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FEB 77 S S CHATTERJEE, B G ATEYA

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EFFECT OF ELECTRODEPOSITED METALS ON THE PERMEATION
OF HYDROGEN THROUGH IRON MEMBRANES

BY

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EFFECT OF ELECTRODEPOSITED METALS ON THE PERMEATION
OF HYDROGEN THROUGH IRON MEMBRANES

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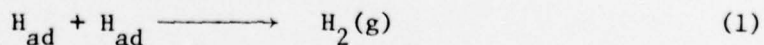
ABSTRACT

The permeability of electrolytically charged hydrogen through annealed Ferrovac E iron membranes was found to decrease significantly upon coating the charging surface of iron with thin layers of either Pt, Cu or Ni (Watts or electroless). The absorption of hydrogen was delayed for a period which depends on the nature and the thickness of the metallic coating. The results show that such coatings do not have to be thick or even continuous to be effective, in which case a catalytic mechanism is proposed to explain the marked reduction in hydrogen permeation through the iron. Experimental confirmation is presented of this catalytic mechanism and of the barrier mechanism which is operative in the presence of a thick continuous coating. It is also shown that the domains of each mechanism can be determined by simple calculations from first principles.

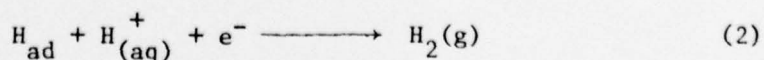
INTRODUCTION

The problem of hydrogen embrittlement of iron and its alloys has recently attracted considerable attention in view of its technological importance (1-4). In attempts to delay the incidence of hydrogen embrittlement, some workers alloyed iron with metals which decreased the diffusivity of hydrogen, e.g., Ni (5) and Cr (6), whereas others coated the base metal with another metal, e.g., electrodeposited Ni (7-13), Cu (7-11, 13-14), Cr (7-11), Pb (9-11), Co (9), Sn (7,10); vapor deposited Cd, Al, Mg, Zn and Zn-Pb alloys (11); and chemically deposited Au and Au-Ni composite layers (11). Various other workers (15-16) have studied the permeability of composite metal membranes to hydrogen charged from the gas phase. With all of these coatings, hydrogen entry into the base metal was delayed and the rate of its permeation decreased. In some of these cases, this was attributed to the barrier effect of the coating. For coatings to be effective barriers, they should be continuous, relatively thick and impervious, much like protective scales on metals.

Another interesting and potentially effective method of reducing hydrogen absorption by iron may be suggested upon reviewing the kinetics of the hydrogen evolution reaction (h.e.r.). For a large number of metals, the rate determining step (r.d.s.) may be either (17-19) chemical desorption (equation 1) or electrochemical desorption (equation 2):



or



It is postulated here that as the rate of the r.d.s. (equation 1 or 2) increases, then, in general, the surface coverage by hydrogen is decreased and, hence, so is the absorption of hydrogen by the metal. While this is an oversimplified description of a complex process, it suggests that a metal like platinum, for which the recombination reaction is very fast (compared to that on iron), might be beneficially deposited over the iron surface. In this event, the bulk of the h.e.r. occurs at the platinum sites with the favorable result that coverage by, and absorption of, hydrogen at iron sites are reduced. This is the basis of the catalytic mechanism of decreasing hydrogen entry into iron.

The purpose of this paper is to investigate the usefulness of metals more noble than iron, e.g., Pt, Cu and Ni, when deposited as thin continuous or discontinuous (square-grid) layers, as a means of decreasing the entry of hydrogen into iron. This is done by directly measuring the permeation transient of hydrogen through the coated iron membrane. This technique provides more resolution than those based on time to cracking (9) or load and deflection (11), and hence, should be more useful for studying the role of thin surface layers for the protection of iron and steels from hydrogen.

EXPERIMENTAL PROCEDURE

A Devanathan and Stachurski cell (20) was used to measure the permeability of hydrogen through Ferrovac E iron membranes coated with Cu, Ni or Pt on the (input) side on which hydrogen is evolved. The membranes were prepared by cutting from a master ingot and cold rolling to the final thickness, cutting to a size somewhat larger than the orifice of the cell, annealing in an evacuated vycor capsule at 800°C for 2 hrs., and air cooling. The thickness of the iron membrane was usually 0.05 cm. The radius

of the orifice and hence of the input area of the membrane was 1.26 cm. Edge effects can be neglected in diffusion through membranes if $L/a < 0.2$, where L is the thickness and a is the radius of the membrane (21). For the membrane thickness used here (0.05 cm), $L/a \approx 0.04$ and, hence, edge effects are negligible.

The charging solution was 0.1N NaOH + 20 ppm As³⁺. The solution in the anodic compartment was 0.1N NaOH. The charging current density was kept at 2mA cm^{-2} in order to avoid internal damage in the specimen and to obtain good reproducibility. At this current density no cracks were observed in the sample (by cross-section metallography) after charging for several hours (without a coating). The solutions were prepared from reagent grade chemicals and conductivity water prepared by the method of Powers (22), and were continuously deaerated by bubbling pre-purified nitrogen. The reference electrodes were Hg/HgO. All experiments were run at room temperature, $25 \pm 2^\circ\text{C}$.

The exit side of the membrane was coated with a thin layer of palladium deposited from $\text{Na}_2[\text{Pd}(\text{NO}_2)_4]$ solution at $100 \mu\text{A cm}^{-2}$ (20). During a run, this side was potentiostated at + 0.1V NHE. Use of other potentials as much as 400 mV more or less noble gave identical transients; hence it is concluded that all of the hydrogen arriving at the exit side is oxidized at 0.1V NHE.

In the absence of metallic coatings, a linear relationship was obtained between the steady state permeation current and the square root of the charging current. This is taken as an indication (23) that the surface absorption process is very fast with respect to diffusion through the iron membrane. Under this condition, the latter process is rate limiting in accord with the finding of a linear dependence of the permeation current on the reciprocal thickness of the iron membrane.

The platinum coatings were deposited at $100 \mu\text{A cm}^{-2}$ from a 1% platinum chloride ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) solution. The platinum thickness was determined coulometrically. Copper plating was done in two stages: (i) a thin, comparatively adherent film of copper was deposited from a "striking" cyanide bath (24) and, (ii) this deposit was built up to the desired thickness by further plating at $200 \mu\text{A cm}^{-2}$ from an acid copper sulfate bath. Nickel was deposited either from a Watts type bath (25) or from an Electroless Nickel type bath (pH 5.0, 90°C) (26). The thickness of the Ni and Cu coatings was determined and their continuity was confirmed by cross-section scanning electron microscopy (SEM) examination.

Fig. 1a is a SEM micrograph of the cross-section of a specimen coated with a $4 \mu\text{m}$ thick Cu layer and Fig. 1b is a SEM micrograph showing the topography of the layer. Both figures reveal the continuity of the coating. Fig. 2 shows the topography of a $0.5 \mu\text{m}$ thick Cu layer on the surface of iron. It is a quasi-continuous layer which covers most of the iron surface.

On some specimens the metals were deposited in a square-grid pattern, c.f. Fig. 7. About 20% of the surface was covered by the following technique: The sample was coated with Shipley photo-resistive chemical (PR) and was baked at 70°C for 20 minutes. Then it was exposed by a KNS Aligner machine fitted with the desired pattern printed on a dark colored glass plate, commonly known as mask. It was developed with AZ developer for 30 seconds and was washed with distilled water. It was dried and baked again at 120°C for 20 minutes. Then electrodeposition on the exposed areas was carried out with the desired metal. After electrodeposition, the PR was removed by washing the specimen surface with acetone.

RESULTS AND DISCUSSION

The upper curve in Fig. 3 shows a typical time-flux transient for hydrogen permeation. The lower curve in Fig. 3 shows the effect of a thin platinum coating on the diffusion transient of hydrogen through the iron membrane. The average thickness of the Pt layer was calculated coulometrically to be about $0.015 \mu\text{m}$. It is seen that the break-through time is much longer and the hydrogen permeability is much less (2 orders of magnitude) than for the uncoated iron sample. This may be attributed to a lower concentration of hydrogen at the entry side of the iron in the presence of the platinum coating.

The beneficial effects of Cu and Ni coatings deposited over the input surface are shown in Figs. 4 and 5, respectively. It can be seen in Fig. 4 that as the coating thickness increases, the permeation current decreases whereas the break-through time and, hence, the time lag increase. Fig. 5 shows a similar effect of thickness on permeation current. This is characteristic of diffusion through composite membranes (27) where diffusion through the coating is at least partially rate limiting.

Barrier Effect

If diffusion of hydrogen through the coating is the rate determining step (r.d.s.), then assuming the applicability of Fick's first law and a constant diffusivity, D , the steady state permeation current i_{∞} , should be a linear function of the reciprocal of the coating thickness. Fig. 6 shows a plot for Cu and Ni (Watts and electroless). The results satisfactorily fit a straight-line relation passing through the origin (infinite coating thickness) for coating thicknesses as low as $1 \mu\text{m}$ Ni and $0.5 \mu\text{m}$ Cu. Analyzing for the r.d.s. on the basis of the mass transfer coefficient $m = D/L$, m of the coating would be significantly less than that for the iron membrane if transport through the coating is rate determining. Taking the

diffusivity of hydrogen in Cu to be $\sim 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, as obtained by extrapolating gas phase values at higher temperatures (28), $m \approx 10^{-5} \text{ cm s}^{-1}$ for the smallest thickness of Cu ($0.5 \mu\text{m}$) for which linear behavior is observed in Fig. 6, whereas for the iron substrate $m \approx 10^{-4} \text{ cm s}^{-1}$. Hence, diffusion through the Cu coating is the r.d.s. Similarly for Ni, using $D = 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 25°C (5) and a thickness of $1 \mu\text{m}$, $m \approx 10^{-5} \text{ cm s}^{-1}$ consistent with diffusion through Ni being the r.d.s. Thus, at thicknesses equal to or greater than $1.0 \mu\text{m}$ for nickel and $0.5 \mu\text{m}$ for copper, both coatings are functioning as barriers. For lower thicknesses than these values, the permeation rate is limited by diffusion through both the coating and the iron substrate.

Fig. 6 also shows that a copper coating is twice as effective as a Ni coating of equal thickness in reducing the rate of hydrogen uptake by iron. This, in principle, may be due to a lower diffusivity and/or a lower concentration at the input surface (catalytic effect) of hydrogen in copper than in nickel. The slope of the plots in Fig. 6 is $\partial i_\infty / \partial (1/L) = F D c^\circ$ where c° is the concentration of hydrogen in the lattice at the outer surface of the coating, F is the Faraday constant, and L in this case is the thickness of the coating. Thus, a large slope indicates a large value of the product $D c^\circ$, i.e., a large diffusivity and/or concentration and obviously a less effective coating. From Fig. 6, $(D c^\circ)_{\text{Ni}} \approx 2 (D c^\circ)_{\text{Cu}}$. An independent confirmation of this conclusion is not possible due to the lack of diffusivity data for hydrogen in Cu at room temperature and of data on the relative solubility of hydrogen in Cu and in Ni under comparable hydrogen charging conditions. However, the data available from gas phase studies at higher temperatures (29) indicate that the solubility of hydrogen in Ni is invariably larger than in Cu at the same temperature and hydrogen

gas pressure. Furthermore, the data compiled in reference (28) indicates that the diffusivity* of hydrogen in Ni is comparable to that in Cu. According to these literature results for somewhat different conditions, the catalytic effect seems responsible for Cu being more effective than Ni in the present work (Fig. 6).

Catalytic Effect

Comparing the results obtained on Ni (Fig. 5) and on Pt (Fig. 3), it is seen that a Pt coating of only 0.015 μm is much more effective in reducing hydrogen permeation than a much thicker Ni coating of about 6 μm . The diffusivity of hydrogen in Pt is comparable to that in Ni (5,30). Furthermore, if one assumes that the Pt layer, albeit thin is continuous, the value of m in Pt ($m = D/L \approx 7 \times 10^{-4} \text{ cm s}^{-1}$) is larger than in Fe ($\approx 1 \times 10^{-4} \text{ cm s}^{-1}$); hence the Pt coating could not be acting as a barrier. This pronounced effect of Pt can only be due to the fact that the h.e.r. occurs much more readily on Pt sites, thereby reducing the activity of hydrogen at both platinum and iron sites, and, thus, decreasing its permeation rate through the iron.

Polarization of the hydrogen evolution reaction on the Pt-coated surface was found to be significantly less than on an iron surface, though it slowly increased (potential drifted in the less noble direction). The latter is consistent with an aging effect (see below), which is understood to be due to a decreasing catalytic activity of Pt surfaces during hydrogen discharge, especially in the presence of cathodic poisons such as,

* Comparison was made of the data produced by the same authors for both metals e.g., the works of Ransley and Talbot, Eichenauer and Rebler, Eichenauer and Katz, see reference (28).

e.g., As^{3+} ion. These results and the above calculation support the catalytic mechanism outlined in the introduction. Clearly, though, Pt at greater thicknesses could also function as a barrier, just as Ni and Cu do.

In order to further confirm the catalytic effect, some iron samples were partially coated with Pt, Cu or Ni on the input side in a regular square-grid pattern, Fig. 7. The area occupied by the electrodeposits was about 20% of the total charging area. It was found that partial coverage of iron by Pt, Ni or Cu is effective in reducing hydrogen entry into the membrane, Fig. 7, particularly at shorter times. After charging for 30 minutes at 2 mA cm^{-2} in the presence of 20 ppm As^{3+} , the presence of a square-grid pattern of Watts Ni decreased hydrogen entry into iron to one-third ($25 \text{ } \mu\text{A cm}^{-2}$) of the value for uncoated iron. Cu and electroless Ni (16 and $13 \text{ } \mu\text{A cm}^{-2}$, respectively) are even more effective than Watts Ni while Pt ($6 \text{ } \mu\text{A cm}^{-2}$) is most effective. Thus, the square-grid pattern of Pt covering only 20% of the membrane area decreases the hydrogen flux through iron by more than 90% at charging times as long as 30 minutes*. As the charging time increases, the protection efficiency⁺ of Pt (in decreasing hydrogen absorption by iron) decreases becoming -75% after one hour and ultimately only 35% after three hours. After such long charging times, the efficiencies of Pt, electroless Ni and Cu become comparable, and better than Watts Ni.

* Had the coating worked only as a barrier, the permeation current would have decreased in proportion to the area covered by the deposit, about 20%, and would be independent of time.

⁺ The definition of protection efficiency here is similar to that used in corrosion terminology, i.e., $p = 100 (1 - i \text{ with coating} / i \text{ without coating})$.

This decrease in protection is a result of the change in catalytic activity of the surface of the coating (aging effect) brought about by continuous hydrogen evolution and enhanced by the presence of arsenic. In the absence of As^{3+} ion in solution, it takes about 17 hrs before the protection efficiency drops to 35%. Before the onset of this aging effect, the effectiveness of the coatings in decreasing hydrogen entry is in the following order:

Pt > electroless Ni > Cu > Watts type Ni

These results are generally in agreement with those of other workers who have tabulated the exchange current density of hydrogen evolution on various metals (17-19), and the relative efficiencies of metals in hydrogen-atom recombination as a function of their initial heat of adsorption of hydrogen (31). The presence of the square-grid coating protects the uncovered iron regions in the sense that they do not absorb hydrogen to the same extent they would in the absence of these catalytic particles. This is understandable in view of the fact that while charging, the electrode potential is more noble in the presence of the coatings in accord with the lower driving force needed for hydrogen evolution off Pt, Cu or Ni. On the other hand, during the aging process, the electrode potential slowly shifts to less noble values. This is consistent with the loss of catalytic activity of the coating. In principle, this catalytic effect should be operative for any coating for which the exchange current density of hydrogen evolution is significantly higher than for iron.

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FIGURE CAPTIONS

- Figure 1a. Cross-sectional SEM micrograph of a 4 μm thick Cu coating on a Ferrovac E substrate.
- Figure 1b. SEM micrograph of the surface of a 4 μm thick Cu coating on a Ferrovac E substrate.
- Figure 2. SEM micrograph of the surface of a 0.5 μm thick Cu coating on a Ferrovac E substrate.
- Figure 3. Effect of a platinum coating (0.015 μm thick) on the permeation of hydrogen through Ferrovac E iron membranes.
- Figure 4. Effect of copper coatings on the permeation of hydrogen through Ferrovac E iron membranes.
- Figure 5. Effect of nickel coatings on the permeation of hydrogen through Ferrovac E iron membranes.
- Figure 6. Dependence of the steady state hydrogen permeation current on the reciprocal of coating thickness for electrodeposited Cu and Ni, and electroless Ni coatings. o Cu, ● Watts Ni, ▽ Electroless Ni.
- Figure 7. Effect of square-grid deposits on the permeation of hydrogen through Ferrovac E iron membranes. Curves 1, 2, 3, 4 and 5 are the permeation transients of uncoated iron and of iron with square-grid deposits of Watts type nickel, Cu, electroless Ni and platinum, respectively.

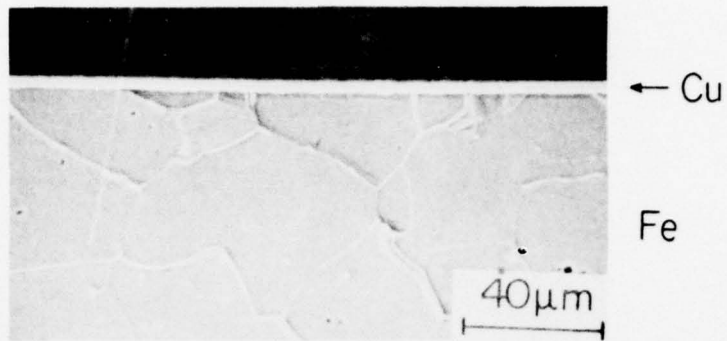


Fig. 1a-Cross-sectional SEM micrograph of a 4 μm thick Cu coating on a Ferrovac E substrate.

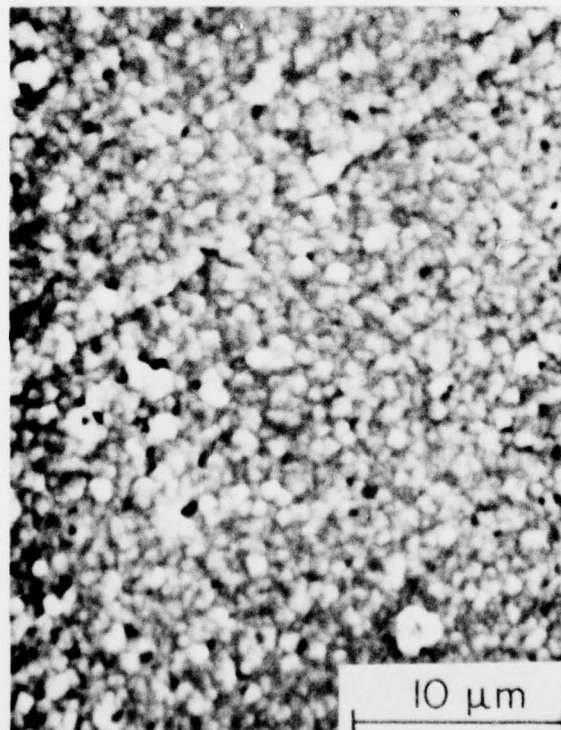


Fig. 1b-SEM micrograph of the surface of a 4 μm thick Cu coating on a Ferrovac E.

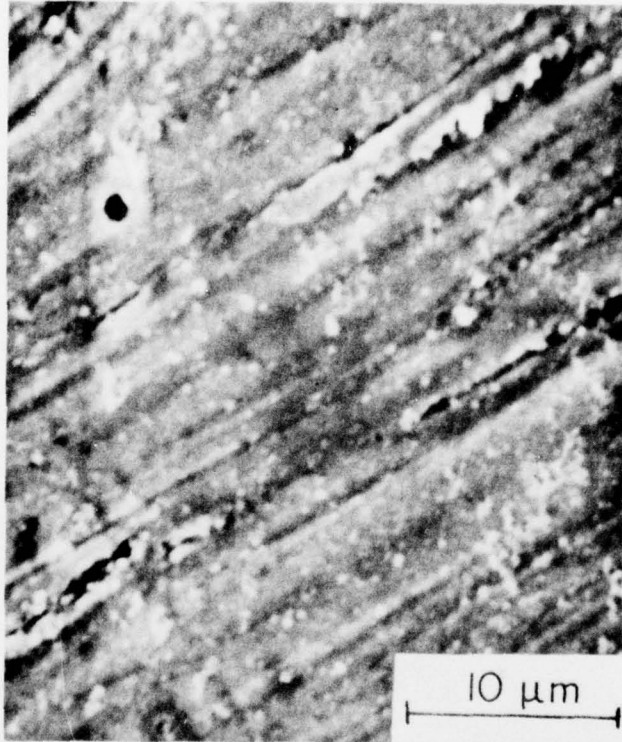


Fig. 2-SEM micrograph of the surface of a 0.5 μm thick Cu coating on Ferrovac E.

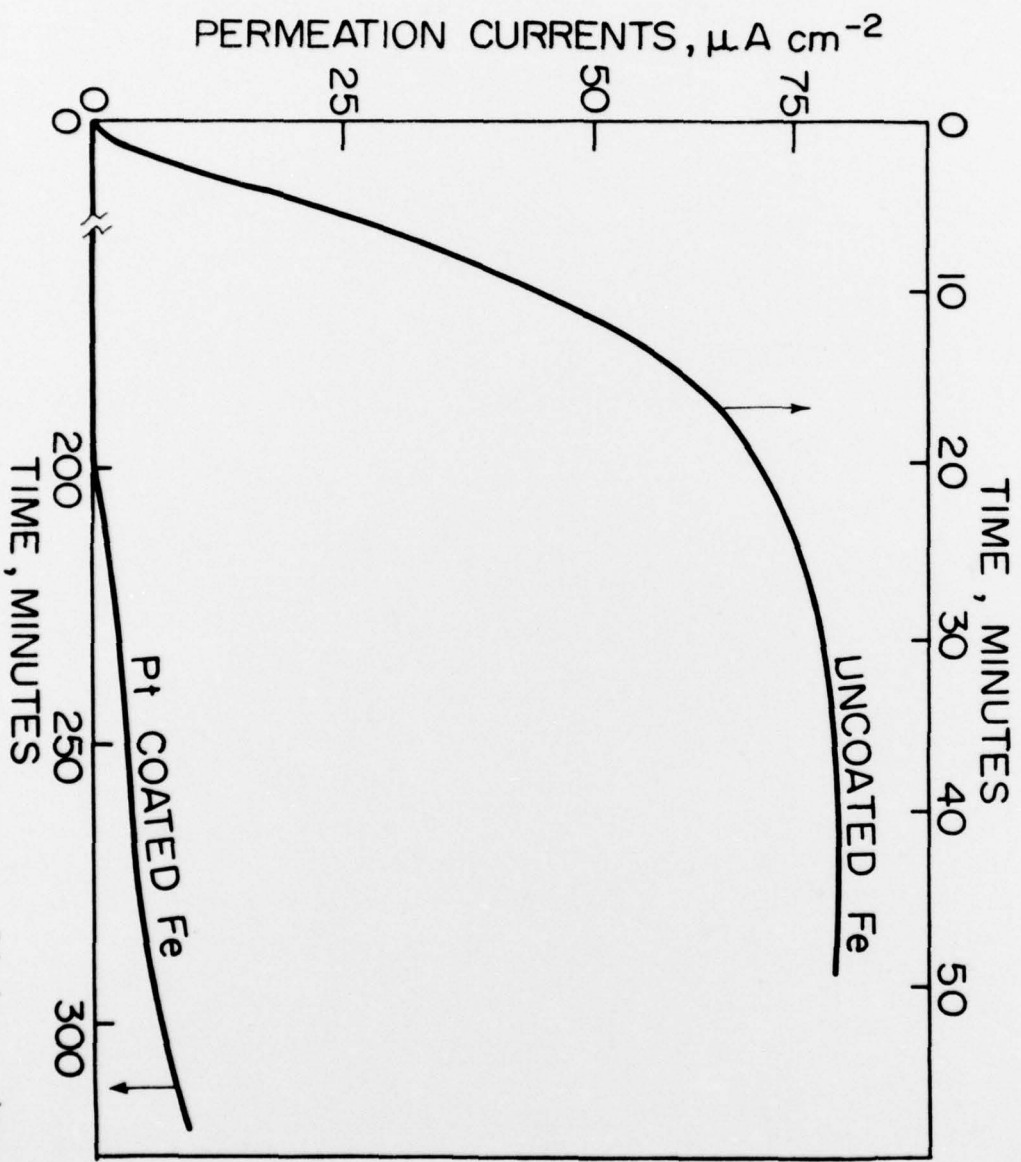


Fig. 3-Effect of a platinum coating on the permeation of hydrogen through Ferrovac E iron membranes.

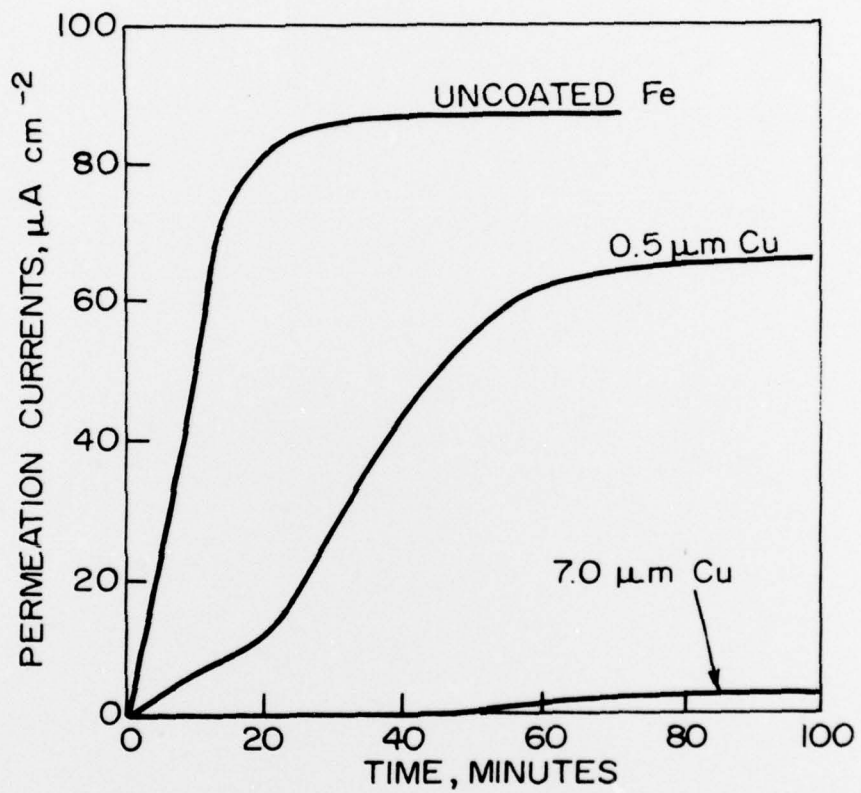


Fig. 4-Effect of copper coatings on the permeation of hydrogen through Ferrovac E iron membranes.

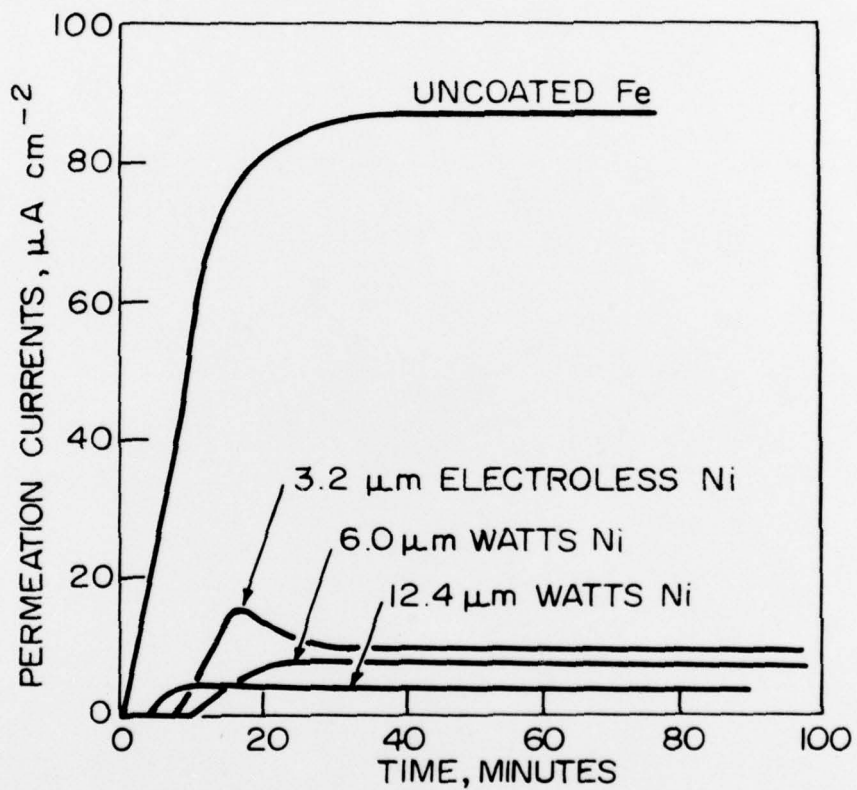


Fig. 5-Effect of nickel coatings on the permeation of hydrogen through Ferrovac E iron membranes.

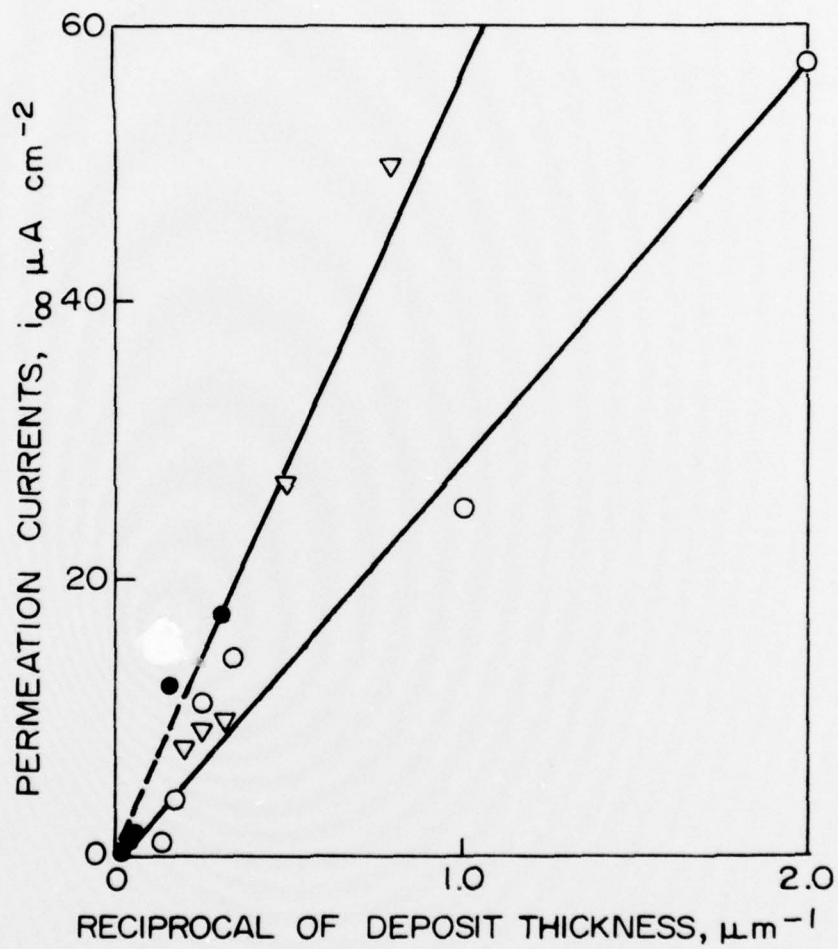


Fig. 6-Dependence of the steady state hydrogen permeation current on the reciprocal of coating thickness for electrodeposited Cu and Ni, and electroless Ni coatings. \circ Cu, \bullet Watts Ni, ∇ Electroless Ni.

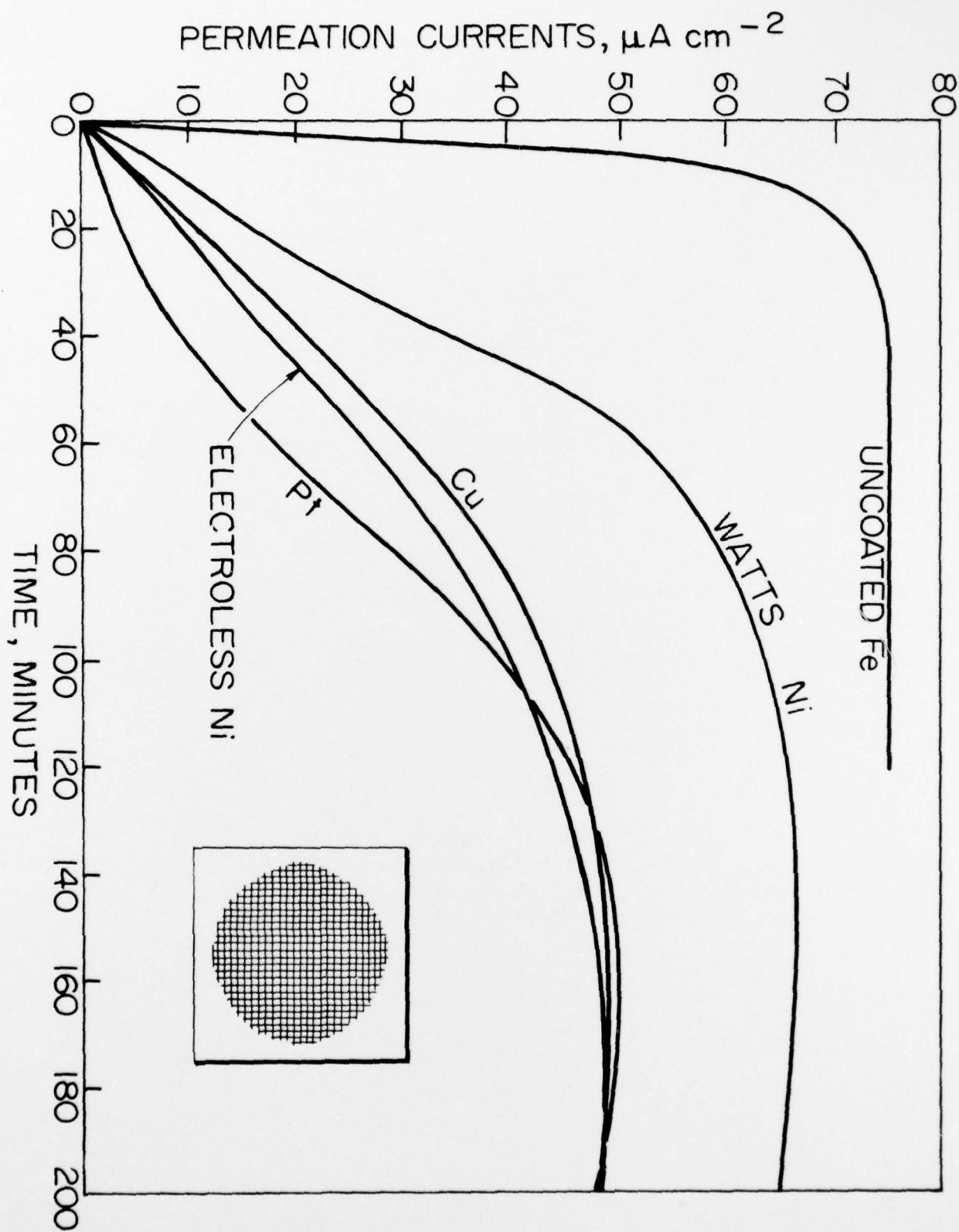


Fig. 7-Effect of square grid deposits on the permeation of hydrogen through Ferrovac E iron membranes. Curves 1, 2, 3, 4 and 5 are the permeation transients of uncoated iron and of iron with square grid deposits of Watts type nickel, Cu, electroless Ni and platinum, respectively.

