughout the deposition time.

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The results in Figs. 7, 8 and 9 were obtained with a platinum wire electrode, whereas those in Figs. 1–6 were obtained with a platinum disk electrode (cf. 2. Experimental).
4.3 Effect of pretreatment on estimated value of nickel deposited

The observation of $Q_p$, corresponding to the net nickel deposited, was conducted under the assumption that the oxidation of hydrogen on nickel scarcely takes place during the potential scanning. The effect of hydrogen on the observed value of $Q_p$ was examined to confirm the assumption, and the nickel deposit was anodically dissolved with or without the cathodic pretreatment at $-0.4 \, \text{V}$ for 30 sec just before the anodic scanning. In Fig. 6, the points shown by $\triangle$ or $\blacktriangle$ were found with or without the pretreatment respectively by the anodic scanning made from $-0.25 \, \text{V}$ (S.C.E.) where hydrogen evolution hardly takes place. As given in Fig. 6, a linear relation holds in both kinds of $Q_p$ observed with or without the cathodic pretreatment, therefore it is confirmed that the observed value of $Q_p$ is hardly influenced by the oxidation of hydrogen evolved during the cathodic pretreatment. Consequently, the nickel deposit on platinum was always subjected to the cathodic treatment prior to the anodic scanning, in order to reduce a trace of the oxide produced during the experimental procedure.

4.4 Dissolution limit for nickel by the first scanning

For the case where the amount of deposit was too large to dissolve by a single scanning, the deposit remained on the substrate was dissolved by the second scanning. In Fig. 9, relating to the results obtained by a single scanning of $0.1 \, \text{V/sec}$, it is found that the charges ($Q_{p*}$) corresponding to the dissolved nickel are about 50 and 70 mcoul/cm² in the case of $Q_d$ of 200 and 300 mcoul/cm² used for the deposition. Consequently, it appears that the maximum dissolution limit obtained with a single scanning is not estimated easily, since the value found by a single scanning varies with $Q_d$.

Fig. 8 Time dependence of $Q_p$ or current sharing during deposition on platinum with $i_c$ of 0.5 mA/cm² from 1.0 M NiSO₄ of pH 2.8 at 39°C

Fig. 9 $Q_d$ dependence of $Q_p$ in observation with too large amount of deposit to dissolve out by a single potential scanning in 1.0 M H₂SO₄ at 30°C. The deposit was prepared in 1.0 M NiSO₄ of pH 2.8 with $i_c$ of 10 mA/cm² at 30°C.

Nevertheless, it can be considered that the observed value of $Q_p$ used for the discussion always corresponds approximately to the net nickel, since nickel is deposited carefully so as to dissolve out by a single potential scanning, as mentioned previously.

Acknowledgement: The authors would like to express their hearty gratitude to Dr. Shigenitsu Nomoto for his valuable discussions throughout the work. The acknowledgements are also due to the Ministry of Education for its financial aid.

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化学関係学協会連合研究発表会

会 告

参考文献:

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と き：10月11日（火）～14日（土）
ところ：京大大学（名古屋市昭和区大村町）
これ関連講演：5月30日（火）
これ関連講演：6月21日（月）

1. 一般研究発表

発表時間1件20分（発表15分、討論5分）。

2. 特別討論会

会場：大学教員会議室

会期：10月11日（火）～14日（土）

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