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Author(s)	MITUYA, Atusi; SAKAI, Toshiyuki
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INVESTIGATION OF THE HYDROGEN ELECTRODE REACTION ON ORDERED AND DISORDERED Ni₃Mn ALLOYS. PART I

By

Atsui MITUYA and Toshiyuki SAKAI^{*})

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THOMPSON¹⁾ studied the transformation temperature, electric resistivities, and magnetisms of ordered and disordered Ni₃Mn alloys. TAOKA and OHTSUKA²⁾, and YAMAMOTO and TANIGUCHI³⁾ worked in detail on the magnetic properties of ordered alloys. KAYA and KUSSMANN⁴⁾ reported the differences in magnetism, while GOLDMANN⁵⁾ observed the Hall-coefficients and electronic specific heats of these alloys, finding appreciable differences between them. Present authors have investigated the hydrogen electrode reaction on these Ni₃Mn alloys for the purpose of finding a key elucidating the effect of metal structure upon the latter process.

Hydrogen electrode reactions have hitherto been observed in most of cases at higher cathodic polarizations above a few hundreds mV. MITUYA and his co-workers^{6,7)} have developed a process of preparing and operating the electrolytic cells completely in vacuum, with which they have consistently observed the hydrogen electrode reaction on mercury and lead cathode at extremely low cathodic polarizations. Usual procedures of excluding air by pure hydrogen stream was now alternatively tried for the observation of the hydrogen electrode reaction on disordered Ni₃Mn alloy in place of the vacuum process by MITUYA and YAHATA^{**)} but with hopelessly fluctuating results. The present authors have thus been obliged to follow the vacuum process as in the previous works^{6,7)} as reported below.

Experimental

Preparation of materials:

^{*}) A. M. and T. S.: Department of Chemistry, St. Paul's University (Rikkyo Daigaku), Ikebukuro, Tokyo.

^{**)} Unpublished paper.

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(1) Electrodes; Ni₃Mn alloys for the cathodes were prepared according to the KAYA-NAKAYAMA method in the laboratory of prof. KAYA of Tokyo Univ. in the form of disks of 1.5 cm diameter and 0.4 cm thick. A lead wire was fixed to one side of the disk by electroplating copper metal on the both to combine them. The surface of the electroplated copper was now covered with methyl methacrylate and further with araldite resins^{*)}. A diagram of the make-up of the ordered and disordered Ni₃Mn electrode is shown in Fig. 1.

The reference electrode and the anode were platinum disks both of 1.5 cm diameter. Their purity was guaranteed by TANAKA Precious

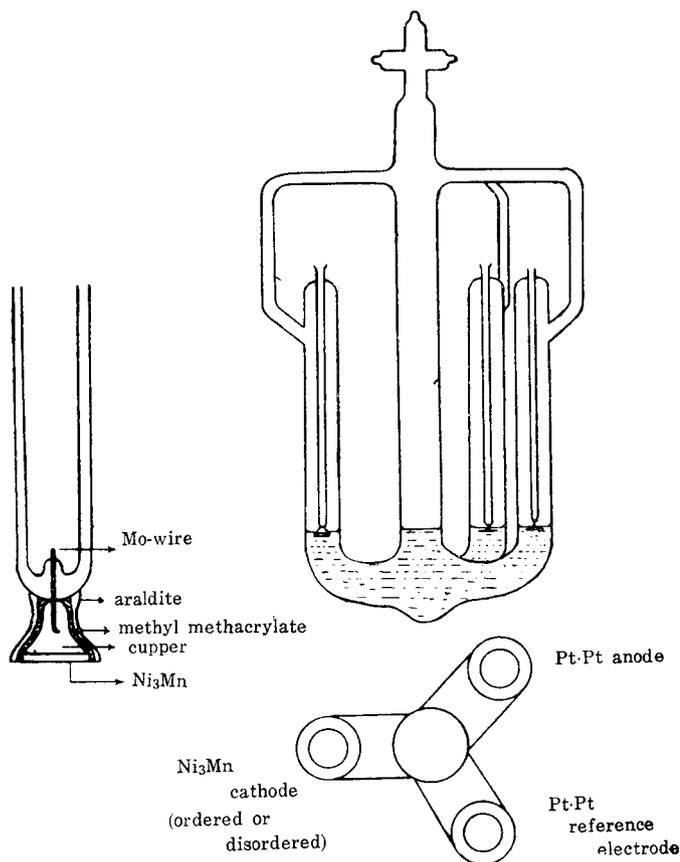


Fig. 1. Diagram of the electrolytic cell.

^{*)} Methyl methacrylate-resin must have been covered with araldite-resin to obtain high vacuum because of its appreciable vapour pressure.

Metal Work Co., Tokyo, as 99.99%. They were platinized and washed as usual, and then electrolytically purified⁶⁾ in pre-electrolyzed 0.1N-HCl solution for more than 60 hours with 0.8 mA current. With this treatment both of the electrodes attained the same potential when immersed in the pre-electrolyzed 0.1N-HCl solution either in the absence or presence of hydrogen.

(2) Hydrogen gas; Cylinder hydrogen was purified by passing it through a palladium thimble and a trap cooled by liquid oxygen.

(3) 0.1N-HCl; 0.1N-HCl was prepared according to the scheme of Diagram 1, which was essentially the same as that described in the previous work⁶⁾.

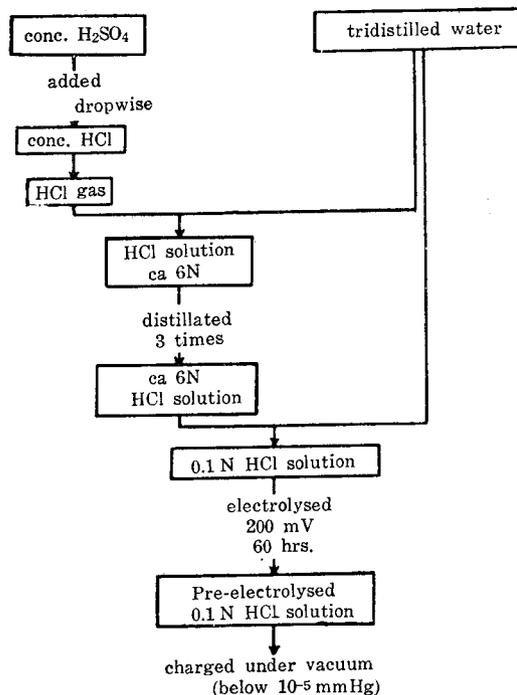


Diagram 1. Schematic diagram of purification of 0.1N HCl for electrolyte.

Preparation of electrolytic cell:

Fig. 1 shows the cell of hard glass used for the determination of the potential-current relation, provided with a Ni₃Mn cathode, platinum anode and reference electrode mentioned above. Tenth normal hydrochloric acid and 720 mm Hg hydrogen gas (at 0°C) were introduced into

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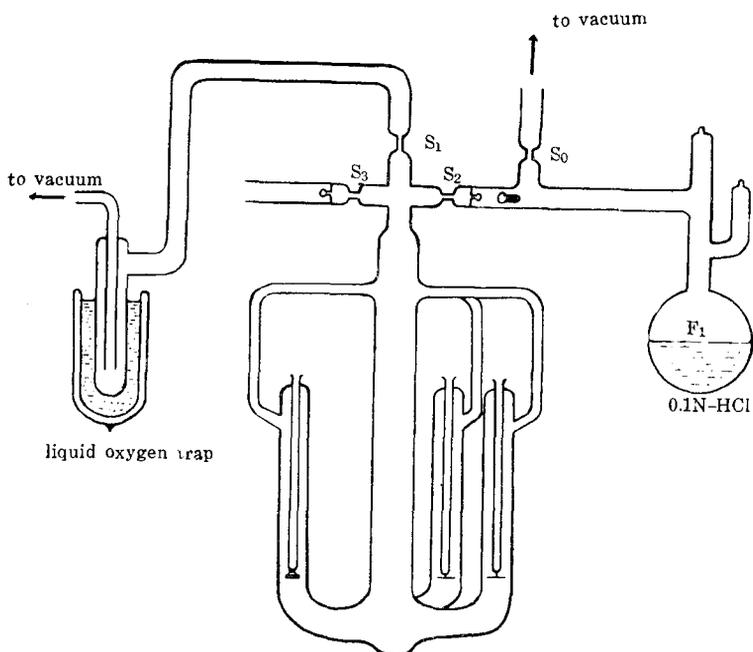


Fig. 2. Diagram of the apparatus for the introduction of 0.1N HCl and H₂ gas into the cell.

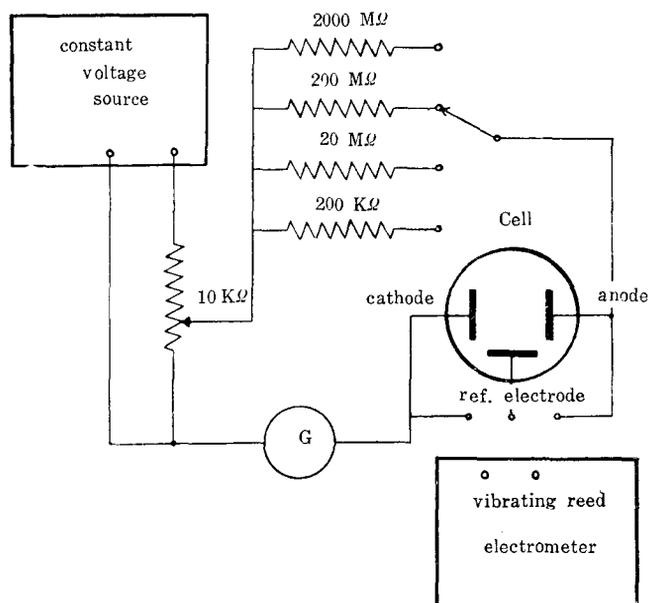


Fig. 3. Diagram of circuit for the cell.

the cell by an arrangement shown in Fig. 2 in vacuum similarly as in the previous work⁶.

Fig. 3 shows the circuit for the determination of the potential-current relation by means of a vibrating reed electrometer and a ballistic galvanometer.

Result

Fig. 4 shows a typical series of η - $\log i$ measurements at 0°C conducted in succession in the order signified by numbers annexed to points of the measurements, where η is the potential of the test electrode

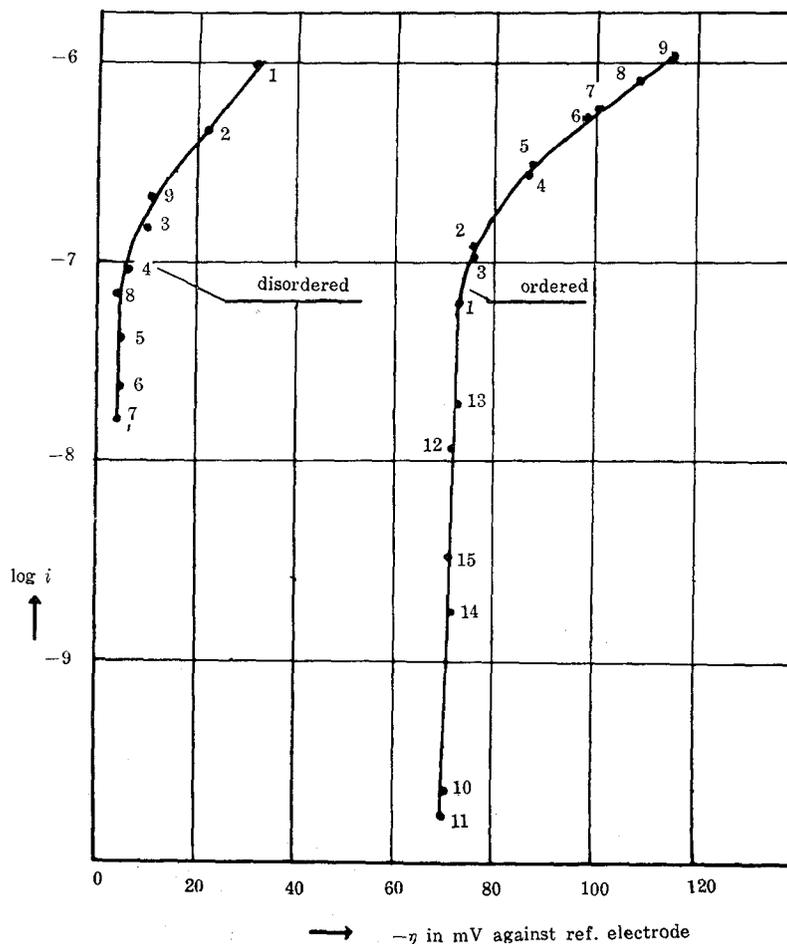


Fig. 4. The results of the η - $\log i$ relation on Ni_3Mn alloy cathodes.

referred to the reference electrode and i the current density. Each measurement was conducted at a constant current to observe η -value finally attained after 24 hours. The final η -value of the points of lowest and second lowest current of disordered alloy fluctuated within 7 and 3 mV respectively, whereas such fluctuation of other points was, if any, within 0.1 mV. Except in a few measurements of the ordered alloy at higher polarization, η gradually increased (decreased) after the constant current was switched on from a higher (lower) constant value of the foregoing measurement as in the case of the previous observation of the hydrogen electrode reaction on mercury⁶⁾. This is interpreted similarly as in the previous case that the gradual change of η is caused by the ionization or deposition of metal on the electrode adjusting the concentration of metal ion in the solution to that of equilibrium at the electrode potential finally attained, the constant current being that of the genuine hydrogen electrode reaction at the potential^{*}). It follows that η is too high or too low in general as attained after a limited time (24 hrs) according as the constant current is lowered or raised just as perceptible in Fig. 4. Nevertheless they together settle closely consistent curves as seen there. On this ground the point of the lowest current is not as well established as those of higher currents.

Results of the similar series were found reproducibly coincident with each other within experimental errors.

The electrode potential of ordered and disordered alloy was found at zero current lower than the potential of reversible hydrogen electrode by 96 mV and 5.6 mV respectively as observed after the series of measurements of Fig. 4. This result is explicable on the basis of the above results similarly as in the case of hydrogen electrode of lead⁷⁾ as follows. The concentration of metal ion in the solution is that of equilibrium of the last measurement which is the lower, the greater the appropriate cathodic polarization. To attain now the equilibrium of

*) At a constant η , the ionization of metal proceeds until the concentration of metal ion attains that at the equilibrium in the case of the solution closed in a vacuum system as in the previous experiments^{5,7)} as well as in the present experiment. When constant η was switched on from a foregoing lower value, the concentration of metal ion must increase to attain the equilibrium. The current should hence be initially small owing to that of metal ionization in the reverse direction tending gradually to a steady value corresponding to the genuine hydrogen electrode reaction. Keeping the current constant instead and switching it on from a foregoing higher value, η should initially be too low but increase gradually up to the steady value.

ionization at zero polarization metal must be more or less ionized to increase the concentration of ion in the solution, being electrically counterpoised by the progress of the hydrogen electrode reaction $2\text{H}^+ + 2\text{e} = \text{H}_2$. The hydrogen electrode reaction is, however, extremely slow particularly at lower polarization as seen from Fig. 4. It follows that the rise of the electrode potential is practically arrested at more or less lower electrode potential than that of reversible hydrogen electrode, depending upon the extent of previous cathodic polarization and the slowness of hydrogen electrode reaction. The arrested potential must be lower, as observed in the case of ordered alloy, when the polarization of the measurements is greater, and the hydrogen electrode reaction is much slower.

Above results show that the hydrogen electrode reaction on ordered alloy is definitely slower than on disordered one.

Résumé

1. By preparing and operating the electrolytic cell exclusively in vacuum instead of relying upon the usual method of excluding air by hydrogen stream, the current (i)-potential (η) relation of the hydrogen electrode reaction on ordered and disordered Ni_3Mn alloy was consistently observed over the cathodic polarizations $-\eta$ below 115 mV and 32 mV respectively.

2. The $\log i$ varies not linearly with η but decreases more rapidly with increase of η .

3. The hydrogen electrode reaction on ordered Ni_3Mn alloy was found considerably slower than that of disordered Ni_3Mn alloy.

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