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The Effect of Ion Implanting on Hydrogen Entry into Metals

S. C. Chou

Makhlouf M. Makhlouf
Worcester Polytechnic Institute, mmm@wpi.edu

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S.C. CHOU and M.M. MAKHLOUF

The effectiveness of platinum ion implanting in mitigating hydrogen entry into 4340 steel is measured and quantified. Data are presented to compare the extent of hydrogen absorption by the substrate during electrolytic hydrogen charging of platinum ion-implanted and unimplanted 4340 steel substrates. Several implanting conditions were used in processing the samples, and the surface-limited mass-transfer coefficient was calculated for each case and used to quantify the effectiveness of each treatment in reducing hydrogen absorption. It is shown that the underlying mechanism for reducing hydrogen absorption by platinum ion–implanted substrates is the catalytic effect of platinum that favors hydrogen evolution at the steel's surface over hydrogen absorption by the metal. Although scattering experiments with low energy helium ions suggest that the platinum content in the first monolayer of platinum-implanted steels is small, the ability of Pt to catalyze the hydrogen evolution reaction is still strong enough to significantly reduce the quantity of hydrogen that enters the metal.

I. INTRODUCTION

THE potential for hydrogen pickup by a metal exists whenever the metal is exposed to a hydrogen-containing environment.[1] However, more severe hydrogen-charging conditions are encountered when the source of hydrogen is an aqueous phase than when it is a gaseous phase. This is because higher hydrogen fugacities may be reached during corrosion reactions than during normal exposure to hydrogen baring gases. During hydrogen charging of steel from an aqueous phase, *e.g.*, during a corrosion reaction, hydrogen adatoms, H_{ads}, form on the steel's surface according to the reaction

$$H^+ + e^- \rightarrow H_{ads} \qquad [1]$$

The adatoms produced *via* Eq. [1] may combine to form hydrogen molecules that evolve as gas bubbles,

$$H_{ads} + H_{ads} \rightarrow H_2 \qquad [2]$$

$$H_{ads} + H^+ + e^- \rightarrow H_2 \qquad [3]$$
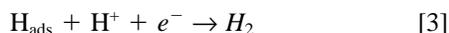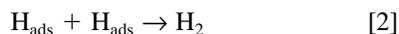
or they may become absorbed into the steel surface,

$$H_{ads} \rightarrow H_{abs} \qquad [4]$$

It is this absorbed hydrogen, H_{abs}, which diffuses into the steel to areas of high triaxial tensile stress, embrittles the metal, and eventually leads to premature failure of steel components. Whether the hydrogen adatom, H_{ads}, follows the path described by Eq. [2], [3], or [4] depends on the energetics of the steel surface. Surface modifications therefore may be designed to reduce the rate of Reaction [4] and enhance the rate of Reactions [2] and [3]. The rate of Reaction [4] is determined by the coverage, θ, of the steel surface by adsorbed hydrogen. Bockris and Subramanyan[2] have shown that when the source of hydrogen is an aqueous phase, θ is related to the hydrogen overpotential, η, by

$$\theta = A e^{-\frac{\beta \eta F}{2RT}} \qquad [5]$$

Where A is the rate coefficient for the hydrogen combination reaction, β is the symmetry factor of the activation barrier for hydrogen discharge, F is the Faraday constant, R is the gas constant, and T is the absolute temperature.

Chattterjee *et al.*,[3] and later Zamanzadeh *et al.*,[4,5] have shown that electrodepositing a metal, with a higher exchange current density for the hydrogen evolution reaction than steel, onto the surface of the steel provides for a lower hydrogen overpotential on the composite surface. The lower hydrogen overpotential on the modified surface provides for lower hydrogen coverage, and consequently less hydrogen is transported from the surface into the bulk of the metal. Chatterjee *et al.*[3] have supported this model with experimental results for platinum electrodeposits on iron. Chatterjee *et al.* electrodeposited platinum, and also nickel, on Ferrovac E iron substrates. After testing the samples for hydrogen permeation, Chatterjee *et al.* found that a platinum coating of only 0.015 μm is much more effective in reducing hydrogen permeation into the iron than a much thicker nickel coating of about 6 μm. Since the diffiusivity of hydrogen in platinum is comparable to that of hydrogen in nickel, Chatterjee *et al.* concluded that the strong effect of the platinum coating in reducing hydrogen permeation must be due to a factor other than its transport properties. They ascribed this strong effect to a catalytic behavior that favors hydrogen evolution on the platinum sites, thereby reducing the overpotential of the composite surface and hence its coverage with hydrogen.

Although catalyzing the hydrogen evolution reaction at the surface of steel by electrodepositing Pt at the surface has shown great potential in mitigating hydrogen uptake, depositing Pt from an electroplating bath seems to be inappropriate since electrodeposition may introduce hydrogen into the steel. Hence, the process, so cleverly designed to protect the metal against hydrogen uptake during service, may potentially undermine the metal during processing. Ion implanting is one way to effectively introduce Pt ions into the steel surface without generating hydrogen atoms, and without affecting the steel's bulk physical and mechanical properties. Unfortunately, scattering experiments with low energy helium ions have shown that the Pt content in the first monolayer of a Pt-implanted steel is typically less than 0.1 at. Pct.[6] Accordingly, the effectiveness of ion-implanted

S.C. CHOU, Graduate Student, and M.M. MAKHLOUF, Associate Professor, are with the Department of Mechanical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609.
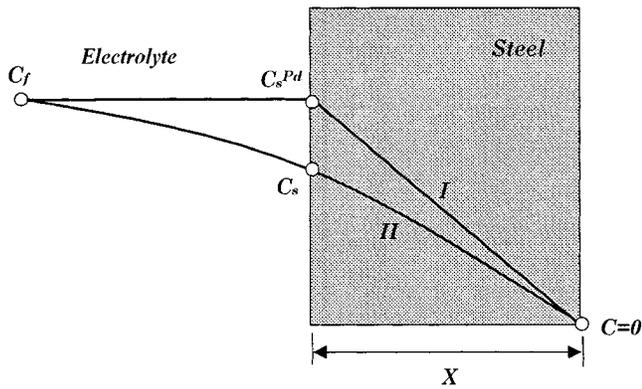
Fig. 1—Schematic representation of the boundry conditions and hydrogen flux during hydrogen charging of palladium-coated and uncoated steel foils in a Devanathan and Stachurski cell.[9] Profile I is for an uncoated foil, and profile II is for a coated foil.

Fig. 2—Schematic representation of the hydrogen charging cell.

Pt in catalyzing the hydrogen evolution reaction on the steel surface may be seriously diminished. In this contribution, the effectiveness of Pt ion implanting in reducing hydrogen uptake by steels is examined. The effect of the depth of the Pt ion-implanted layer, as well as the Pt ion concentration, is quantified in terms of the surface-limited mass-transfer coefficient, h_m.[7] The surface-limited mass-transfer coefficient was first introduced by Makhlouf and Sisson[8] to account for all surface effects during hydrogen charging, including catalytic effects, as well as chemical reactions and interactions between the metal and the environment.

Surface-Limited Mass-Transfer Coefficient

Figure 1 is a schematic representation of the concentration profile of hydrogen atoms during electrolytic hydrogen charging.* Two cases are depicted in Figure 1. In one case,

*An example of this is in an electrolytic hydrogen-charging cell similar to the one developed by Devanathan and Stachurski.[9]

the surface of the steel foil is coated with palladium. Palladium has a very high solubility for hydrogen, and therefore will effectively eliminate all surface effects.[10] Accordingly, in this case, the concentration of hydrogen in the steel at the surface, C_f^{Pd}, is approximately equal to the fugacity of hydrogen in the electrolyte, C_f. In the other case, no palladium is deposited on the surface of the steel. In the absence of palladium, surface processes may be rate limiting and may reduce the concentration of hydrogen in the metal at the surface to a value C_s. The steady-state flux for the first case is given by

$$J_\infty^{Pd} = -D \frac{\Delta C}{\Delta X} \approx -D \frac{C_s^{Pd} - 0}{X} = -D \frac{C_s^{Pd}}{X} \quad [6]$$

Similarly, for the second case, the steady-state flux is given by

$$J_\infty = -D \frac{C_s - 0}{X} = -D \frac{C_s}{X} \quad [7]$$

Also,

$$J_\infty = -h_m(C_f - C_s) \quad [8]$$

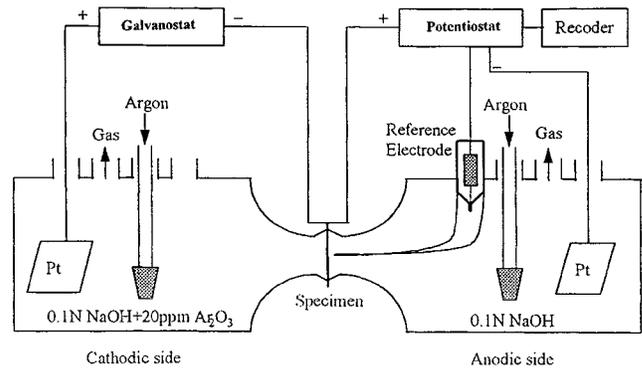So, from Eqs. [7] and [8]

$$J_\infty = -D \frac{C_s}{X} = -h_m(C_f - C_s)$$

and

$$C_s = \frac{h_m C_f X}{D + h_m X}$$

Substituting for C_s into Eq. [7] gives

$$J_\infty = -D \frac{C_f}{X} \left(\frac{h_m}{D/X + h_m} \right) \quad [9]$$

Substituting Eq. [6] into Eq. [9] gives

$$\frac{J_\infty^{Pd}}{J_\infty} = 1 + \frac{D}{h_m X} \quad [10]$$

In Eq. [10], the quantity $D/h_m X$ is dimensionless, and is analogous to the reciprocal of the Biot number for heat transfer. The physical significance of this dimensionless quantity lies in the fact that it is the ratio of bulk diffusion to surface impedance; i.e., it is the ratio of internal resistance to external resistance.

The surface-limited mass-transfer coefficient, h_m, corresponding to a particular surface condition may be calculated by experimentally measuring the steady-state flux for the specimen of interest (J_∞), and also for a similar specimen with a thin layer of palladium deposited on its surface (J_∞^{Pd}). These experimentally determined values, together with D and X, may then be substituted into Eq. [10] to yield h_m.

II. EXPERIMENTAL

An electrolytic hydrogen-charging cell similar to that developed by Devanathan and Stachurski[9] was used for measuring the hydrogen flux through the steel as a function of time. The apparatus, which is shown schematically in Figure 2, consists of two electrochemical cells separated by the test sample. The cathodic cell was filled with an electrolyte of 0.1N sodium hydroxide to which 20 ppm arsenic trioxide was added. Arsenic trioxide acts as a hydrogen recombination poison and reduces the rate of recombination of hydrogen atoms to form hydrogen molecules, thus the arsenic trioxide increases the quantity of hydrogen atoms available to enter the steel.[9] The anodic cell was filled with 0.1N sodium hydroxide. Pure argon gas was bubbled in both

procedures to HRC50. All specimens were hand polished with 600 grit silicon carbide paper, then ultrasonically cleaned and degreased in acetone followed by Freon prior to surface modification, and again prior to hydrogen charging. One side of each foil was implanted with either Pt ions or N ions.* The energies and the doses used in the implanting

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*Implant Sciences Corporation, Wakefield, MA.

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process are shown in Table I, and the profiles of the implanted ions are presented in Figure 3. The foils were implanted under a vacuum of 4×10^{-6} torr, and the temperature of the specimens during implanting did not exceed 100 °C. In addition, one side of some specimens was electroplated with a thin layer of palladium. The chemical composition of the electroplating bath and the electroplating parameters are presented elsewhere.[12] All specimens were stored in a desiccator while awaiting hydrogen charging.

cells to remove oxygen and to circulate the electrolytes. The experimental technique used for measuring the hydrogen flux through the steel foil was essentially that developed by Devanathan and Stachurski[11] for studying the kinetics of the hydrogen evolution reaction. Prior to a measurement, the solutions were pre-electrolyzed in auxiliary cells under an atmosphere of pure argon using platinum electrodes for a minimum of 24 hours. The test samples were AISI 4340 steel foils approximately $3.5 \times 3.5 \times 0.1$ cm. The foils were quenched and tempered according to standard commercial

III. RESULTS AND DISCUSSION

Figure 4 shows the effect of palladium electrodeposited onto the surface of AISI 4340 steel on the hydrogen permeation flux through the foil. The magnitude of the steady-state hydrogen permeation flux in the palladium-coated foil is almost two times that in the uncoated foil. The higher
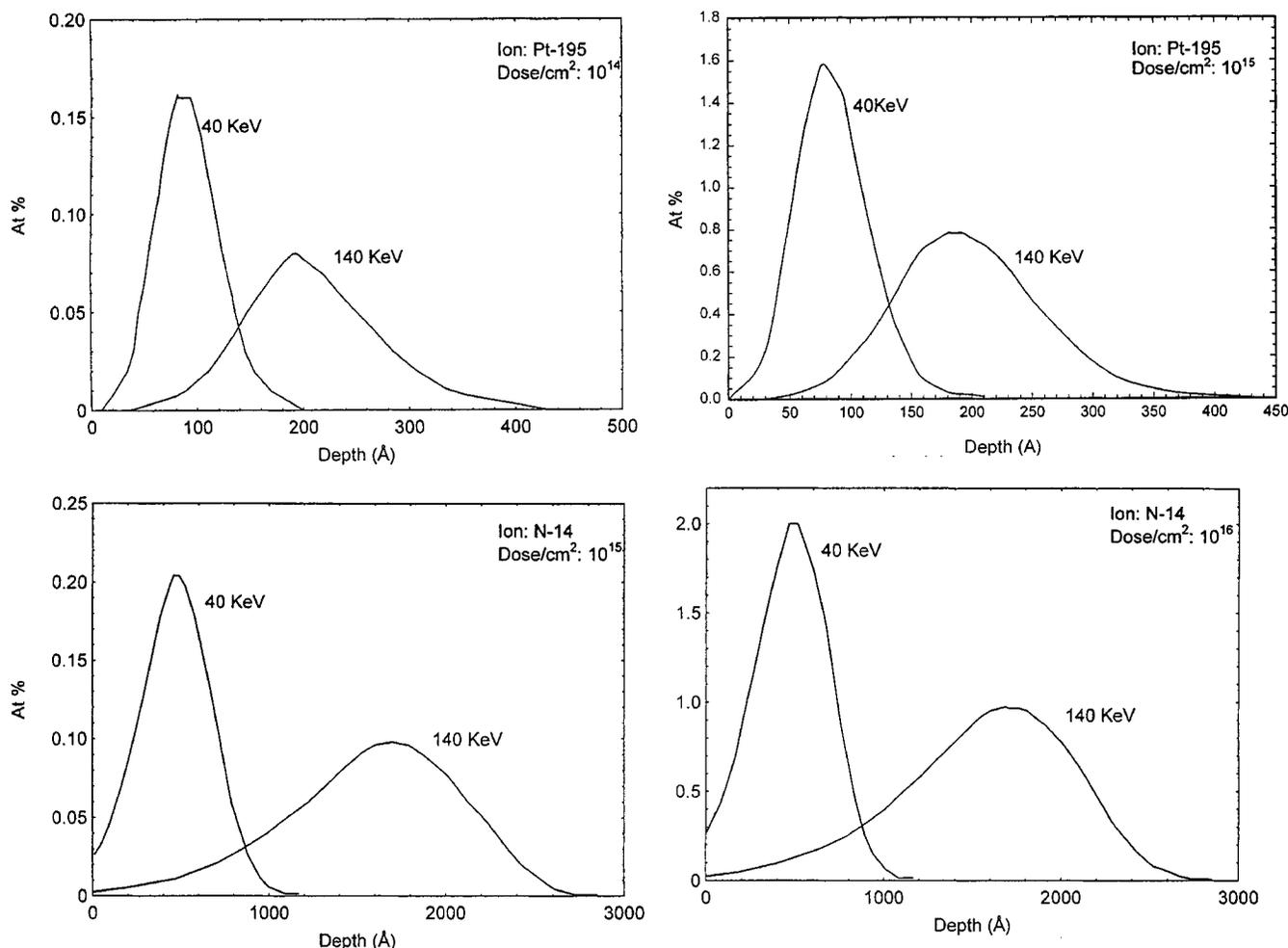

Fig. 3—Profiles of platinum and nitrogen ions implanted in AISI 4340 steel foils. The implanting parameters are shown in Table I.
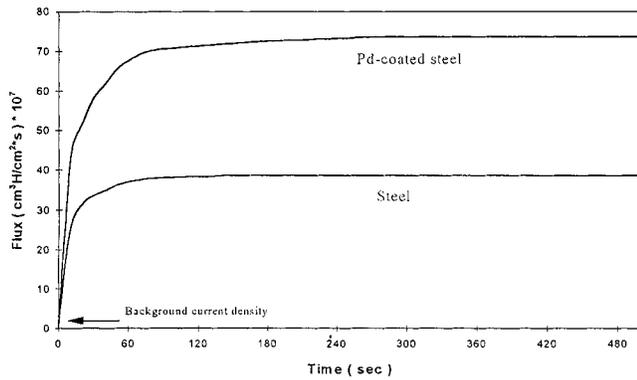
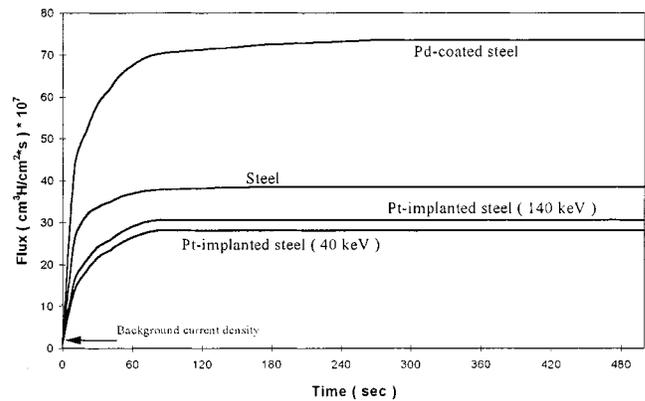Fig. 4—The effect of palladium coating on hydrogen uptake by AISI 4340 steel.

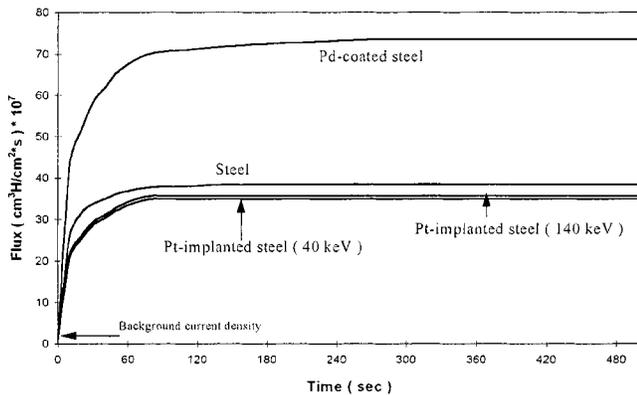Fig. 5—The effect of platinum ion implanting on hydrogen uptake by AISI 4340 steel. Ion dose = 10^{14} ions/cm^2.

Fig. 6—The effect of platinum ion implanting on hydrogen uptake by AISI 4340 steel. Ion dose = 10^{15} ions/cm^2.

steady-state permeation flux in the Pd-coated specimen is attributed to the high solubility of hydrogen in palladium.[10] Kumnick and Johnson[13] and Johnson et al.[14] also argue that, in addition to the high solubility of hydrogen in palladium, palladium is a very effective catalyst for the decomposition of hydrogen molecules into hydrogen atoms. Hence, when palladium is present on the surface of the foil, there is an increased coverage of the foil surface with hydrogen atoms. Therefore, it can be assumed that Pd effectively eliminates all surface impedance to hydrogen entry into the steel foil.

Figures 5 and 6 show the effect of platinum ion implanting on hydrogen entry into AISI 4340 steel. It is clear from these figures that platinum ion implanting reduces the magnitude of the steady-state hydrogen flux in the steel foil. This is in agreement with the findings of Chatterjee et al. for electrodeposited platinum on iron.[3] The exchange current density of the hydrogen evolution reaction is higher on platinum than on iron.[15] During hydrogen charging, the overpotential required to support the charging current is low when the exchange current density is high.[3,4] The low overpotential results in a low coverage of the surface of the steel foil by adsorbed hydrogen atoms, and hence, a low rate of absorption of hydrogen atoms into the surface. Consequently, the magnitude of the steady-state hydrogen permeation flux is lower for foils whose surface is implanted with Pt ions than for foils whose surface is not Pt ion implanted.

Figures 5 and 6 also show that the lower the Pt ion implanting energy, the lower is the magnitude of the steady-state hydrogen permeation flux. This may be explained by examining Figures 3(a) and (b), which show the profiles of Pt ions implanted into the steel foils using 40 KeV (Figure 3(a)) and 140 KeV (Figure 3(b)). It is clear from Figures 3(a) and (b) that the lower the ion implanting energy, the closer is the peak of the Pt ion distribution curve to the foil's surface. Therefore, it is reasonable to assume that the catalytic effect of Pt ions on the hydrogen evolution reaction is more effective when the peak concentration of Pt ions is closer to the foil surface than when it is deeper into the foil's bulk. Comparison of Figures 5 and 6 shows the effect of the Pt ion dose on hydrogen permeation into the steel. The high Pt ion dose (10^{15} Pt ions/cm^2) results in a lower steady-state hydrogen permeation flux than the low Pt ion dose (10^{14} Pt ions/cm^2). This is because the higher dose implies that there are more Pt ions available at the steel surface to catalyze the hydrogen evolution reaction.

In order to confirm that the catalytic mechanism proposed by Chatterjee et al.[3] is responsible for the reduction in hydrogen entry into platinum ion–implanted steel, AISI 4340 steel foils were implanted with nitrogen ions. The exchange current density for the hydrogen evolution reaction is lower on nitrogen than on iron.[6] Since during hydrogen charging the overpotential required to support the charging current is inversely proportional to the exchange current density, a higher overpotential should be created on the nitrogen-implanted surface than on the unimplanted surface. The high overpotential should cause a high coverage of the surface by adsorbed hydrogen atoms, and hence, a high rate of absorption of hydrogen atoms into the surface. Consequently, the magnitude of the steady-state flux should be higher for foils whose surface is implanted with nitrogen ions than for foils whose surface is not nitrogen ion implanted. Figures 7 and 8 show the effect of nitrogen ion implanting on hydrogen entry into AISI 4340 steel foils. Contrary to Pt ion implanting, nitrogen ion implanting increases the steady-state hydrogen flux in the AISI 4340 steel foils, confirming that the catalytic mechanism is active on the ion-implanted surface.

Figures 7 and 8 also show that the higher the nitrogen ion implanting energy, the higher is the magnitude of the steady-state hydrogen permeation flux. Similar to the case
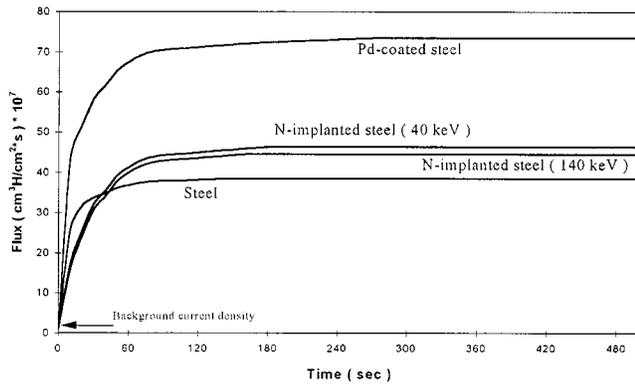
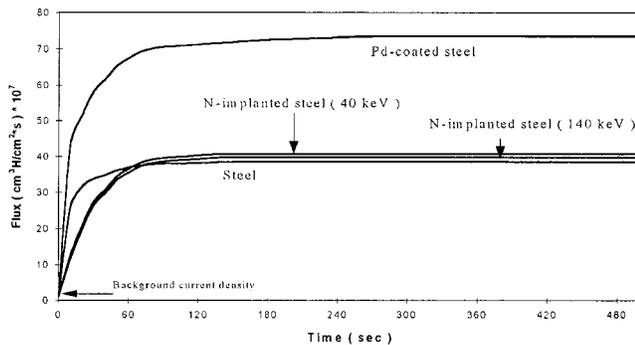Fig. 7—The effect of nitrogen ion implanting on hydrogen uptake by AISI 4340 steel. Ion dose = 10^{15} ions/cm^2.

Fig. 8—The effect of nitrogen ion implanting on hydrogen uptake by AISI 4340 steel. Ion dose = 10^{16} ions/cm^2.

Table II. Surface-Limited Mass-Transfer Coefficient (h_m) and Steady-State Flux for AISI 4340 Steel with Various Surface Modifications

Surface Treatment	Ion Concentration (At. Pct)	Depth (nm)	Steady-State Hydrogen Flux 10^7 (cm^3 H/cm^2 s)	h_m 10^6 (m/s)
Pd-coated	—	—	73.59	
N-implanted	2.000	48.2	46.42	19.9
N-implanted	0.972	169.5	44.59	17.9
N-implanted	0.204	49.0	40.81	14.5
N-implanted	0.098	169.8	39.78	13.7
Steel	—	—	38.51	12.8
Pt-implanted	0.079	19.3	35.78	11.0
Pt-implanted	0.163	8.4	34.96	10.5
Pt-implanted	0.781	18.5	30.60	8.3
Pt-implanted	1.580	7.9	28.08	7.2

Table III. Protection Efficiency for Various Platinum Ion-Implanting Conditions

Surface Treatment	Ion Concentration (At. Pct)	Depth (nm)	Steady-State Hydrogen Flux 10^7 (cm^3 H/cm^2 s)	ηp (Pct)
Steel	—	—	38.51	—
Pt-implanted	0.079	19.3	35.78	7.1
Pt-implanted	0.163	8.4	34.96	9.2
Pt-implanted	0.781	18.5	30.60	20.5
Pt-implanted	1.580	7.9	28.08	27.1

with platinum ion implanting, this is because the higher the implanting energy, the closer is the peak of the nitrogen ion distribution curve (Figures 3(c) and (d)) to the foil's surface. The poisoning effect of the nitrogen ions on the hydrogen evolution reaction is more effective when the peak concentration of the nitrogen ions is closer to the foil surface. Comparison of Figures 7 and 8 shows the effect of the nitrogen ion dose on hydrogen permeation in the steel. As expected, the higher dose results in a higher steady-state hydrogen permeation flux, because the higher dose provides more nitrogen sites at the steel surface to poison the hydrogen evolution reaction.

Quantifying the Effect of Ion Implanting on Hydrogen Uptake by AISI 4340 Steel Quenched and Tempered to HRC50

Table II shows the magnitude of the surface-limited mass-transfer coefficient (h_m) corresponding to each of the surface conditions. These h_m values were calculated using Eq. [10]. The diffusion coefficient was assumed to be that for pure Ferrovac iron, *i.e.*, $D = 1.2 \times 10^{-9}$ m^2/s.[16] It can be seen from Table II that the magnitude of the surface-limited mass-transfer coefficient for each of the platinum-implanted foils is somewhat lower than that for the unimplanted foil. It can also be seen from Table II that the magnitude of the surface-limited mass-transfer coefficient for each of the nitrogen-implanted foils is higher than that for the unimplanted foil.

The effectiveness of platinum ion implanting in reducing

hydrogen entry into the steel may be determined by defining a protection efficiency, η_p,

$$\eta_p = 100 \left(1 - \frac{j_\infty^{\text{implanted}}}{j_\infty^{\text{unimplanted}}} \right)$$

where j_∞ is the steady-state flux. Table III shows the effect of the various platinum ion-implanting conditions on the protection efficiency against hydrogen entry. As the concentration of platinum ions increases, and as the depth of the ion implanted layer decreases, the protection efficiency of platinum increases. A platinum ion concentration of only 1.58 at. Pct at a depth of 7.8 nm results in a protection efficiency of 27 Pct.

IV. CONCLUSIONS

Hydrogen entry into AISI 4340 steel depends to a large extent on the energetics of the steel's surface. Therefore, surface modifications may be designed to alter the surface energetics in such a way as to effectively mitigate hydrogen entry into the steel and reduce the subsequent embrittlement of the metal. The presence of platinum ions at the steel's surface favorably alters the surface energetics. Platinum, which has a higher exchange current density for the hydrogen evolution reaction than iron, catalyzes the hydrogen evolution reaction at the steel's surface and thus reduces the coverage of the steel's surface by hydrogen adatoms. Ion implanting is an effective way of introducing platinum ions

into the steel's surface. Ion implanting does not alter the metal's bulk properties, and, in contrast to electrodeposition, does not expose the metal to hydrogen atoms.

Although scattering experiments with low energy helium ions have shown that the platinum content in the first monolayer of the implanted surface is typically less than 0.1 at. Pct, the ability of platinum to catalyze the hydrogen evolution reaction at the steel's surface is still strong enough to significantly affect hydrogen entry into the metal. The fact that the observed effect of platinum ions on hydrogen entry into the metal is due to platinum's catalytic effect on the hydrogen evolution reaction, and not due to any other surface effect,*

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*Such as creating a state of stress at the steel's surface that limits hydrogen entry.

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was confirmed by implanting nitrogen ions into the steel's surface. Nitrogen, which has a lower exchange current density for the hydrogen evolution reaction than iron, poisoned the hydrogen evolution reaction and enhanced hydrogen entry into the metal.

The catalytic effect of platinum on the hydrogen evolution reaction is more pronounced when the platinum ion concentration is high, and when the peak concentration of the platinum ions is closer to the steel's surface. Consequently, high platinum ion doses and low implanting energies result in high protection efficiencies. A protection efficiency of 27 Pct was achieved by implanting 10^{15} platinum ions per cm^2 (1.58 at. Pct) into the surface of AISI 4340 steel at 40 KeV.

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