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Author(s)	MACHIDA, K.; ENYO, M.
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## HYDROFLUORIC ACID-LEACHED RANEY Ni MATERIALS FOR WATER ELECTROLYSIS CATHODE

By

K. MACHIDA\*) and M. ENYO\*)

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We have reported recently that a series of amorphous Ni-Ti and Ni-Zr alloys after a treatment with aq. HF show a high electrocatalytic activity for the hydrogen electrode reaction (HER). This is mainly due to a porous nickel layer formed on their surface during the acid treatment, a similar manner as in usual Raney Ni electrodes<sup>1,2)</sup> which are usually prepared from Ni-Al or Ni-Zn alloys by leaching Al or Zn out with alkaline solutions. In this note, comparison will be made on electrochemical properties of Raney Ni electrodes which are prepared by development either with aq. NaOH or with aq. HF. Double-layer capacitance measurements and surface characterizations by XPS observations are also conducted.

Two types of Raney Ni electrodes were prepared by heating pure Ni wires and plates with Al powder (99.999%) at 1100~1200 K for 30 min in purified He, followed by leaching in 3 M NaOH or in 1 M HF at room temperature for several hours. Electrochemical measurements were carried out in a three compartment Pyrex glass electrolysis cell under a stream of H<sub>2</sub> at 303 K according to the technique described elsewhere.<sup>1)</sup> The electrolytic solution (1 M NaOH) employed was prepared from a special grade NaOH (Merck Japan, Ltd.) with water from a Millipore pure water system. A platinized Pt was used for the reference hydrogen electrode. The roughness factor (RF) of the test electrode was evaluated from the double layer capacitances assuming 18  $\mu\text{F cm}^{-2}$  (true). Surface analysis of the Raney Ni electrodes was performed using an ESCA apparatus (VG-III) with Al K $\alpha$  X-ray radiation. Surface sputtering by Ar<sup>+</sup> ion bombardment was carried out at 1.5 KeV and 7.5  $\mu\text{A cm}^{-2}$  for 10 min (the estimated sputtered depth is about 80 Å). The binding energy values recorded were calibrated using 4f<sub>7/2</sub> signal (83.8 eV) from a gold plate employed as an internal standard.

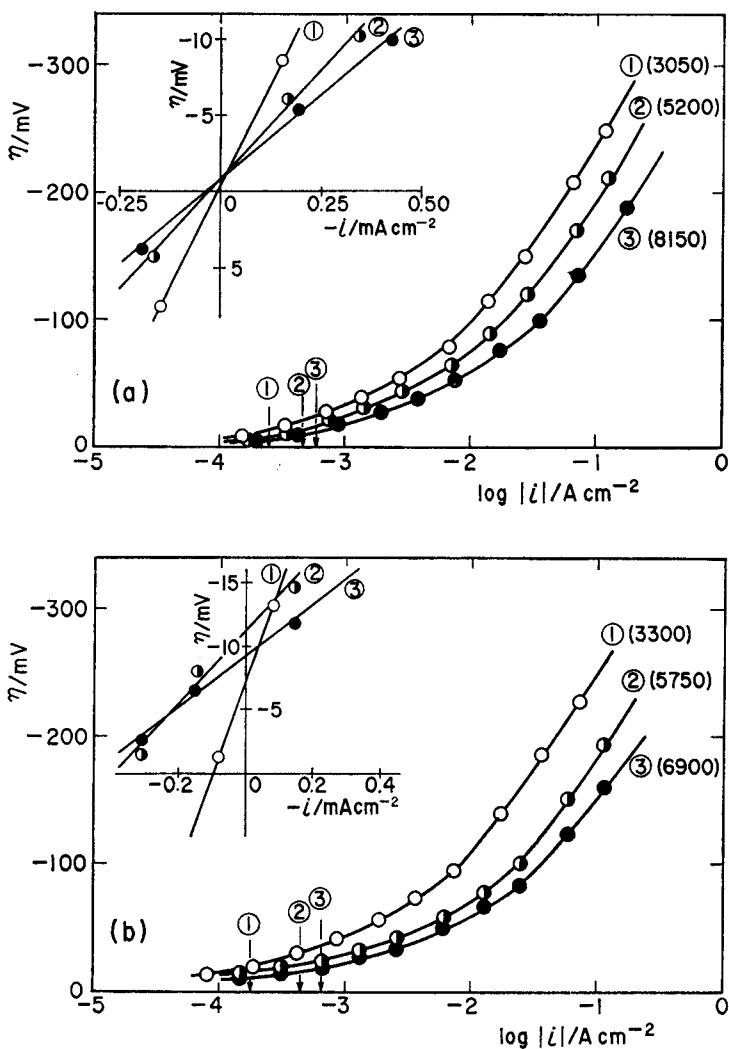
Each electrode obtained in this work gave a potential near the reversible HER potential within several hours after setting up the electrochemical cell but did not

\*) Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan.

K. MACHIDA and M. ENYO

precisely realize the reversible potential: They, particularly the HF-treated specimens, had a rest potential slightly deviated to the cathodic side ( $\sim -12$  mV). Such a rest potential may perhaps be due to ionization (dissolution) of aluminium residue in the specimens.

Cathodic polarization behaviours of the total overpotential  $\eta$  on the NaOH- and



**Fig. 1.** Cathodic polarization behaviours of a series of (a) NaOH- and (b) HF-treated Raney Ni electrodes with different degrees of roughness. The arrows on the abscissa indicate  $i_0$  obtained at low overpotentials (the inset figures) and numerals in the parentheses represent the RF values of the electrodes.

*Raney Ni for Water Electrolysis Cathode*

HF-treated electrodes with various RF values are shown in Figs. 1(a) and 1(b), respectively. Both the specimens exhibited very high values of electrocatalytic activity, and the exchange current density  $i_0$  obtained from the polarization resistance  $r$  by the relation\*)  $i_0 = (RT/2F)/r$  was as high as  $10^{-4}$ – $10^{-3}$  A cm $^{-2}$  (apparent).

Evidently, such a high electrocatalytic activity was caused by very large RF values. The relation between the current density  $i$  (at  $\eta$  chosen at  $-100$  mV) on Raney Ni electrodes and their RF values are plotted in Fig. 2, in which those obtained on amorphous Ni-Ti and Ni-Zr alloys reported earlier<sup>1)</sup> are also shown from comparison. Both the  $i$  values on the NaOH- and HF-treated Raney Ni electrodes agree with each other and they are essentially proportional to their surface roughness (the slope was some  $3.8 \times 10^{-6}$  A cm $^{-2}$  (true)). Thus, no significant difference in the electrocatalytic activity appeared to exist between the different developers used. Hence, aq. HF as well as aq. NaOH, may well be used as a developer in preparation of Raney-type Ni catalysis.

It is to be noted that the data presented in Fig. 2 of the amorphous Ni-Ti and Ni-Zr alloys, prepared by development with aq. HF have much a steeper slope. Or, the current density values per true unit surface area are much larger than those of

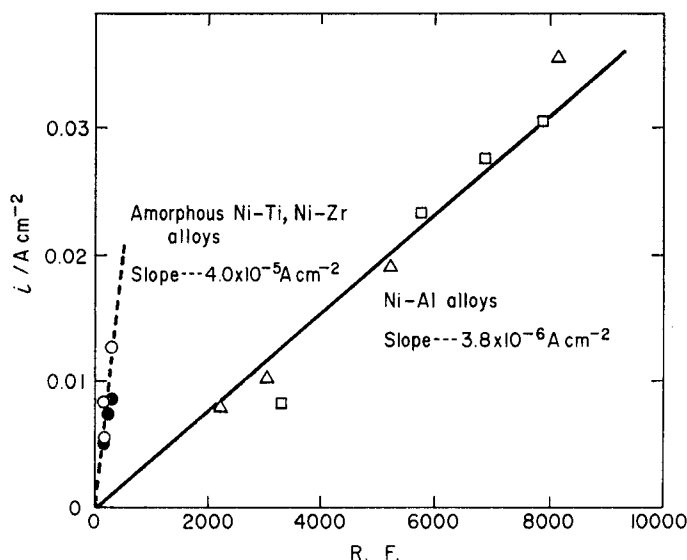


Fig. 2. The relationship between the current density (at  $\eta = -100$  mV) and RF values of the Raney Ni electrodes treated with aq. NaOH ( $\Delta$ ) or HF ( $\square$ ). Data of amorphous Ni-Ti and Ni-Zr alloys (open and closed circles)<sup>1)</sup> are given for comparison.

\*) The HER on Ni proceeds *via* the Volmer-Tafel route with mixed rate-determining characteristics but the reaction rate near the reversible HER potential is practically determined by the Tafel step.<sup>3)</sup> This introduces the factor 2 in this relation.

ordinary Raney Ni electrodes prepared from Ni-Al alloys. This difference should indicate a moderate degree of contribution of Ti or Zr in the alloys to the electrocatalytic activity, namely the "synergistic effect" between Ni and Ti or Zr.

XPS measurements of the Raney Ni specimens were carried out in the study of their surface characteristics. Figure 3 shows the XPS patterns of the  $Ni_{2p}$  electrons on the NaOH- and HF-treated specimens before and after the  $Ar^+$  ion bombardment. The NaOH-treated specimens gave two spectrum bands at 856.7 eV ( $2p_{3/2}$ ) and 874.2 eV ( $2p_{1/2}$ ) which were ascribed to  $Ni(OH)_2$ , while the spectra of the HF-treated specimens mainly consisted of those of  $NiF_2$ :  $2p_{3/2}$ , 859.0 eV;  $2p_{1/2}$ , 876.6 eV. After the  $Ar^+$  ion bombardment, the additional spectra derived from metallic Ni and NiO were observed at the peak positions of 853.3 and 855.3 eV for  $2p_{3/2}$  or 870.5 and 873.7 eV for  $2p_{1/2}$ ,

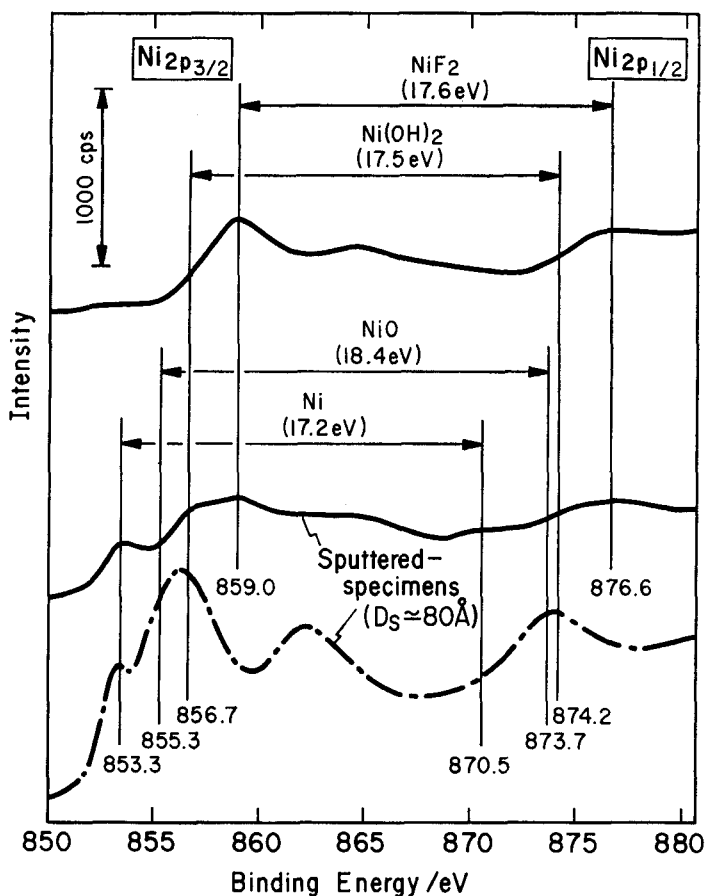
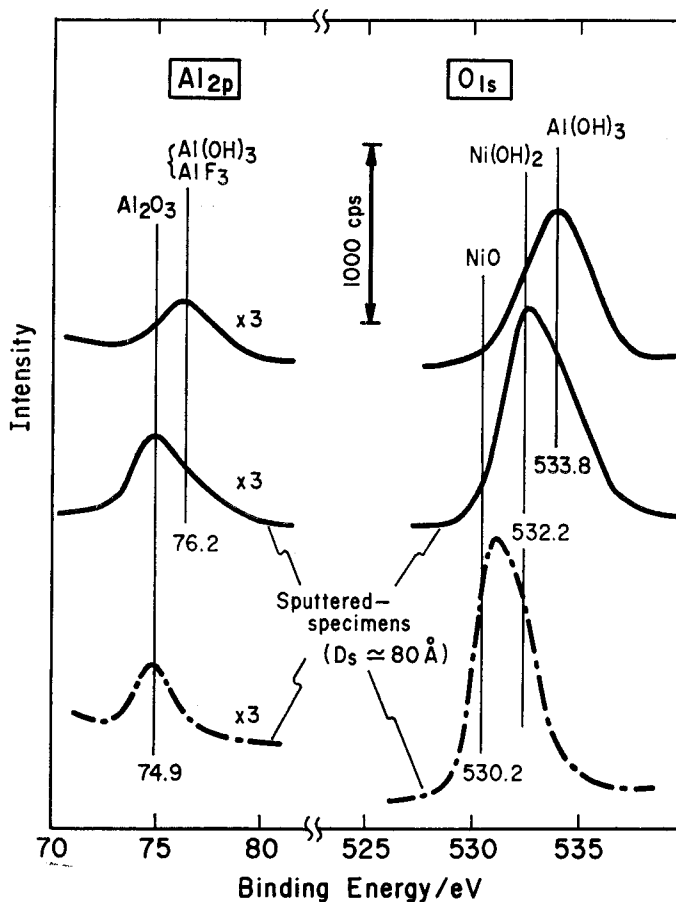


Fig. 3. XPS patterns of the  $Ni_{2p}$  electrons on the Raney Ni specimens treated with aq. NaOH (broken line) and aq. HF (solid lines).

*Raney Ni for Water Electrolysis Cathode*

respectively. The differences in the binding energy values between the  $2p_{3/2}$  and  $2p_{1/2}$  spectrum peaks in each valence state were as follows: metallic Ni, 17.2 eV; NiO, 18.4 eV;  $\text{Ni(OH)}_2$ , 17.5 eV;  $\text{NiF}_2$ , 17.6 eV. These peak positions and binding energy differences perfectly agreed with the XPS data listed in a handbook<sup>4)</sup> or in the literature.<sup>5)</sup> It is concluded, therefore, that most of the nickel on the surface of the HF-treated specimens exist as  $\text{NiF}_2$ , while the surface of the NaOH-treated one is covered with  $\text{Ni(OH)}_2$ . However, since  $\text{NiF}_2$  and  $\text{Ni(OH)}_2$  are both expected to be reduced to metallic Ni by cathodic polarization and since the amount of  $\text{NiF}_2$  is small, the NaOH- and HF-treated electrodes would show, as actually observed, the electrochemical properties similar to each other.

XPS signals from the Al residue were also detected on both the NaOH- and HF-



**Fig. 4.** XPS patterns of  $\text{Al}_{2p}$  and  $\text{O}_{1s}$  electrons on the Raney Ni specimens treated with aq. NaOH (broken lines) and aq. HF (solid lines).

K. MACHIDA and M. ENYO

treated specimens (Fig. 4). The  $Al_{2p}$  spectra from the HF-treated specimens have a peak at about 76.0 eV, which is attributed to  $Al(OH)_3$  or  $AlF_3$ , although the NaOH-treated one gives only the spectra derived from  $Al_2O_3$  (the  $Al_{2p}$  signal is observed at 74.9 eV). Furthermore, the signals from the  $Al_2O_3$  on the HF-treated specimens were increased by the  $Ar^+$  ion bombardment, contrary to the decrease of those from  $Al(OH)_3$  and  $AlF_3$ .

Strong signals of  $O_{1s}$  were observed on the Raney Ni specimens, as shown in Fig. 4. The spectra from hydroxyl groups of the specimens before the  $Ar^+$  ion bombardment were assigned to  $Ni(OH)_2$  for the NaOH-treated specimens and  $Al(OH)_3$  and  $Ni(OH)_2$  for the HF-treated specimens, respectively, where  $Ni(OH)_2$  gave a band at 532.2 eV and  $Al(OH)_3$  at 533.8 eV. The  $Ar^+$  ion bombardment also gave rise to an additional peak derived from NiO at 530.2 eV. Signals from the oxygen of  $Al_2O_3$  were not clearly observed.

In summary, aq. HF can effectively be employed in preparation of some Raney Ni alloys, as same as aq. NaOH and KOH. This suggests that new Raney Ni electrodes with some additional properties, *e.g.* high hydrogen absorbability and improved electrocatalytic activity, can be prepared starting with Ni-based alloys which contain other components than Al or Zn which are hardly leached out in alkaline solutions.

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