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Effect of Catalytic Poisons on the Production of Nickel Hydride by Electrolytic Charging of Nickel with Hydrogen

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A comparative experimental study has been performed of the action at room temperature of several poisons, when added in small proportion to 1 *N* sulfuric acid solution, on the depth of the nickel hydride formation in electrodeposited nickel layers during cathodic charging. The results show the following sequence of decreasing thickness of the hydride layer produced in the presence of different additions: thiourea (about 30 to 35 μ), selenium dioxide (about 28 μ), sodium sulfide (about 27 μ), phosphine (about 6 μ), tellurium dioxide (about 5 μ), and arsenious trioxide (about 2 μ). The mean limiting concentration of hydrogen in the hydride layer is a little greater when charging in the presence of arsenic ($H/Ni = 0.8$), than in that of thiourea ($H/Ni = 0.7$). The cause of these variations is not known.

As shown in previous works (*1, 2*), a surface layer of compact polycrystalline nickel, up to about 35 μ thick, may be transformed at room temperature into nickel hydride having an approximate formula $NiH_{0.7}$ to $NiH_{0.8}$. This transformation occurs when a nickel cathode is charged electrolytically with hydrogen in the presence of catalytic poisons.

The nickel hydride is unstable under ordinary conditions. It has a f.c.c. crystal lattice with a spacing about 6% greater than that of nickel (*3, 4*).

In the absence of catalytic poisons, i.e., during electrolysis of pure acid solutions, the nickel cathode absorbs very little hydrogen, and the nickel hydride is not formed, or rather, only traces of it are produced at the surface of the cathode. On the other hand, if traces of some elements of the V and VI periodic groups are present in the acid solution or at the interface, and the cathodic current density is high enough, the formation of nickel hydride proceeds into the bulk of the nickel cathode, until a limiting thickness of the hydride phase is obtained.

Catalytic poisons are thought to inhibit the hydrogen recombination reaction $2H \rightarrow H_2$, and thus to increase the chemical potential of atomic hydrogen at the working cathode. Another possibility considered by some authors (*5*) is that the formation of a Me–Ps boundary (Me, metal; Ps, poison) has a weakening effect on the Me–Me boundary and thereby facilitates the penetration of hydrogen into the bulk of the metal phase.

Baukloh and Zimmermann (*6*) ascribed the strongest poisoning effect to selenium, while Polukarov (*7*) thought the same of tellurium. Smialowski and Szklarska-Smialowska (*8*) established the following sequence of decreasing ability to promote secondary effects of hydrogenation* in iron cathodes: P, S, As, Se, Te, Bi.

Anions SO_4^{2-} and PO_4^{3-} having a high degree of oxidation and stability are not reduced at the cathode and do not influence

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* By "secondary effects of hydrogenation" is meant plastic deformation of iron and steel samples. The magnitude of the deformation elicited by cathodic hydrogen depends on the catalytic poisons applied.

the process of hydrogen penetration, but lower oxides, such as sulfur dioxide, and oxides and oxidized anions of other elements mentioned, give by cathodic reduction free elements and hydrides, for instance:

$$As_2O_3 \xrightarrow[\text{reduction}]{} As \xrightarrow[\text{reduction}]{} AsH_3$$

Evidently, the formation of a volatile hydride is decisive for the poisoning effect and for the increase of the ability of hydrogen to penetrate into the cathodic metal. Certain organic compounds, as for example thiourea, decompose at the cathode giving hydrogen sulfide.

This paper reports results of a comparison of effects of different poisons on the depth of hydride formation in nickel.

Methods

All experiments were performed using the following method, similar to that described previously (*1, 2*).

Copper wires, 0.1 cm in diameter and 100 cm in length, were bent into coils of 1 cm diameter and degreased for 10 min in a 10% aqueous solution of potassium hydroxide and in absolute alcohol, and electropolished for 2 min in orthophosphoric acid solution (density of the acid 1.4, current density 0.13 amp/cm^2). After this procedure the coils were quickly immersed in distilled water and in absolute alcohol, dried, and heated for 1 hr at 400°C at normal pressure in a pure hydrogen atmosphere. After cooling to room temperature the copper wires were coated electrolytically by a nickel plate. A solution of 75 g ammonium-nickel sulfate per liter at 40 to 45°C and a current density of 0.004 amp/cm^2 was used. The electroplated copper wires were further heated for 1 hr at 300°C in air at a low pressure, about 0.01 cm Hg. The prepared specimens were charged electrolytically at room temperature in an aqueous solution of 1 N sulfuric acid to which the poison was added. A

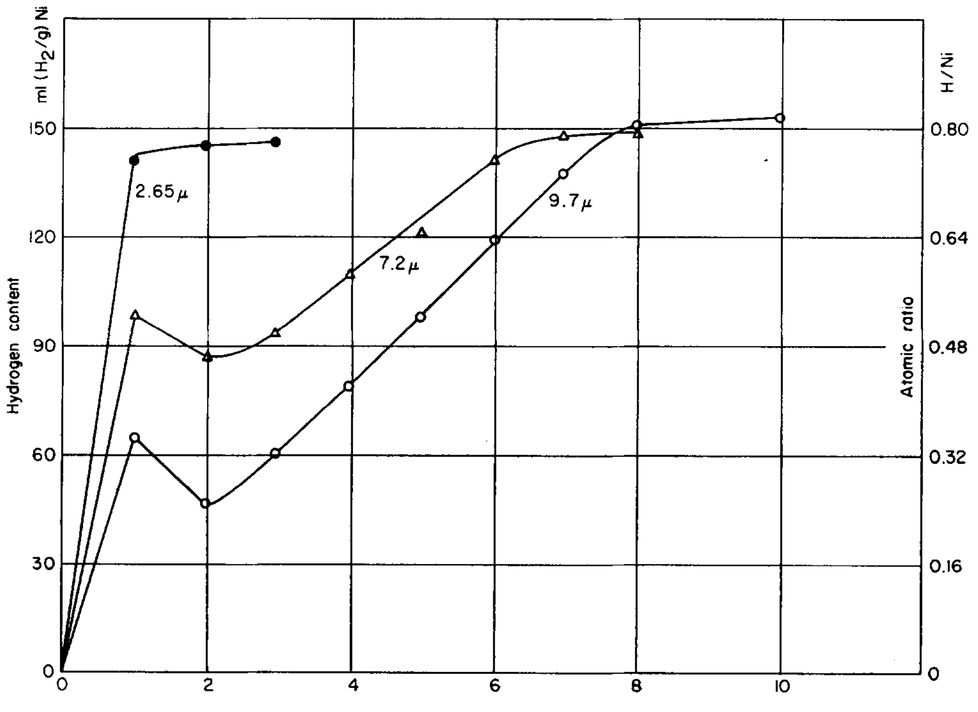

FIG. 1. Dependence of the hydrogen content in nickel layers differing in thickness upon the number of cathodic chargings. Charging time, 2.5 hr each. Poison, 0.001 g SeO_2/liter. Cathodic current density, 0.02 amp/cm^2.

platinum wire served as anode. The charging was usually performed several times before the maximum hydrogen content was attained. After charging, the coils were quickly rinsed with distilled water, and the hydrogen content was determined by measurements of the volume of desorbing gas at 25°C and at normal atmospheric pressure. The volume of evolved hydrogen was determined with an accuracy of 0.01 cm^3. Measurement of the volume of desorbed hydrogen begins always 1 min after charging has been terminated.

RESULTS

Effect of Selenium Oxide

A constant amount of 0.001 g selenium dioxide was used as an addition to 1 liter of 1 *N* sulfuric acid. As shown in a previous study (*8*), this concentration greatly exceeds the limit below which the effect of cathodic hydrogenation begins to decrease. Two charging times were used, namely, 2.5 hr for nickel layers up to 10 μ thick, and 19 hr for thicker ones. For each experiment, a fresh electrolyte was always used.

As shown in Fig. 1, a nickel layer of 2.65 μ thickness attains after the first 2.5 hr of charging at a current density of 0.02 amp/cm^2 the limiting atomic ratio H/Ni equal about 0.75 to 0.8. In the case of thicker layers, up to about 10 μ, the first charging occasioned absorption of a smaller amount of hydrogen than that corresponding to the maximum H/Ni ratio, but always greater than that attained during the second 2.5 hr charging. After 6 to 8 chargings, the maximum atomic ratio H/Ni of about 0.8 was reached.

Figure 2 illustrates the behavior of nickel layers, 22.6, 30.0, and 35.2 μ thick, charged

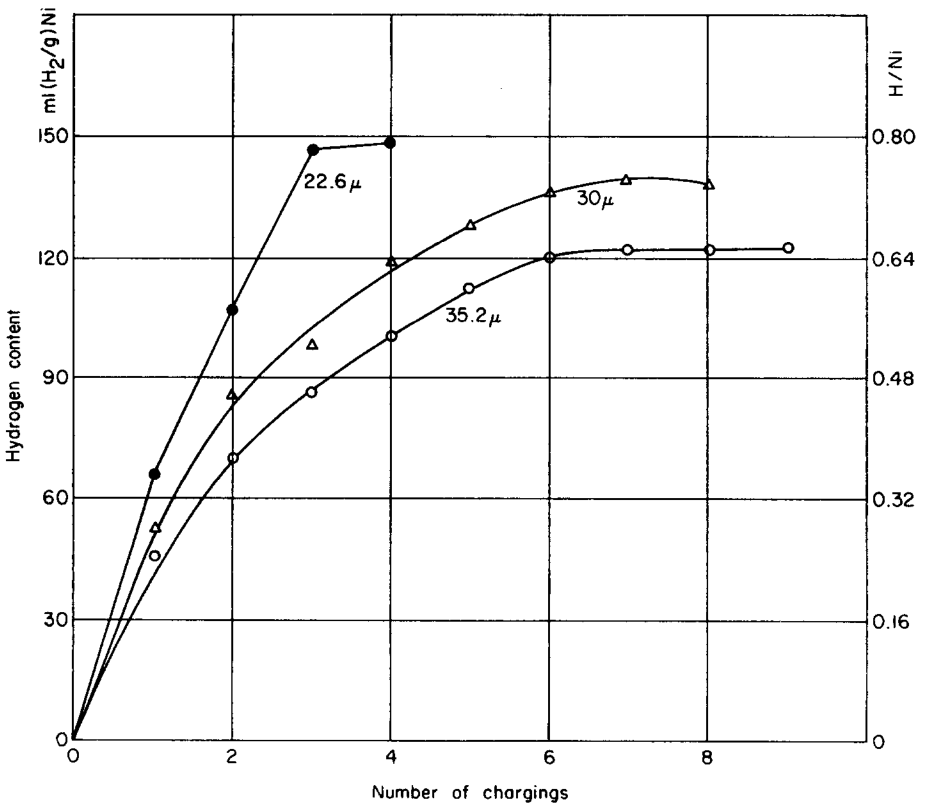

FIG. 2. Dependence of the hydrogen content in nickel layers differing in thickness upon the number of cathodic chargings. Charging time, 19 hr each. Poison, 0.001 g SeO$_2$/liter. Current density, 0.02 amp/cm^2.

cathodically several times for 19 hr. As may be seen, the sample having a 22.6 μ thick nickel layer attained the atomic ratio H/Ni = 0.7 during the third charging. In the case of the 30 and 35.2 μ thick nickel layers, the maximum hydrogen concentration was reached after the seventh charging. The maximum atomic H/Ni ratio was 0.73 in the case of the 30 μ thick nickel layer, and 0.64 in that of the 35.2 μ thick nickel layer.

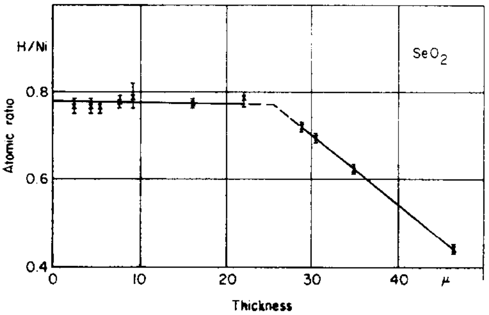

FIG. 3. Dependence of the hydrogen content attained after a prolonged cathodic charging of nickel layers upon their thickness. Poison, 0.001 g SeO_2/liter.

In Fig. 3, the dependence is given of the hydrogen concentration in repeatedly charged nickel layers on their thickness. There, results of some 100 experiments are taken into account, with deviations from the mean values. The curve is similar to that obtained in previous work (*1, 2*), during charging in the presence of thiourea, but it differs, a little, in the maximum H/Ni ratio, in the thickness of the hydride phase produced, and in the slope of the declining part (see Fig. 4).

Effect of Sodium Sulfide

Preliminary experiments showed that the amount of $Na_2S \cdot 10H_2O$ necessary to attain a degree of hydrogenation which was nearly independent of further addition of sodium sulfide to the electrolyte was about 1 g/liter of 1 *N* sulfuric acid solution. The effect of

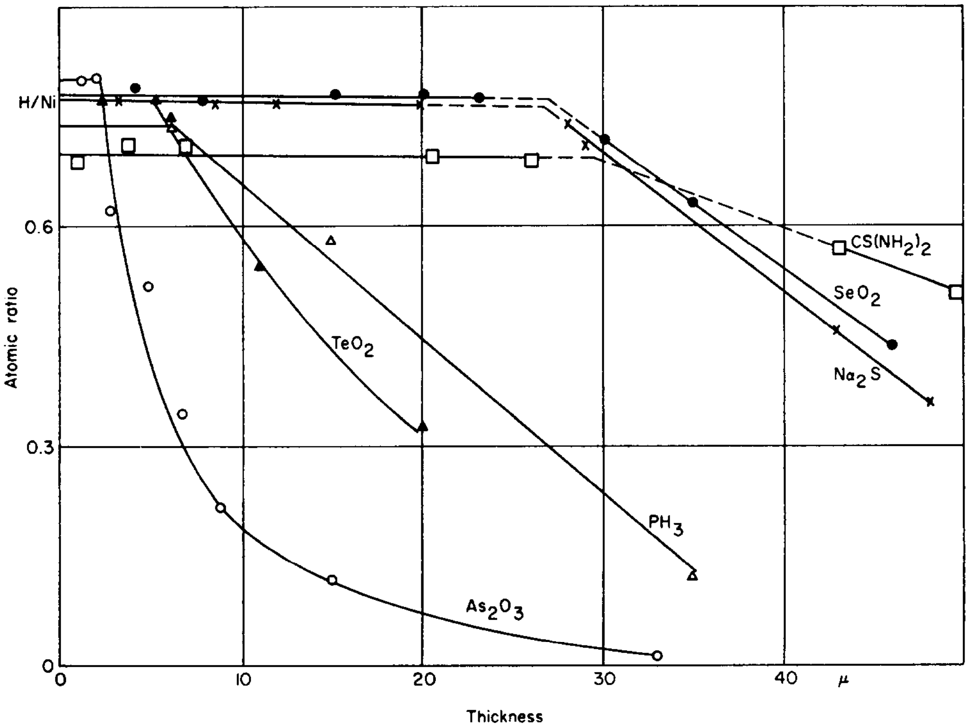

FIG. 4. Relationship between the mean limiting content of hydrogen in nickel after a prolonged cathodic charging in the presence of different poisons, and the thickness of the nickel layer. The curve for thiourea is plotted according to results obtained in a previous work (*1, 2*).

this poison on the hydrogen content in layers of different thickness is represented in Fig. 4, together with effects produced by other poisons studied.

Effect of Phosphine

Gaseous phosphine was produced in a suitable additional vessel by the action of hot potassium hydroxide solution on yellow phosphorus, and bubbles of the gas were passed through the electrolyte at charging. In this case, a cathodic current density of 0.04 amp/cm^2 and a charging period of 2.5 hr was used. The relationship between atomic H/Ni ratio and the thickness of nickel layers is illustrated in Fig. 4, curve PH_3.

Effect of Arsenic

It has already been shown in a previous study (*1, 2*) that the thickness of the nickel layer which may be transformed into nickel hydride is only of the 1 to 2 μ order. Boniszewski and Smith (*9*) wrote that a thickness of 10 μ was observed in their experiments, but they did not give any information as to the method used to determine this (*10*). Our recent results, obtained with the addition of 0.05 g of As_2O_3 per liter, are represented in Fig. 4.

Effect of Tellurium Oxide

Usually, 0.001 g of tellurium oxide was added to the electrolyte, but since the effects of this addition were irreproducible, greater and smaller concentrations of TeO_2 were used, too. The irreproducibility of results was probably due to the fact that tellurium hydride, which evidently is the active poisoning compound, is highly sensitive to the experimental conditions, such as temperature, presence of reducing and oxidizing agents, light, etc. A great number of experiments were performed, but no clear conclusions could be drawn from them. Some mean results are given in Fig. 4, curve TeO_2.

DISCUSSION

As shown in Fig. 4, different poisons have a varied effect on the production of nickel hydride at cathodic charging. The depth of hydride formation is the greatest in the case of thiourea (about 30 μ), and the smallest in that of arsenic (about 2 μ), but the maximum H/Ni ratio seems to be greater in the case of arsenic than in that of thiourea. Other poisons studied show intermediary effects between those characterizing arsenic and thiourea. It is interesting to note, too, that the slope of the declining part of the curve, H/Ni atomic ratio versus thickness of the nickel layer, is influenced by the poison used.

In general, there seems to be a very complex effect of poisons on various phenomena related to the process of cathodic hydrogenation. Results of experiments on the diffusion rate of hydrogen through metals and alloys suggest that the presence of arsenic produces hydrogen having a greater mobility in the bulk of the metal phase than hydrogen evolved in the presence of the sulfide ion. This could be the cause of a smaller stability of the nickel hydride produced in the presence of arsenic as compared with thiourea, sodium sulfide, and selenium dioxide.

Unfortunately, the present knowledge of the action of catalytic poisons on one hand, and of the mechanism of cathodic hydrogen evolution on the other hand, is too narrow to allow us an accurate interpretation of the above results. A further experimental study of these phenomena seems indispensable, and this is now in progress.

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