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Passivation treatment for inhibition of hydrogen absorption in chromium-plated steel

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Hydrogen permeation transients for passivated chromium-plated steels were measured at room temperature as a function of cathodic charging current density. The passivated film on chromium plating is shown to be an effective barrier to hydrogen at low cathodic charging current density (40 and 100 μA cm^{-2}). The passivated film can be reduced to chromium at higher cathodic charging current density (1 and 10 mA cm^{-2}), promoting hydrogen absorption significantly. .

1. Introduction

It is well known that ferrous alloys are susceptible to hydrogen degradation [1–4]. Surface modification has been used to reduce hydrogen-induced failures [5–12]. The permeability of hydrogen through steel can be decreased significantly by coating with a thin layer of effective barrier, and the absorption of hydrogen can also be delayed for a period that depends on the property and the thickness of the coating. Hydrogen-impermeable coatings would effectively impede hydrogen entry into steels. To protect steels from hydrogen embrittlement, some researchers used a coating of another metal to lower the hydrogen permeability. A hard chromium coating offers excellent corrosion and wear resistance, and appearance, owing to its passive film of Cr_2O_3. The chromium oxide film is thought to act as a barrier between the metal and the corrosive environment or atmosphere. Without a passive film, chromium-plated steel cannot prevent hydrogen embrittlement, and even more severe hydrogen embrittlement can result from chromium coating [13, 14]. In this study, an electrochemical hydrogen-permeation technique was used to evaluate the effect of passivation treatment on the hydrogen transport in chromium-plated steel for improving the hydrogen-embrittlement resistance.

2. Data analysis

2.1. Permeation

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

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

The permeation rate [6] is defined by

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

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

2.2. Diffusion

For effective diffusivity, D_{eff} is related to time lag by [15]

$$D_{\text{eff}} = \frac{L^2}{6t_L} (\text{m}^2\,\text{s}^{-1}) \qquad (3)$$

where t_L is the lag time [15] and D_{eff} is determined from the transient, t_L.

3. Experimental procedure

3.1. Specimen preparation

The test material was cold-rolled mild steel (0.05% C, 0.67% Si, 0.23% Mn, 0.01% S). The steel sheets (0.78–0.82 mm × 3.0 cm × 5.0 cm) were ground with grinding paper down to 1000 grit. Surface preparation prior to chromium electroplating involved the following steps: (1) alkali cleaning (60–80 °C), (2) water cleaning, (3) acid pickling, (4) rinsing and drying. Chromium electroplating was applied on the hydrogen entry side of each specimen, A chromium layer was deposited from a Bornhauser plating bath [16] (300 g^{-1} CrO_3, 0.8 g^{-1} H_2SO_4, 50 g^{-1} NaOH, 1 ml l^{-1} C_2H_5OH) at room temperature and a plating current density of 2 KA m^{-2}. The exit side of each specimen was electroplated with a thin nickel layer (0.2 μm) to minimize the background current [6].

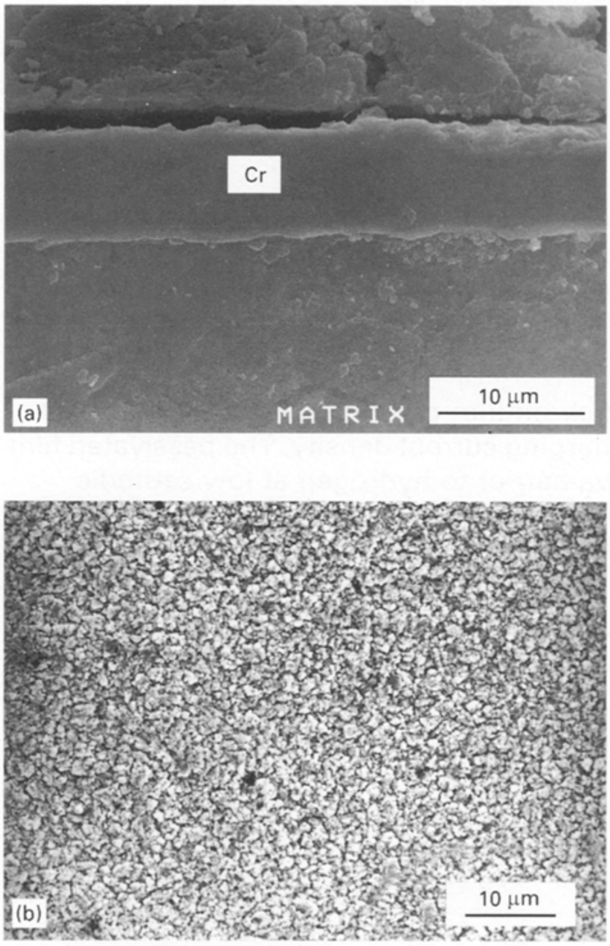


Figure 1 Scanning electron micrographs of (a) the cross-section of a passivated chromium layer plated on a steel substrate, and (b) the surface view.

TABLE I Permeation data of chromium-plated steel in 0.1N NaOH with and without promoter solutions

Thickness of chromium plating		0.1N NaOH	0.1N NaOH + 1 g $^{-1}$Na$_2$S·9H$_2$O
No plating	Permeation rate $J_\infty L$ (mol H m^{-1} s^{-1})	2.55×10^{-10}	6.24×10^{-10}
	Fraction of $J_\infty L$ (%)	100	245
7 μm Cr plating	Permeation rate $J_\infty L$ (mol H m^{-1} s^{-1})	3.06×10^{-9}	3.22×10^{-9}
	Fraction of $J_\infty L$ (%)	1200	1260

Charging current density 10 mA cm^{-2}, temperature 25 ± 1 °C, specimen thickness 0.8 mm, effective diffusivity of unplated steel 1×10^{10} m^2 s^{-1}.

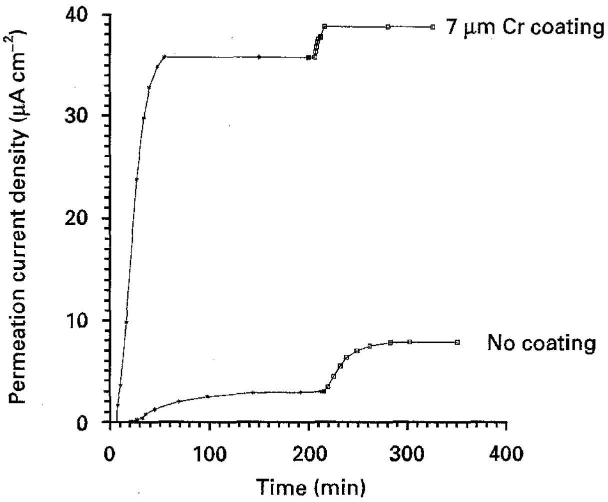


Figure 2 Permeation current density versus time at a constant charging current density (10 mA cm^{-2}) in 0.1N NaOH (□) with and (∗) without 1 g^{-1} Na$_2$S·9H$_2$O.

After plating, the thickness of the coating layer was measured using a Mitutoyo Coating Thickness Gauge. The thickness of the chromium electrodeposit on the hydrogen entry side was controlled at 7 μm. Examination showed that the chromium plating was a dense structure. To obtain a passive film on chromium-plated steel, some chromium-plated specimens were also passivated in 20 vol% HNO$_3$ at 55° C for 30 min [17]. Fig. 1 shows the cross-section of a passivated chromium-plated steel.

3.2. Hydrogen permeation

The instrumentation and procedures were similar to those described elsewhere [18]. The cathodic side, or hydrogen entry side, of the cell was galvanostatically polarized at various constant charging current densities (40, 100 μA cm^{-2} and 1, 10 mA cm^{-2}) in 0.1N NaOH with 1 g^{-1} Na$_2$S·9H$_2$O added as a hydrogen-recombination poison. The anodic side of the cell was held at a constant potential of 250 mV (SCE) in 0.1N NaOH. The potentiostat 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 [19] are thought to result from initial filling of deep traps.

4. Results and discussion

4.1. The effect of chromium plating

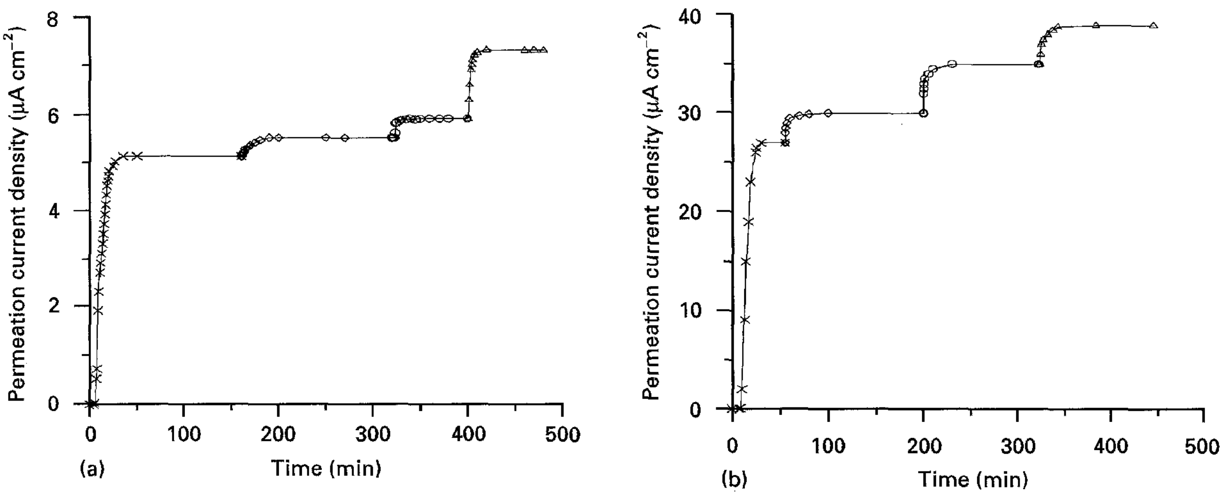
In hydrogen-permeation measurement, the cathodic solution of the entry cell was added with a promoter. The promoter acts as a hydrogen-recombination poison, and can delay the hydrogen atom state from forming the hydrogen molecular state. Permeation data of unplated and chromium-plated steels with and without promoters (Na$_2$S·9H$_2$O) are listed in Table I. Permeation current density versus time for chromium plated steel with and without promoter is shown in Fig. 2. The permeation rates of unplated and chromium-plated steels with promoters are higher than without adding promoter.

Hydrogen permeation-rate measurements on chromium-plated steel show that hydrogen absorption is about one order of magnitude higher than that on unplated steel. It is difficult to explain why the chromium surface suppresses the recombination reaction and enhances permeation in steel.

TABLE II Permeation data

		Charging current density (mA cm^{-2})			
		40	100	1	10
No plating	Measured potential (V, SCE)	− 1.23	− 1.32	− 1.65	− 2.89
	Permeation rate, $J_\infty L$ (mol H m^{-1} s^{-1})	4.36×10^{-10}	4.70×10^{-10}	5.05×10^{-10}	6.24×10^{-10}
7 mm Cr plating	Measured potential (V, SCE)	− 1.36	− 1.46	− 1.65	− 2.84
	Permeation rate, $J_\infty L$ (mol H m^{-1} s^{-1})	2.30×10^{-9}	2.54×10^{-9}	2.97×10^{-9}	3.31×10^{-9}
	Fraction of $J_\infty L$ (%)	528	540	588	530
7 mm passivated Cr plating	Measured potential (V, SCE)	− 1.30	− 1.36	− 1.63	− 3.06
	Permeation rate, $J_\infty L$ (mol H m^{-1} s^{-1})	0[a]	0[a]	1.52×10^{-9}	3.22×10^{-9}
	Fraction of $J_\infty L$ (%)	0[a]	0[a]	301	516

Temperature 25 ± 1 °C, specimen thickness 0.8 mm, Cathodic solution 0.1N NaOH + 1 g^{-1} $Na_2S \cdot 9H_2O$.
[a]Below the detection limit of instrumentation.



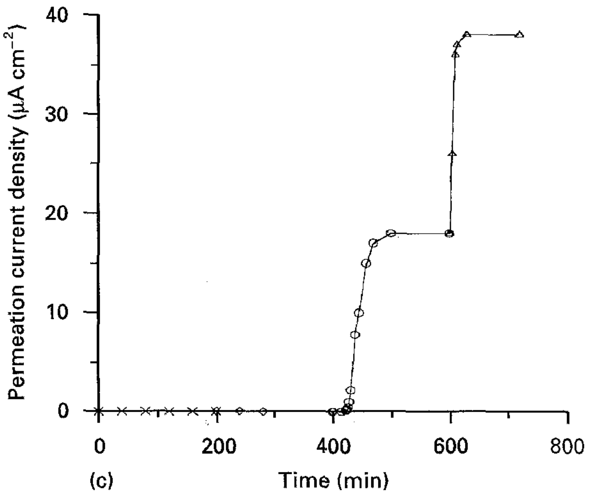


Figure 3 The effect of cathodic charging current density on the permeation transient for (a) unplated steel, (b) chromium-plated steel, (c) chromium-plated steel with passivation treatment. (×) 40 μA cm^{-2}, (◇) 100 mA cm^{-2}, (○) 1 mA cm^{-2}, (△) 10 mA cm^{-2}.

Mindvuk *et al.* [14] have reported that the hydrogen permeability of metals depends on their unpaired d- and p-electrons of the outer ionic shells of the metallic lattice. Chromium has a very high density of unpaired electrons, and thus shows an extremely high hydrogen permeability [13], promotes hydrogen entry into steel, and increases hydrogen solubility significantly.

4.2. The effect of passivation treatment

The effects of cathodic charging current density and passivation treatment on permeation rates of unplated and chromium-plated steel is listed in Table II and shown in Fig. 3.

If the impermeable coatings are formed as continuous and pore-free layers, the entry of hydrogen into steel can be minimized. No hydrogen diffusion has been detected through the chromium-plated steel with passivation treatment at lower charging current densities (40 and 100 mA cm^{-2}). This is a characteristic of diffusion through composite membranes, where diffusion through the passive film of Cr_2O_3 is the rate-determining step. The hydrogen-barrier efficiency of chromium-plated steel approached 100% when passivated in 20 Vol % HNO_3 at 55 °C for 30 min, due to the extremely low permeation rate and diffusivity of hydrogen in Cr_2O_3 film. The permeation of hydrogen through some passivated metals is also controlled chiefly by the kinetic processes in the passive film [20].

It can be seen that as the charging current density increases, the permeation rate and absorption rate also increase for chromium-plated steel without passivation treatment. High permeation rates of passivated chromium-plated steel resulted from the reduction of a passive film of Cr_2O_3 with high charging current densities. The calculated potential of reduction of Cr_2O_3 to chromium is -1.64 V(SCE). It is quite close to the measured potential at a charging current density of 1 mA cm^{-2}. To protect steels from hydrogen damage, passivated chromium plating provides a significant beneficial effect. However, destruction of a passive film of Cr_2O_3 should be avoided in hydrogen environments.

5. Conclusions

1. Hydrogen absorption is significantly reduced due to the barrier effect of a passivated film on chromium-plated steel. The passivated chromium-plated steel shows an undetectable low permeability due to the low hydrogen absorption rate of the passivated film. To inhibit steels from hydrogen-induced failure, treatment with an extremely low hydrogen-permeable passivated chromium plating is a feasible method.

2. A passivated film of chromium-plated steel can be reduced to chromium at higher charging current density, and this causes more severe hydrogen damage.

3. Chromium-plated steel cannot prevent hydrogen embrittlement. More severe hydrogen damage can result from chromium plating in hydrogen environments without passivation treatment.

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References

1. F. FONDEUR, T. A. MOZHL and B. E. WILDE, *Corr. Sci.* **28** (1988) 461.
2. B. C. POUND, *Corrosion* **45** (1989) 18.
3. D. B. McDONNELL, V. S. SASTRI, C. TIAN and J. BEDNAR, *Metall. Trans.* **16A** (1985) 1694.
4. D. L. JOHNSON and J. K. WU, *J. Mater. Energy Sys.* **8** (1987) 402.
5. J. M. CHEN and J. K. WU, *Plating Surface Finish.* **79**(10) (1992) 74.
6. J. M. CHEN and J. K. WU, *Corr. Sci.* **33** (1992) 657.
7. S. S. CHATTERJEE, B. G. ATEYA and H. W. PICKERING, *Metall. Trans.* **9A** (1978) 389.
8. M. ZAMANZADEH, A. ALLAM, C. KATO, B. ATEYA and H. W. PICKERING, *J. Electrochem. Soc.* **129** (1982) 284.
9. M. ZAMANZADEH, A. ALLAM, H. W. PICKERING and G. K. HUBLER, *ibid.* **127** (1980) 1688.
10. B. E. WILDE and T. SHIMADA, *Chin. J. Mater. Sci.* **19** (1987) 107.
11. C. MERGEY, *Br. Corr. J.* **19** (1984) 132.
12. R. H. SONG and S. PYUN, *J. Electrochem. Soc.* **137** (1990) 1051.
13. Y. C. WU, W. Y. WEI, J. M. CHEN and J. K. WU, *Tatung J.* **19** (1989) 191.
14. A. K. MINDVUK, E. I. SVIST. V. P. KOVAL, I. I. VASILENKO and Y. I. BABEI, *Fiz.-Khim. Mekh. Mater.* **8** (1972) 99.
15. J. CRANK, "The Mathematics of Diffusion" (Oxford University Press, Oxford, 1977) pp. 44–9.
16. D. L. WANG, "Practical Electroplating" (Hsus Foundation Press, Taiwan, 1992) p. 511.
17. "Metals Handbook," 9th Edn, L. J. Korb and D. L. Olson, Vol. 13 (ASM International, Metal Park, OH, 1988) p. 552.
18. M. A. V. DAVANATHAN and Z. STACHURSKI, *Proc. R. Soc.* **A270** (1962) 90.
19. S. X. XIE and J. P. HIRTH, *Corrosion* **38** (1982) 486.
20. S. I. PYUN and R. A. ORIANI, *Corr. Sci.* **29** (1989) 485.

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