Electrode Potential of NiH

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THE electrode potential variation in nickel foils and wires has been recorded during hydrogen diffusion and also during subsequent outgassing. The results are discussed in terms of Gurneys' model of metal dipped in a solution.

THE electrode potentials of hydrogenated nickel for different amounts of hydrogen content were measured by Szlarska-Smialowska and Smialowska[1]. Their procedure can be summarised as follows : A 0.5 mm thick copper foil was electroplated to form about 0.017 mm thin layer of nickel. The nickel plated foil was subjected to cathodic hydrogen diffusion using the method of Baranowski and Smialoski[2] for a known time. Thereafter its electrode potential was measured by dipping it in 0.1 N H_2SO_4 solution against a hydrogen electrode. The hydrogen content of the foil was determined by a volumetric method. A curve is thus obtained for electrode potential versus hydrogen diffusion. Similar studies have been made with nickel metal foils and nickel wires instead of copper foils plated with nickel. The two show different behaviour. If a hydrogeneated nickel foil or wire is left to itselt, it loses hydrogen with time. This process is called outgassing. We have measured the electrode potentials not only during hydrogen diffusion but also during outgassing.

The difference in the behaviour of foils and wires has been discussed on Gurney[3] model of electrode potential. In a foil surface states will dominate and hence the former will behave differrently from a wire.

EXPERIMENTAL

Sample preparation : For obtaining a stable and reproduceable electrode potential in case of nickel wires, it was essential to anneal them in high vacuum. About 20 cm lengths of Ni-wires having diameter 0.2 mm were sealed in glass capsules under 10^{-6} Torr vacuum and subjected to three hours of annealing at the desired temperatures (240, 340 and 470°C) and subsequently furnace Cooled. Samples annealed thus were chemically polished using the following procedure recommended by de Jong[4]. In an ice cooled beaker are added the following substances in the order given below :

a) Conc. H_2SO_4 10 c.c.

b) Conc. HNO_3 30 c.c.

c) Glacial Acetic Acid 50 c.c.

d) Orthosphosphoric acid 10 c.c.

The solution is then heated to boiling and the annealed wires are supended in it for $\frac{1}{2}$ a minute or less, then taken out, washed first with distilled water and then with methanol. Nickel foils of different thickness were supplied by M/s. Vacuum Geschmelze, Hanau, W. Germany. They did not require annealing and were used as such directly.

Hydrogen diffusion : The electrolytic cell consisted of two platinum electrodes in a solution of 0.2 gm of thiourea and 10 c.c. of H_2SO_4 in 1 liter of distilled water. Nickel sample was fixed at the cathode. The current was kept fixed at 30 mA from a 6 volt battery. Hydrogenated Ni foils are brittle and difficult to handle. A special sample holder of glass as described earlier[5] was used. This ensured safe handling of the hydrogenated foils. About 24 hours of electrolysis in foils (3, 4 and 6 microns thick) brought a state of saturation of hydrogen while the wires needed 3 days time.

Measurement of electrode potential : During hydrogen diffusion, the samples were taken out from time to time, washed by methanol and dipped at once in the solution for measurements. The solution in one series of experiments was 0.1 N H_2SO_4 in distilled water and the second series of measurements were done by a saturated solution of nickel sulphate (A.R.) in distilled water. The solution was connected to a saturated calomel electrode via a KCl bridge. The potentials were read on a Toshniwal Titration Potentiometer model CI 106A. Each measurement took 30 seconds time at the maximum. After the measurement the sample was taken out of the solution, washed with

methanol and placed in the electrolytic cell for further electrolysis.

Observations during hydrogen outgassing were also recorded. During the outgassing the samples was exposed to air. For measurement of the electrode potential, each time the sample was dipped in the required solution.

RESULTS AND DISCUSSION

Foils : Fig. 1a shows the variation of the electrode potential with time of hydrogen diffusion

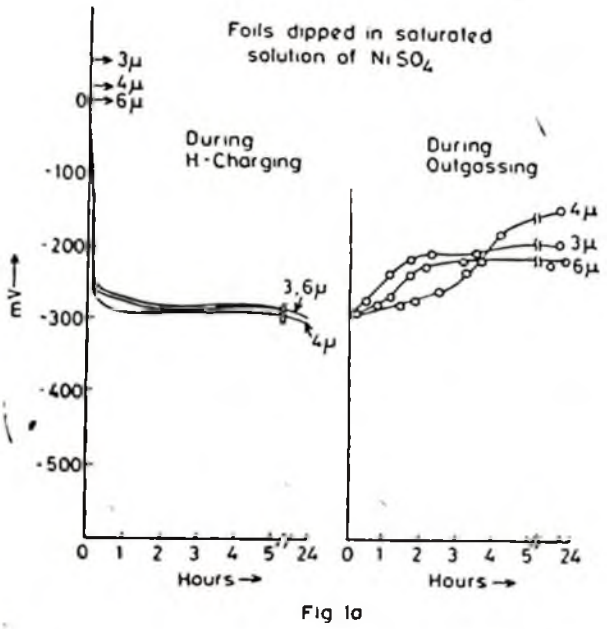


Fig 1a

Fig. 1(a) Variation of electrode potential of nickel foil during and after hydrogen diffusion when the foil is dipped in saturated solution of $NiSO_4$

for foils dipped in a saturated solution of nickel sulphate. Each foil gave a curve with similar shape. Slight variations in the initial potentials do occur. The right hand side of each figure represents the variation of the electrode potential during hydrogen outgassing. Fig. 1b shows the above variation for foils dipped in 0.1 N H_2SO_4. Fig. 1c is a reproduction of the results of Szlarska-Smialowska and Smialowska[1] for the sake of comparison. The outgassing curves of these workers have not been drawn because they outgassed hydrogen in an alkaline medium where the rate of outgassing is greatly accelerated.

Wires : Figs. 2a and 2b are the curves obtained for nickel wires. The extra hump is a feature characteristic of the wires and is absent in case of

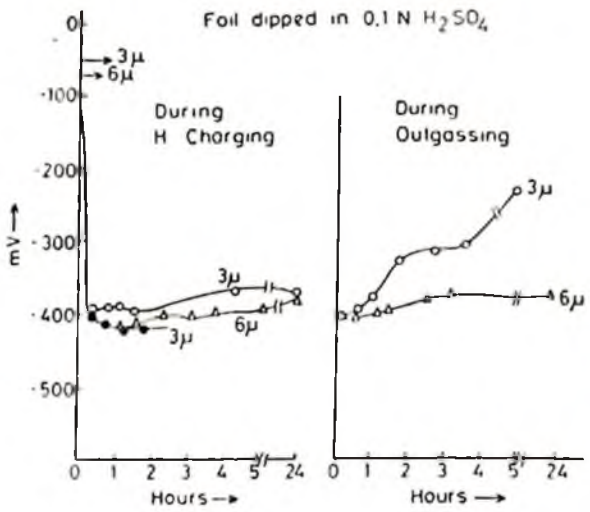


Fig 1b

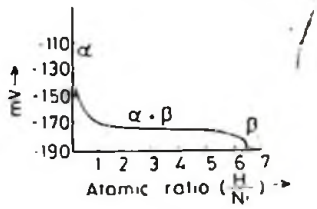


Fig 1c

Fig. 1(b) Variation of electrode potential of nickel foil during and after hydrogen diffusioe when the foil is dipped in 0.1 H_2SO_4

Fig. 1(c) Comparison of the curve obtained by authors of ref.(1)

foils. Foils thicker than 6 microns do show this hump and the wires thinner than this dimension do not show this hump. During outgassing of hydrogen, oxide layer will be formed at the surface whose thickness is highly irreproduceable. Hence the curves for outgassing corresponding to different samples can never coincide.

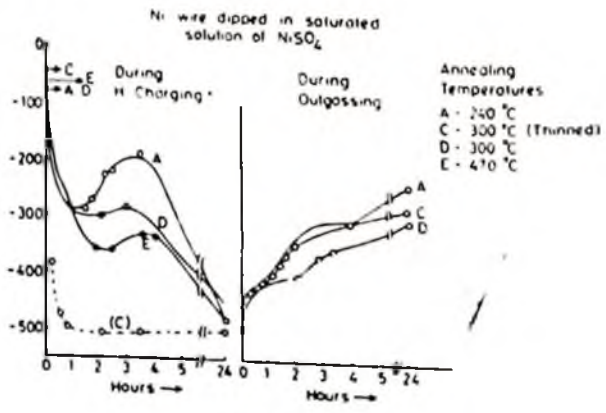


Fig 2a

Fig. 2(a) Variation in electrode potential of nickel wire during and after hydrogen diffusion when the wire is dipped in saturated solution of $NiSO_4$

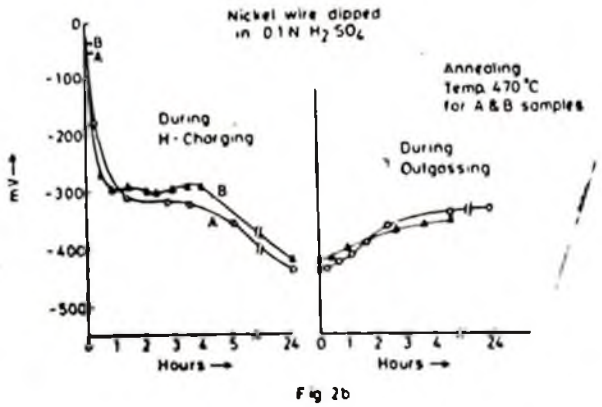


Fig. 2(b) Variation in electrode potential of nickel wire during and after hydrogen diffusion when the wire is dipped in 0.1 N H_2SO_4

The process of hydrogenation of nickel involves the filling-in of the vacant part of the d-band of the metal by the electrons donated by the diffusing hydrogen. For this reason, it would be more appropriate to discuss the present results in terms of the quantum mechanical model of metal in a solution as proposed by Gurney[3] instead of using the conventional thermodynamic approach.

For a metal dipped in a solution, Gurney considers the potential energy curves for the metal ions at the surface of the metal in relation to the corresponding curve for the metal ion in solution, Fig. 3. If the solution curve is at a greater height, the solution will deposit ions on the metal surface. If the reverse holds, there will be a dissolution of the metal into the solution. Based on these concepts, Gurney[3] derived the following expressios for the electrode potentiel of a Metal :

$$V = \frac{kT \log \beta c}{me} + \frac{U_m - U_s}{me} \qquad (1)$$

where β is the ratio of the transition probabilities for deposition to dissolution, c the concentration, U_m is the energy level of ion in the metal, U_s is the energy level of the metal ion in solution, m and e are electronic mass and charge respectively. Here we have neglected Fowler's correction for concentration which is given as an appendix in Gurney's paper. The reason for this is that in our case, the solutions used are of fixed concentrations.

This model of Gurney has been slightly modified by Gerischer[6] only in so far as the Fig. 3 is concerned, the essential ooncepts remain the same. The potential energy curves of the above figure are replaced by the Fermi distribution function curve for the metal and the Maxwell-Boltzmann distribution curves for the solution. This is illustrated in Fig. 4.

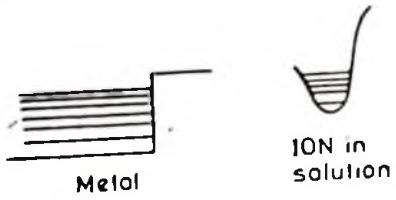


Fig 3

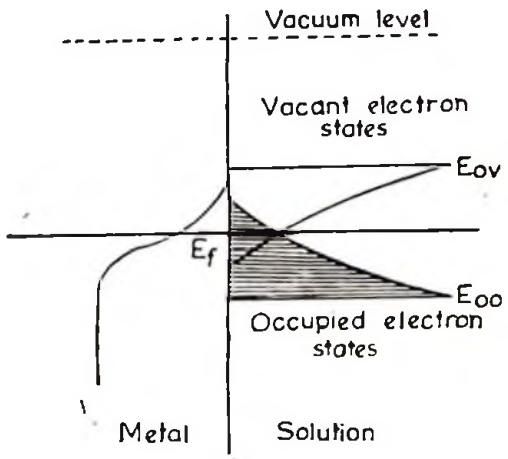


Fig. 4

Fig. 3 Electronic energy levels of metal and ion according to ref. (3)

Fig. 4 Electronic density of states distribution in metal and soiution according to ref. (6)

Now, going just a step further, Fermi distribution curve can be replaced by the actual d-band density of states curve showing the filled and unfilled parts in Fig. 5. By dotted line is shown the density of states curve for the surface state of chemisorbed hydrogen. With this back ground the difference in the behaviour of wires and foils can be understood.

In the present set of experiments, considering the geormetic areas only) the current densities in case of foils is about 5 mA/cm² and in case of wires about 24 mA/cm². Since even the value of 5 mA/cm² is quite high, the charging in both wires as well as in foils is controlled by diffusion of hydrogen (and not by the current density). When a wire is

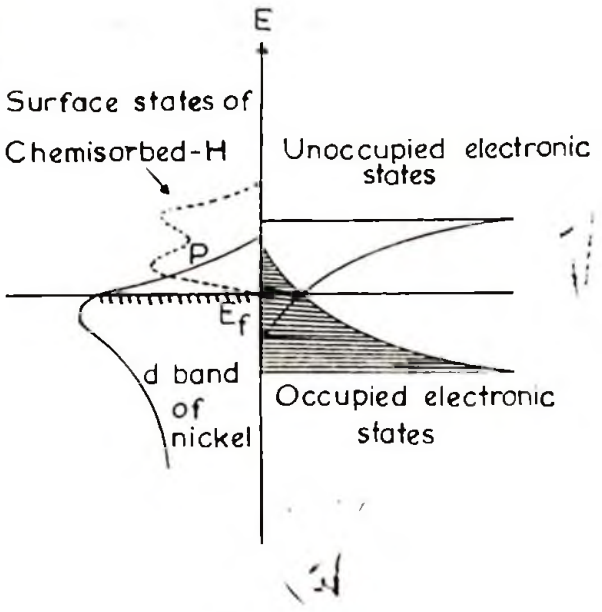


Fig. 5

Fig. 5 Proposed electronic density of states in nickel metal and solution Surface states are shown by dashed curve

subjected to cathodic polarisation, it gets charged with hydrogen over a distance depending on the time of polarisation i. e. the time available for inward diffusion. The thermodynamic activity of hydrogen at the surface is high (10^3 atmospheres) and becomes zero at the centre as long as saturation is not reached. On stopping the current, surface hydrogen is partly lost and the surface overvoltage falls. When such a wire is dipped in $NiSO_4$ solution the highly active hydrogen reacts with Ni^{++} ion of the solution.

$$2H + Ni^{++} \longrightarrow Ni + 2H^+$$

The surface hydrogen is exhausted but is replaced by hydrogen supplied from the interior. The metal gets a potential between −0.15 V (Active H) to about +0.15 V (Ni^{++}/Ni). With reference to the Calomal electrode the potential would have to be between −0.1 V and −0.4 V as is observed. The process is illustrated in Fig. 6 showing the conc. of hydrogen against the distance diffused in two cases: a) just after charging and b) after dipping in $NiSO_4$. These are not drawn to scale and are hypothetical. In terms of Fig. 5, the above process implies the following. The d-band filling in will raise the Fermi level in the metal and the potential will become more negative. The reaction written above implies the electron transfer to the solution energy levels above the dashed line (right hand side) and the observed potential is seen to rise (Fig 2). This process continues as long the filling in takes place in the neighbourhood of E_F where the density of states is high and so is the probability of electron transfer from metal to solution. As soon as the upper part of the d-band is approached, the density of states is lowered (such as at the point P in Fig. 5) and hence the transfer probability is also lowered, the levels on the left hand side start rising above E_F and the potential is again negative.

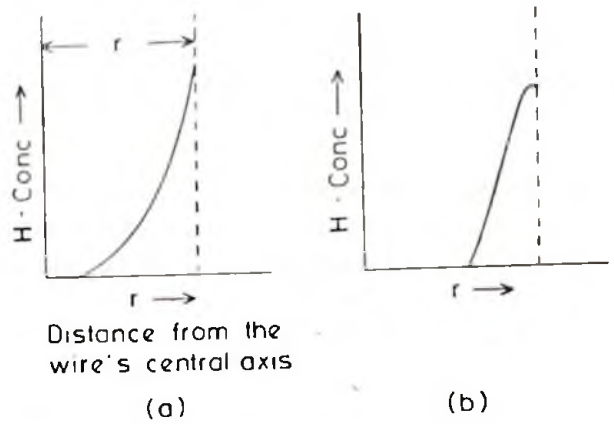


Fig 6

Fig. 6 Distribution of H-conc. inside a wire

A foil surface will have an oxide layer. However the obsorved hydrogen will build up a two dimensional lattice giving rise to the surface states of the chemisorbed hydrogen. These are shown by dotted lines in Fig. 5 and they will dominate the electrical behaviour of the foil. A qualitative quantum mechanical discussion and the utility of such states is given by Horiuti and Toya[7]. The shape shown in Fig. 5 is only tentative. It is similar to the metal surface states showing a dip in the middle. No quantitative calculations exist for these states of the chemisorbed hydrogen. The probability of transfer of the electrons from the metal surface to the solution thus remains low. In the initial stages the filling in is slow due to low density of states and the potantial is nearly constant at a negative value (Fig. 1). As the filling in proceeds further, the potantial shows a tendency of becoming more negative. The left hand side levels in Fig. 5 will rise above E_F in the dotted part of the curve and the potential will be negative.

The above explanation is phenomenological only.

Acknowledgement

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REFERENCES

1. Z. Szlarska-Smialowska and M. Smialwska, *Jour. Electr. Chem. Soc.*, 110 (1963) 444
2. B. Baranowski and M. Smialowski, *Jour. Phy. Chem. Solids*, 12, (1969) 206.
3. R. W. Gurney, *Proc. Roy. Soc.* (London) A136 (1932) 378.
4. J. J. de Jong, *Metallen*, 9 (1954) 2.
5. A. N. Nigam and R. Rani, *Zeit. Naturforsch.*, 30a (1975) 1787.
6. H. Gerischer, In C. Gatos' book 'The Surface Chemistry of Metals and Semiconductors', John Wiley and Sons New York (1969).
7. J. Horiuti and T. Toya, Solid State Surface Science Vol. 1, Ch. 1, 1969, Ed. by M. Green, M. Dekker, Inc. New York.