The Application of Electroplating for Prevention Of Hydrogen Embrittlement in AISI 4140 Steel

By Jin-Ming Chen and Jiann-Kuo Wu

In order to control the hydrogen embrittlement problem of high-strength steel, electrochemical hydrogen permeation and precharging techniques were performed on Ni-, Ag-, Sn- and Cu-plated AISI 4140 steels to evaluate the benefits of impermeable coatings. From permeation and tensile results, the effectiveness of hydrogen impermeable coatings is in the order Cu, Sn, Ag and Ni. To protect high-strength steels from hydrogen embrittlement, coating with a low-hydrogen-permeable metal is a practical method.

It is well known that high-strength steels are susceptible to hydrogen embrittlement (HE).[1-4] Surface modification has been used to reduce hydrogen-induced failures.[5-8] Wilde and Shimada reported a surface modification technology to impede hydrogen ingress into the steel and the results are feasible.[5] Electroplating appears to be a potential control technique. Hydrogen transport through electroplated metals, such as tin and nickel, etc., have been proposed in association with the delay of hydrogen-induced cracking.[6,7]

In this study, an electrochemical hydrogen permeation technique was utilized to measure the permeation rate and effective diffusivity of hydrogen in Ni-, Ag-, Sn- and Cu-plated AISI 4140 steels. The four differently plated steels investigated for improving HE resistance were also evaluated by cathodic charging and subsequent tensile testing.

Data Analysis

Permeation

For this study, the flux of hydrogen through the specimen was measured in terms of current density i_p and converted to hydrogen permeation flux according to the following equation

$$J_\infty = \frac{i_p^\infty}{nF} \quad (\text{mol H m}^{-2}\,\text{sec}^{-1}) \qquad (1)$$

The permeation rate is defined by

$$J_\infty L = \frac{i_p^\infty L}{nF} \quad (\text{mol H m}^{-1}\,\text{sec}^{-1}) \qquad (2)$$

where i_p^∞ is the steady-state permeation current density, n is the number of electrons transferred, F is Faraday's constant, L is specimen thickness, and J_∞ is steady state flux.

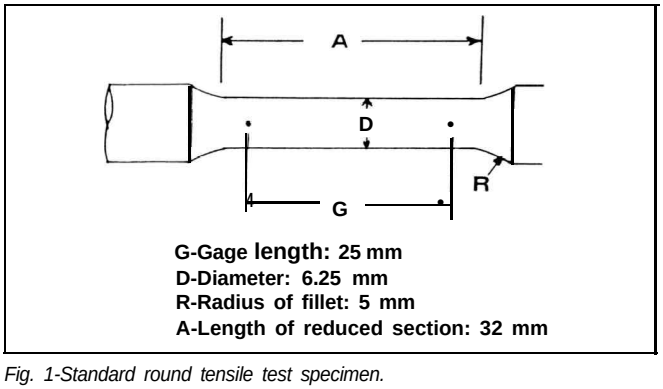


Fig. 1-Standard round tensile test specimen.

Table 1
Composition of AISI 4140 Steel (wt%)

C	Si	Mn	P	S	Cr	Mo
0.41	0.25	0.70	0.03'	0.03	1.05	0.25

Diffusion

For effective diffusion, the rate limiting step D_{eff} is related to time lag by'

$$D_{eff} = \frac{L^2}{6t_1} \quad (\text{m}^2\,\text{sec}^{-1})$$

where t_1 is lag time and D_{eff} is determined from the transient t_1.

Experimental Procedure

Materials

The material chosen for this stud was commercial AISI 4140 low-alloy steel. The chemical compositions (wt percent) are listed in Table 1. Permeation specimens were cut from round bars and machined to 25 mm in diameter and thickness between 0.75 and 0.85 mm. All sheet specimens were austenized at 850°C for 30 min, followed by air cooling to obtain a normalized structure. The specimens were then ground with SiC grinding paper down to 1000 grit. The surfaces were rinsed with distilled water, cleaned ultrasonically in acetone, and dried quickly by warm air. The exit side of each specimen was electroplated with a thin nickel layer. The thickness of the nickel layer was one μm, so that the hydrogen permeation current density could be obtained correctly and the background current density minimized. All tensile specimens were also austenized at 850 "C for 30 rein, followed by air cooling. The dimensions of the round bar tensile specimen are shown in Fig. 1.

Electroplating

Surface preparation prior to electroplating involved the following steps: (1) alkali cleaning (60 to 80°C); (2) water cleaning;

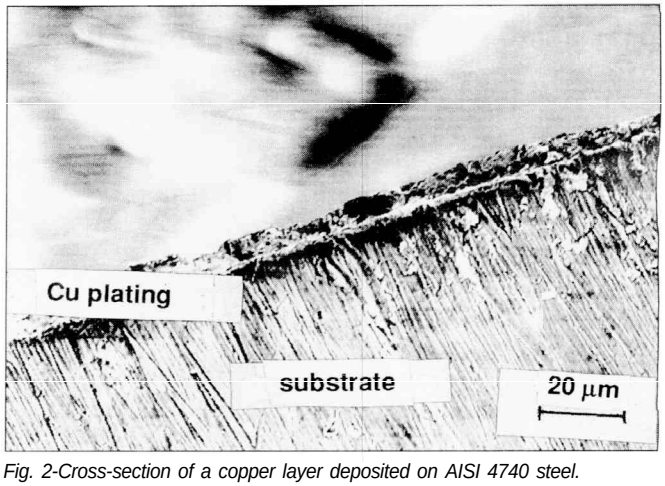
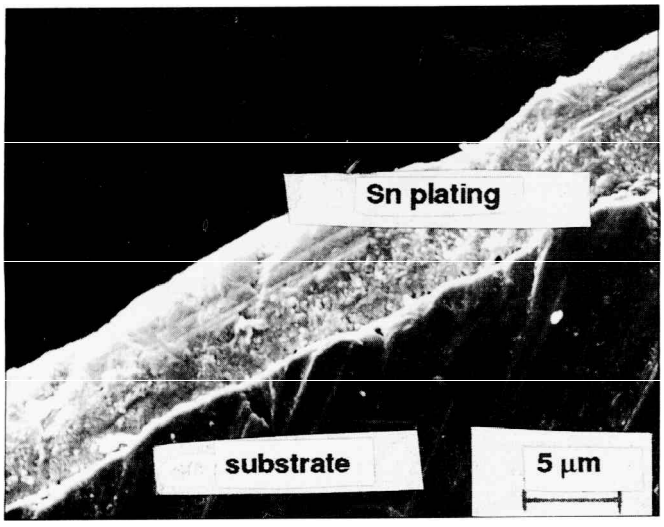


Fig. 2-Cross-section of a copper layer deposited on AISI 4740 steel.



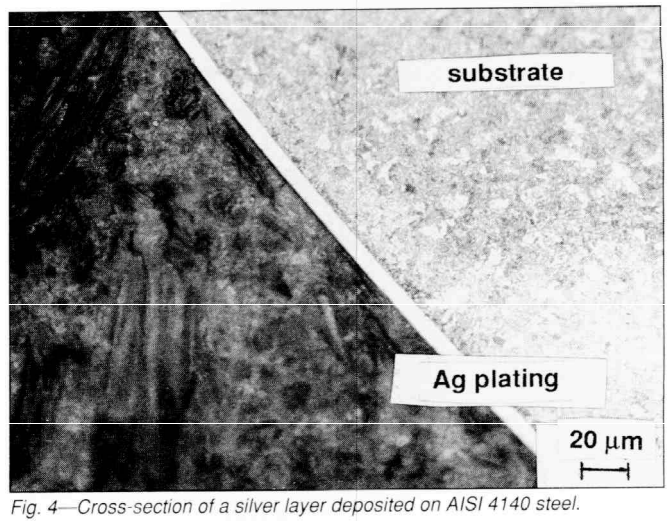


Fig. 4—Cross-section of a silver layer deposited on AISI 4140 steel.

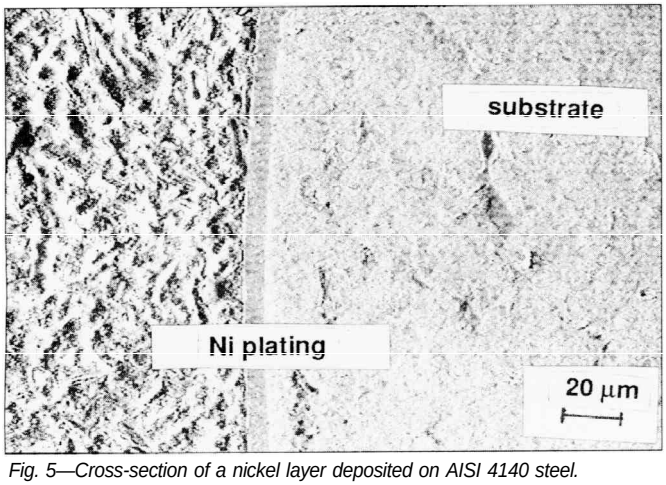


Fig. 5—Cross-section of a nickel layer deposited on AISI 4140 steel.

Tab! 2
Solutions and Conditions for Test Specimens

Metal	Electrolyte Composition	T (°C)
Ni	270 g/L $NiSO_4$; 40 g/L $NiCl_2$; 30 g/L H_3BO_3; pH = 4-5	55
Ag	40 g/L AgCN; 70 g/L KCN; 40 g/L K_2CO_3; 20 g/L KOH	25
Sn	75 g/L $SnCl_2$; 25 g/L NaF; 50 g/L KF; 45 g/L NaCl; pH = 2.7	65
Cu	310 g/L Cu pyrophosphate; 17 g/L KOH; 3 g/L NH_4OH; P_2O_7/Cu = 7 (PH = 8.5)	55

(3) acid pickling; (4) rinsing and drying. After plating, the thickness of the coating layer was measured. If the thickness was excessive, the layer was polished with Al_2O_3 powder to reduce it. Each coating was plated on the hydrogen entry side of all discs and tensile specimens. The four electroplating solutions and conditions for each coating are listed in Table 2. Hydrogen embrittlement of steel may occur during electroplating, so a bake-out treatment for removal of hydrogen from plated steels was carried out at 200 "C for four hr. Figures 2-5 show the cross-sections of Ni, Ag-, Sn- and Cu-plated steel. The thickness of various coatings in this study was only seven pm.

Electrochemical Permeation

The instrumentation and procedures were similar to those described elsewhere.[10] The cathodic side, or hydrogen entry side, of the cell was galvanostatically polarized at a constant charging current density (30 mA/cm^2) in 0.1N NaOH with one g/L of thiourea added as a hydrogen recombination poison. The anodic side, or hydrogen exit side, of the cell was held at a constant potential of 250 mV (SCE) in 0.1N NaOH. The potentiostatic current gave a direct measure of the hydrogen flow rate. The cell assembly was immersed in a constant temperature bath maintained at 25 ±1 °C. Both sides of the membrane were deoxygenated. Permeation transients were recorded on a strip chart recorder. Preliminary experiments indicated good reproducibility after an initial charging run was made on each sample. Similar observations reported by Xie and Hirth are thought to result from initial filling of deep traps.[11]

Hydrogen Charging and Tensile Testing

Hydrogen charging was done a room temperature in a 0.1 N NaOH solution poisoned with one g/L of thiourea. Platinum served as the counter electrode. During cathodic charging, the whole specimen was immersed in the solution. A schematic of the equipment is shown in Fig. 6. Two of each specimen were

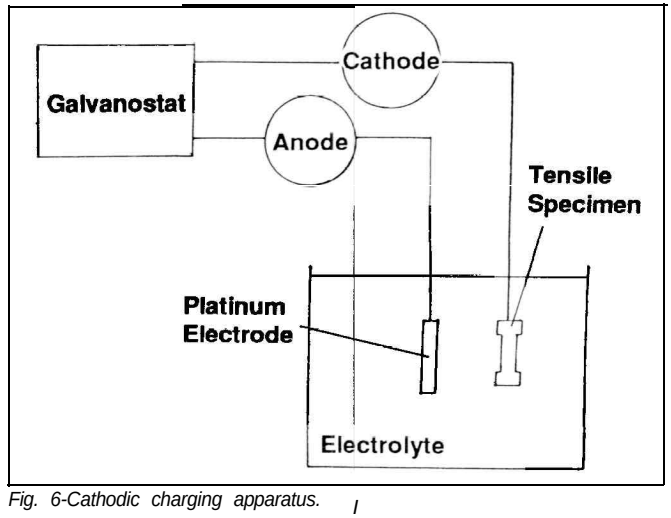


Fig. 6-Cathodic charging apparatus.

Table 3
Effective Diffusivity and Permeation Rate of Plated Specimens
(charging current density: 30 mA/cm²)

Coating metal	Steady state permeation current density ($\mu A\ cm^{-2}$)	Lag time (minutes)	Diffusivity D_{eff} ($m^2\ sec^{-1}$)	Permeation rate (mol H $m^{-1}\ sec^{-1}$)	Impermeable efficiency (%)
Unplated	84	73	2.68×10^{-11}	7.31×10^{-9}	—
Ni-plated	48	79	2.48×10^{-11}	4.18×10^{-9}	43
Ag-plated	23	88	2.33×10^{-11}	2.01×10^{-9}	73
Sn-plated	18	96	2.04×10^{-11}	1.56×10^{-9}	79
Cu-plated	6	92	2.00×10^{-11}	5.22×10^{-10}	93

charged with a galvanostat for 24 hr at a constant current density of 30 mA/cm². The specimens were then removed from the electrolyte, rinsed with distilled water, then with acetone, and dried with cold air. Within five min after hydrogen charging was completed, a tensile load was applied to the specimen. The initial strain rate for all these tests was one msec.

Results and Discussion

Permeation Test

If the impermeable coatings are deposited as thin continuous layers, entry of hydrogen into the metal can be minimized. Figures 2-5 show that the various platings are dense, with continuous structure. Grain diameters of these electrodeposits in the planes parallel to the substrate ranged from 0.1 to 0.5 µm. The permeation data of four differently plated AISI 4140 steel are listed in Table 3. From the values of J~L and D_{eff} the effectiveness of the impermeable coatings studied is in descending order: Cu, Sn, Ag and Ni. This is a characteristic of diffusion through composite membranes where diffusion through the metal coating is the rate-determining step. The efficiencies were calculated and a significant beneficial effect of copper coatings was found.

Tensile Testing

Tensile properties of hydrogen-charged and uncharged specimens are shown in Tables 4 and 5. The charged AISI 4140 steel showed significant degradation in elongation, area and strength. In examining the hydrogen effect for tensile properties, the Cu, Sn, and Ag coatings for AISI 4140 steel also show significant improvement in HE resistance in the same order as previously after 24 hr cathodic charging. These results confirm earlier reports of tests using copper, tin or silver Coatings[6,8] to combat hydrogen embrittlement of working steel parts, but nickel-plated steel still experiences hydrogen damage."

Table 4
Tensile Properties for Different Hydrogen Charging Times of Unplated AISI 4140 Steel

Test Term: Charging time (hr)	Elongation %	Reduction area (%)	RAL* (%)	UTS** (MPa)	YS*** (MPa)
o	20.2	53.1	—	1160	890
6	17.5	46.1	13.2	1130	850
12	17.1	45.4	14.5	1130	850
18	16.8	44.8	15.6	1100	830
24	15.7	44.5	16.2	1080	830

*Reduction Area Loss
**Ultimate Tensile Stress
***Yield Stress

Table 5
Tensile Properties of Hydrogen-Charged AISI 4140 Steels with Various Coatings

Test Term: Plating	Charged or uncharged	Reduction area (%)	RAL* (%)	UTS (MPa)	Coating thickness (µin)
unplated	uncharged	53.1	—	1160	0
	charged	44.5	16.2	1080	7
Ni-plated	charged	46.5	12.4	1120	7
Ag-plated	charged	49.9	6.0	1140	7
Sri-plated	charged	50.0	5.8	1140	7
Cu-plated	charged	50.0	5.8	1160	7

Conclusions

1. From permeation and tensile data, the effectiveness of the hydrogen-impermeable coatings is in descending order: Cu, Sn, Ag and Ni.

2. To protect high-strength steels from hydrogen-induced fracture, "coating with a low-hydrogen-permeable metal is a feasible method.

Acknowledgment

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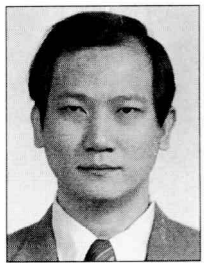

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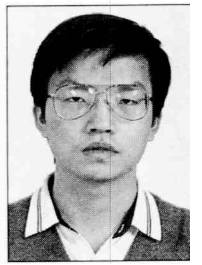

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