*On the Relation between the Hydrogen Overpotential and the Magnetic Susceptibility of Copper-Nickel Alloys**

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Introduction

In the case of the catalytic hydrogen electrode reactions, the present author paid special consideration to the influences of the two chief factors governing the general catalytic reactions, one of which is the so-called "geometric factor" and the other the "electronic factor." About the former the present author and Mukaibo previously discussed[1,2] the experiments on the variation of the slope of the Tafel line due to the steric hindrance caused by the adsorbed organic catalytic poisons.

It is the object of the present paper to explain how the latter-the "electronic factor"-has influences upon the catalytic electrode reaction.

Now, according to Couper and Eley[3] the metal *d*-orbital may be expected to give a stronger bond to a hydrogen atom than an *s*-orbital. On this standpoint, if the recombination process between two hydrogen atoms on the metal surface is the rate determining step of the hydrogen electrode reaction, it is reasonable to assume that the change of the adsorption energy of hydrogen atoms caused by the change of the electronic structure of *d*-band of the metal has a great effect upon the rate of the above reaction.

For this reason we can expect for the series of binary solid solutions containing one of the elements of the eighth group together with one of those of the first group, that the hydrogen overpotential depends largely on the number of holes in the *d*-bands of the alloy.

Since the values of the lattice constants of copper and nickel are very much alike and moreover nickel-copper alloys form a face-centred cubic lattice with no superstructure for any compositions, by selecting such alloys we are able to observe the effect of the "electronic factor" on the hydrogen overpotential without much anxiety about that of the "geometric factor."

Experimental Procedures

Hydrogen Overpotential

Apparatus.—The cell for the measurement of the hydrogen overpotential was divided into three rooms separated from each other by diaphragms of glass filter. The sample alloy cathode, having an available area of approximately 4.9 cm², was placed between two auxiliary platinum electrodes in the middle room. Hydrogen purified by passing over heated palladium asbestos was bubbled through the apparatus during measurements for removing air and oxygen. The alloy cathode was attached to the end of a glass tube and could be easily replaced. The tip of a fine capillary tube connected with the reference saturated calomel electrode was kept constantly at 1.0 mm. distance from the test cathode, so as to keep the ohmic fall of voltage involved in the measurement at a given current constant.

Materials.—As for the electrolyte normal sulphuric acid, saturated with hydrogen, was used during the experiments, which was produced from G. R. sulphuric acid and redistilled water.

Four nickel-copper alloys, which covered the whole composition range at 15–25% intervals together with the pure metals, were prepared by electrolytically refined nickel and copper; these alloys and the pure metals were rolled into sheets of 0.097 cm. thickness and were annealed at 900°C to remove strain. The Debye Scherrer rings of the needle samples polished out from the alloys were taken and it was observed that the measured lattice parameter-composition relationship does not depart from the Vegard's law appreciably as shown in Fig. 1. This shows the complete homogeneity of the composition of alloys.

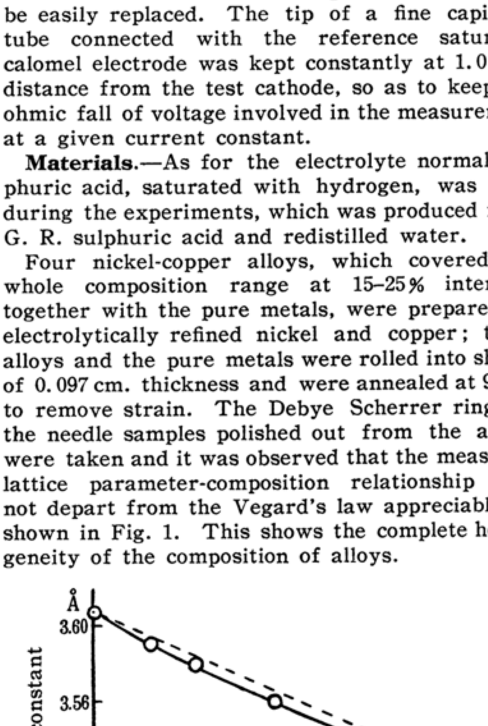

Fig. 1. The lattice constants of nickel copper alloys. (Verification to the Vegards law. ------)

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* This paper was read at the discussion meeting of the Chemical Society of Japan and the Electrochemical Society of Japan on November 19, 1954.

1) M. Oikawa and T. Mukaibo, *J. Electrochem. Soc.*, Japan, **20**, 568 (1952).

2) T. Mukaibo and M. Oikawa, *Bull. Chem. Soc. Japan*, **26**, 524 (1953).

3) Couper and Eley, *Nature*, **164**, 578 (1949).

Procedure.—It is most important to find a measuring method of the Tafel line which is satisfactorily reproducible. Prior to taking the data the present author tried the following two ways.

(1) The potential, whether constant or not, was measured one minute after the adjustment of the current. This method was rapid but the slope of the obtained Tafel line was rather abnormally large and could not be relied upon.

(2) The cathode was prepolarized at the current density of 1.1×10^{-4} amp./cm^2 and continued until a steady potential value was attanined, usually after 1–3 hr. Steady potentials at the higher current densities were then measured within a few minutes after adjustment of current.

In the present work, method (2) was employed and found to give reproducible and reasonable η-log c.d. plots.

Thermoelectric Power

The thermoelectric power of the alloy ribbon cut out from the sample was measured by a student type potentiometer. In each case the test sample was welded to a pure copper wire and the thermal e.m.f. was taken at temperature range between minus 40 to plus 90°C under the basis of a Standard Chromel-Alumel thermocouple.

The two such junctions, the temperatures of which were fixed one at minus 40°C and the other at plus 90°C, were suspended in two glass tubes, one of which was dipped in Dewar's vessel filled up with ethyl alcohol saturated with dry-ice for the cold junction and the other in boiling water for the hot junction.

Magnetic Susceptibilities

The magnetic susceptibilities of nickel-copper alloys were determined by the inductance method, —the change of induction of a coil when the test piece was placed in the coil was measured by a flux meter. To eliminate the effect of oxygen, the alloy plates,—the section of which were made 10 mm. × 0.95 mm.—, were previously annealed at 300°C in pure hydrogen, followed by sufficient outgassing at the same temperature.

Results

Thermoelectric Power s.—As shown in Fig. 2. the homogeneity of composition of these nickel-copper alloys was satisfactorily checked by the values of thermoelectric power s. If copper is added to nickel, the positive holes in the *d*-band are partially filled up, consequently the energy density of *d*-electron levels, will rapidly decrease with the increasing composition of copper and as in Fig. 2. s will become larger gradually until about 60 per cent composition of copper is reached, when the positive holes are all full. We should then expect⁴⁾ s to drop rapidly to a value comparable with that of copper, as the signs of s for nickel and copper are opposite to each other.

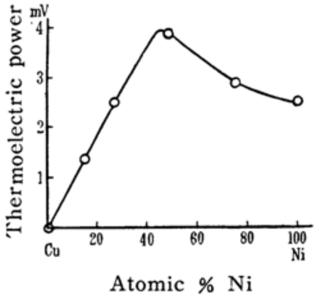

Fig. 2. Thermoelectric power s, in millivolts, of nickel copper alloys, at −40∼+90°C, against pure copper.

Magnetic Susceptibilities of Alloys.—According to the theory of solid⁸⁾ the number of positive holes in the *d*-band of transition metals is equal to the saturation moment in Bohr magnetons. For this reason we are able to represent the number of positive holes by the value of the Bohr magneton. The magnetic susceptibilities of these alloys were obtained by the inductance method and are shown in Fig. 3. The point *x* in Fig. 3. shows the experimental result agreeing with theoretical assumption⁸⁾ mentioning that in nickel there are about 9.4 electrons in the *d*-band (giving 0.6 holes, the vacant *d*-orbitals) and 0.6 electrons in the *s*-band. By alloying nickel with approximately 60 atomic per cent. of copper the *d*-band is filled with electrons completely as the copper atom contains one electron more than the nickel atom.

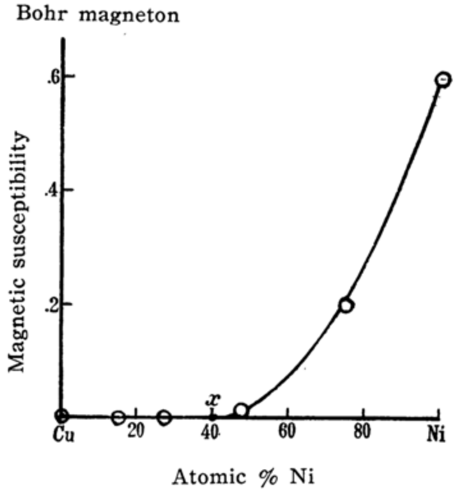

Fig. 3. The quenching of the magnetization of nickel by the addition of copper.

Overpotential-log (Current Density) Relation.—1. *Reproducibility*—The mean deviation from the mean value over the whole series of the experiment is ±0.01 V.

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4) Mott and Jones, "The theory of the properties of metals and alloys," London, (1936) p. 314.

8) Mott and Jones, "The theory of the properties of metals and alloys," London (1936).

2. The plot of over potential against log (c.d.) is linear for all alloys. The mean value of b, the inclination of Tafel line, is about 0.11 for nickel rich alloys and 0.094 for copper rich alloys. These values and those of the Tafel constant a, which were obtained in the present work, almost agree with the results of Hillson[5], Bockris[6] and Wetterholm[7].

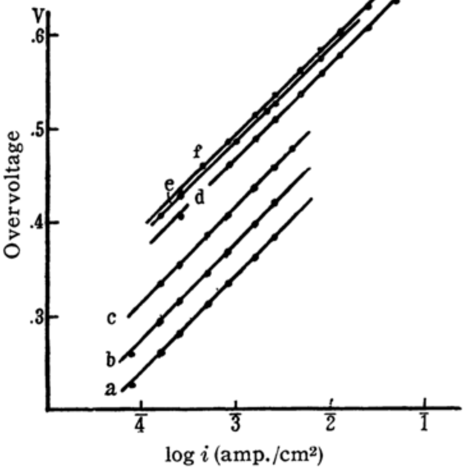

Fig. 4. Hydrogen overpotential on nickel copper alloys in N H_2SO_4 solution. Variation with alloy composition.

a:	100% Ni	d:	27% Ni
b:	75% Ni	e:	15% Ni
c:	48% Ni	f:	pure copper

Discussion

In any attempts to apply the theories of solid to catalitic reaction, it is easiest to assume, in the first instance, that the electronic structures of the bulk metal persist unchanged into the surface layer where catalysis occurs.

Now the metal *d*-orbital would be expected to give a stronger bond to a hydrogen atom than an *s*-orbital because of[3] (a) its lower energy, (b) a possible greater overlapping with the *s*-electron of the H-atom. Moreover, according to the simplest Bloch-type picture of metals, which is chiefly due to Mott and Jones[8], it is supposed that in nickel-copper alloys the added copper atom passes its electron into the *d*-band of the nickel, because of the higher density of energy levels in this band, compared with that of the overlapping *s*-band as shown in Fig. 5.

Then, for nickel-copper alloys, we can except that the adsorption energy of the hydrogen atom decreases with the increasing composition of copper. For this reason, in the catalytic hydrogen electrode reaction as in the case of nickel[9], the richer the composition of copper in the alloy becomes the greater becomes the free energy forming the activated complex in the combination reaction between the two hydrogen atoms[10] and so the hydrogen overpotential becomes higher.

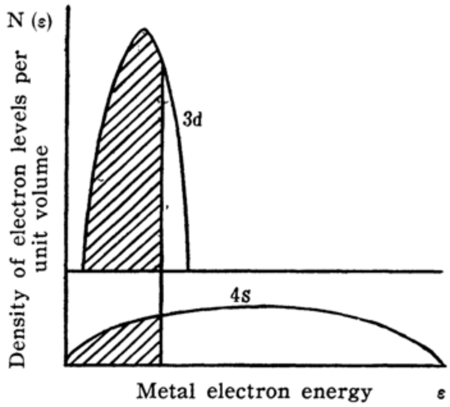

Fig. 5. The energy density of the s- and d-bands in nickel.

The shaded regions represent the levels that are filled by electrons.

Fig. 6. shows the rate of hydrogen electrode reaction at the definite hydrogen overpotential, 0.42 volts, as a function of alloy composition. The broken line denotes the feromagnetic susceptibility, or the number of positive holes. As expected, the rate of hydrogen electrode

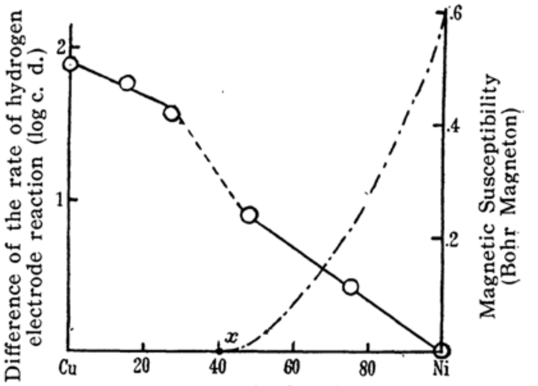

Fig. 6. Rate of hydrogen electrode reaction at the definite hydrogen overpotential, 0.42 volts, as a function of alloy composition.

The broken line (— · — ·) denotes the magnetic susceptibility in Bohr Magneton units.

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[5] P.J., Hillson, *Trans. Farad. Soc.*, **48**, 462 (1952).

[6] J.O.M. Bockris, *Trans. Farad. Soc.*, **43**, 417 (1947).

[7] A. Wetterholm, *Trans. Farad. Soc.*, **45**, 861 (1949).

[9] J. Horiuti, G. Okamoto and K. Hirota, *Sci. Papers Inst. Phys. Chem. Res.*, (Tokyo), **29**, 223 (1936).

[10] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," (1941).

reaction decreases with the increasing composition of copper until about 60 atomic per cent. composition of Cu is reached, when the positive holes are all full as denoted by point x. Then the reaction velocity approaches abruptly to that of copper as the energy of adsorption falls down to that of pure copper owing to the extinction of positive holes.

Summary and Conclusion

Experiments were carried out on the relation between the hydrogen overpotential and the electronic structure of nickel-copper alloys.

We can classify these alloys into two groups, depending upon whether or not they contain more nickel than 60 atomic per cent., that is whether they have positive holes or not in their d-band.

The hydrogen overpotential of nickel rich alloys (more than 60 atomic percentages of nickel) is rather low because of their small activation energy caused by the large adsorption energy due to the strong bond between metal d-orbital and H-atom. For copper rich alloys the hydrogen overpotentials are high and are almost identical owing to the extinction of positive holes.

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