Sign Reversal of Thermo EMF on Hydrogen Diffusion in thin Nickel Foils

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On cathodic hydrogen diffusion thin foils of nickel (6 micron thickness) show a sign reversal in their thermo electric power. The original value $-17\ \mu V/^{\circ}C$ changes to $+3\ \mu V/^{\circ}C$ after diffusion. The results are interpreted in terms of a possible 4p band filling by the electrons donated by hydrogen. Annealed foils retain hydrogen longer than the unannealed ones.

Introduction

In an earlier paper [1] the effect on thermo emf of cathodic hydrogen diffusion in annealed and unannealed nickel wires was reported and the results were interpreted in terms of the filling-in of d-band by electrons donated by hydrogen. The sign of the thermo emf before and after hydrogen diffusion remained negative – only the magnitude changed. In that paper it was mentioned that nickel foils show a sign reversal in the thermo emf after hydrogen diffusion. The present note describes the experiments and their results for foils.

Experimental

Foil stripes, 20 cm long, 3 mm wide and 6 microns thick, were subjected to cathodic hydrogen diffusion by electrolysis. Hydrogenated foils are brittle and difficult to handle. A special sample holder made of glass was constructed. This is shown in Figure 1. A ladder-shaped structure of 2 mm glass rods is made and bent into the form shown in the figure. The foil strip is made to pass through the horizontal stripes of glass alternately above and below as shown. This arrangement ensures safe handling. The entire system was placed in the electrolysis cell. A platinum wire was attached to the nickel foil as a lead. Another platinum wire forming the anode, was dipped in the solution. The solution of the electrolyte was acidulated water with traces of thiourea; the importance of the latter has already been stressed by Nigam and Garg [1]. Current was supplied by a 6 volt battery and was kept at 30 mA. Previous work [2, 3] has shown that such foils get saturated with hydrogen after 24 hours of electrolysis. After hydrogenation the sample holder was removed from the cell and fixed in position, as shown in Fig. 2, for thermoelectric measurements by a standardised 10-wire potentiometer. The cold junction was maintained at the temperature of melting ice and the hot one at room temperature. Junction temperatures were recorded by thermometers dipped in mercury. These are not shown in the figure. The variation in thermo emf with time was recorded. To get the absolute value of the thermoelectric power the value of copper $(+3.3\ \mu V/^{\circ}C)$ was subtracted from the measured values. When hydrogenated foils are left to themselves they lose hydrogen and slowly return to their original state.

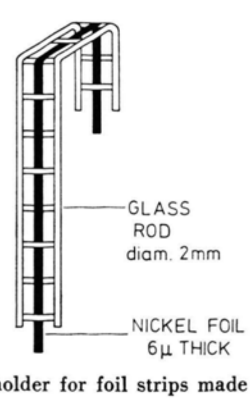

Fig. 1. Sample holder for foil strips made out of glass rods.

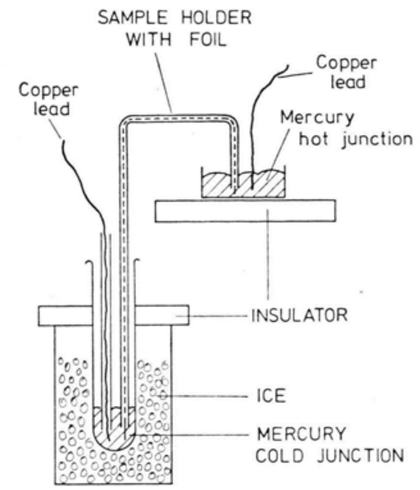

Fig. 2. Schematic setting of the sample holder for thermoelectric measurements.

Results and Discussion

The variation of thermo electric power with time is shown in Figure 3. There is a sign reversal of thermo electric power. Before hydrogen diffusion the foils gave the value $-17\ \mu V/^{\circ}C$. After hydrogen diffusion this value is $+3\ \mu V/^{\circ}C$ for unannealed and $+2\ \mu V/^{\circ}C$ for annealed samples.

It is still an open question why foils should behave differently from wires? A wire is drawn while a foil is rolled. The x-ray diffraction patterns

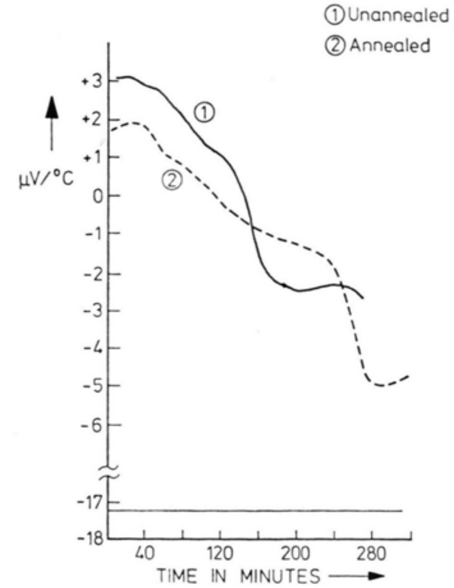

Fig. 3. Time variation of thermoelectric power for hydrogenated foils.

of the two are different. Pole figure studies of the two have not been carried out as yet. Yet there is a different aspect: The wires used in (1) had a diameter of 250 microns while the foils were 6 microns thick. The foil reaches saturation earlier than the wire. After the filling of d-band is complete the probability of 4p band filling is larger in a foil than in a wire. In case this can happen the sign reversal in thermo emf can be explained as follows. The thermo electric power is given by [1]

$$d\theta/dT = -\sigma/\varepsilon \qquad (1a)$$

where

$$\sigma = \frac{\pi^2 k^2 T}{\zeta} + \frac{1}{3}\,\frac{\pi^2 k^2 T}{\zeta^{1/2}}\left(\frac{\partial n_s}{\partial E} + \frac{\partial n_d}{\partial E}\right), \qquad (1b)$$

T is the absolute temperature, k the Boltzmann constant, ζ the Fermi energy, n the density of states of the electron in a band whose suffix is added to n and E the band energy. In case of wires, only 3d band filling occurs and $\partial n_d/\partial E$ remains negative. If 4p band starts filling up, $\partial n_p/\partial E$ will have a positive sign. This is one possible way of looking at the sign reversal. It can also happen that after the d band is full the conduction process is dominated by the free protons of diffused hydrogen. The sign of ε in (1a) will change and so also that of thermo emf. Which of these mechanisms is true can be decided by a Hall Effect measurement on hydrogenated foils. The authors are planning experiments in this direction.

One notes that the annealed and unannealed foils behave differently. We had done a vacuum annealing at 288 °C for three hours followed by furnace cooling. The annealing process affects the grain boundries and the orientation of the grains. The packing becomes more close. Now, the process of hydrogen diffusion has two aspects: a) the filling in of the conduction band and b) the passage of hydrogen through the grain boundaries. The fact that annealed foils return to their original state after 4 days while the unannealed ones after just a day, shows that the former can retain hydrogen longer than the latter. This can happen only when the annealed foil offers a greater resistance to hydrogen outflow than the unannealed one. Greater resistance implies narrowing of the grain boundaries' space; a reduction of the density of discontinuities. The internal friction measurements [4] on hydrogenated nickel support this line of arguments.

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