

Corrosion and wear properties of electrodeposited amorphous chrome

YONG CHOI

Department of Metallurgical Engineering, Sun Moon University, Asan-City, Chung-Nam 336-840, Korea

Amorphous chrome was electrodeposited onto AISI 1025 steel substrates in a modified Sargent bath containing formic acid after electropolished in several electrolytic solutions. The average carbon content of the deposited layer was 2.0 wt %, which is higher than the carbon content of a chrome layer deposited in the modified Sargent bath. The hardness and wear resistance of the amorphous chrome layer are improved by annealing up to about 600 °C due to the precipitation hardening effect resulting from the formation of chromium carbide. The chrome layers electropolished in a modified Sargent bath for 2 min showed the longest neutral salt spray life amongst the chrome layers prepared in the same solution. Electropolishing in the modified Faust solution also improved the neutral salt spray life of chrome plated steel more than did the electropolishing in the plating bath. A chrome layer electropolished in the modified Faust solution for 2 min at a current density of 0.6 Acm⁻² and 53 °C showed the highest corrosion resistance amongst the samples prepared in this study. The contamination of the plating bath with a modified Faust solution reduces the cathodic current efficiency.

1. Introduction

Chrome plating is widely used in the manufacture of machine parts and instruments in the automobile and other industries in order to improve the wear and corrosion resistance of metallic surfaces [1,2]. As is discussed in reference [3] Sargent *et al.* developed a modified chrome plating method using a plating bath based on chromium trioxide (CrO₃), which forms dichromic acid (H₂Cr₂O₇) in aqueous solutions, containing a sulphate catalyst. This modified Sargent bath produces a crystalline chrome layer on a metal substrate. The microstructure and the properties of the chrome layer are significantly influenced by small amounts of chemical agents in the bath [4].

Recently, Furuya *et al.* [5] and Morikawa and Eguchi [6] observed that the electrodeposited chrome was amorphous when formic acid or certain other organics were added to the sulphate-catalysed chromic acid electrolyte. The amorphous chrome layer has fewer defects, smoother surfaces, a greater resistance to corrosion by hydrochloric acid solutions and increased hardness at elevated temperature than a modified chrome layer [7]. Since the chrome structure significantly depends on the initial surface condition of the steel, a smooth and mirror-like surface is required in order to make a high quality chrome plate [4,8]. The roughness of a mechanically polished surface can be reduced by applying the electropolishing technique. Electropolishing in a Faust solution gives a smoother surface than electropolishing in a conventional production bath [8]. Morikawa and Eguchi observed that electropolishing in a modified Faust

solution induces the deposition of a dense chrome layer, which has fewer defects, smoother surfaces, and more effectively protects substrate metal alloys such as steel and Inconel [6]. Although considerable literature exists concerning amorphous chrome deposits, little information is available on the characteristics of the chrome layer. In this study, a challengeable electrochemical solution was selected and applied to the electropolishing of the substrate steel before hard chrome plating. Conventional and amorphous chrome layers were electrodeposited in a Hull cell. The corrosion and wear tests of the layers were performed with a neutral salt fog spray tester and a Taber wear tester, respectively. Attention is focused on (i) any annealing effect on the hardness and wear properties of the amorphous chrome layer and (ii) any effect of the electropolishing in the modified Faust solution and conventional Sargent bath on chrome plating efficiency and neutral salt fog spray life.

2. Experimental procedure

2.1. Electropolishing

Two kinds of electropolishing solution were prepared in this study. The solutions have the bath chemistries listed in Table 1.

Plates of size 100 × 100 mm were polished with 180, 240, 320, and 600 grit sand papers. Each plate was electropolished at a current density of 0.6 Acm⁻² for 0.5, 1, 2, and 3 min at 53 °C. Since the modified Faust solution contained orthophosphoric acid, each sample surface was immediately neutralized with 2% sodium

TABLE 1 Bath chemistries for electropolishing

Composition (wt%)	
1	Faust solution ($\text{H}_3\text{PO}_4:\text{CrO}_3:\text{H}_2\text{O} = 70:10:20$)
2	Plating bath ($\text{CrO}_3:\text{H}_2\text{O}:\text{organic acid} = 70:20:10$)

hydroxide solution after electropolishing and rinsed with distilled water.

The samples used to find the optimum electroplating time in the Faust solution were directly chrome plated after the rinsing process. In order to simulate a real chrome plating situation, the samples used to compare the electropolishing effect between the Faust solution and the conventional Sargent bath were electropolished in the plating solution for 30 s after the rinsing process.

2.2. Electrodeposition

The chrome deposits were obtained on AISI 1025 steel substrates by the method described by Holflund *et al.* [9] The conventional chrome layers were prepared by electroplating chrome in a Sargent bath containing 250 g l^{-1} of chromic acid and 2.5 g l^{-1} of sulphuric acid at a temperature of 53°C and a current density of 0.6 A cm^{-2} for 3 h. The amorphous chrome layers were prepared by electroplating chrome in the modified Sargent bath containing up to 20 ml per L of formic acid at a temperature of 30°C and a current density of 0.6 A cm^{-2} for 1 h.

The plating cell was made of acrylic with dimension of $120 \times 200 \times 200 \text{ mm}$. The anode was an lead-5% antimony alloy plate with dimensions of $100 \times 100 \times 5 \text{ mm}$. The anode and the steel cathode were vertically situated at the ends of the cell. The electroplating of each sample was carried out with a potentiostat (Hokuto Denko HAB-151). Fig. 1 shows a schematic diagram of the apparatus for the amorphous chrome plating procedure.

2.3. Characterization of the deposited chrome

After deposition, the samples were ultrasonically cleaned in acetone and ethanol and then annealed at temperatures up to 600°C in a $1.333 \times 10^{-3} \text{ Pa}$ vacuum for 1h. The carbon content in the chrome was determined by a carbon-sulphur determinator (LECO-777). The phase identification and the morphology observation of the deposited chrome were carried out with an X-ray diffractometer (Rikoku 100) and a scanning electron microscope (Jeol 35-C). Knoop microhardness testing was conducted on the cross-sectional areas of the chrome deposits at 100 g. (Micromet-3), and each hardness value is the average of several measurements, which did not vary significantly. Wear resistance was determined using a Taber abrasive wear tester (Taber D-505) in accordance with ASTM C-501. For the samples with a chrome thickness of about 0.08 mm, a neutral salt fog spray test was carried out by a batch process following ASTM B-117. Considering the phosphoric acid contamination in the

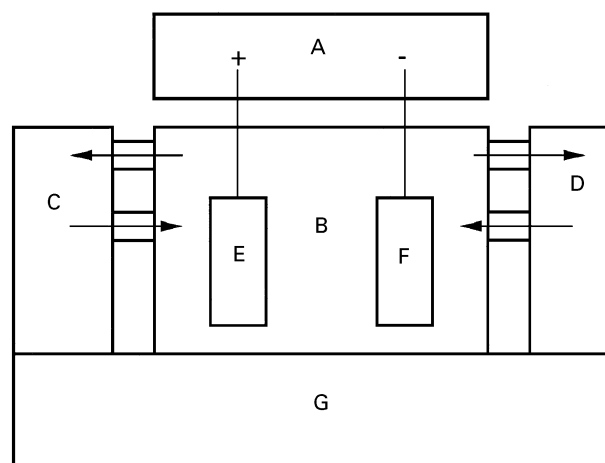


Figure 1 Schematic diagram of amorphous chrome plating apparatus A: D.C. rectifier, B: Plating bath, C: Chrome solution reservoir, D: Organic solution bath, E: Lead anode, F: Specimen, G: Heater and temperature controller unit.

chrome solution, the cathodic current efficiency was determined by a Hull cell with the modified Faust solution content in the modified Sargent bath.

3. Results and discussion

The chrome layers were shiny white in colour. Fig. 2 shows the variation of carbon concentration in the deposited chrome layer with various concentrations of formic acid. The carbon content of the chrome deposits increases with increasing the concentration of formic acid. For a given plating condition, the maximum carbon content in the chrome layer deposited in a solution containing the formic acid is about 2.0 wt%. This is almost one hundred times a higher value than that of the 0.02 wt% in the modified Sargent bath. Since the equilibrium solubility of carbon in chrome is less than 0.02 wt% [10], the excess carbon is supersaturated in a chrome layer deposited in the modified Sargent bath containing the organic compound.

The hardness of the chrome deposited in the organic bath is 935 Knoop at 100 g load, which is almost equal to the conventional chrome hardness, 920 Knoop at the same scale. Fig. 3 shows the hardness change of the chrome layers annealed for 1 h at $1.333 \times 10^{-1} \text{ Pa}$ at various temperatures. As is shown in Fig. 3, the hardness of a chrome layer deposited in the modified Sargent bath decreases with annealing temperature. This hardness reduction is attributed to the combined effects of the softening of metallic chrome and the formation of microcracks [2, 3]. However, the hardness of the chrome prepared in the modified Sargent bath containing the organic compound increases with annealing temperature. In order to understand the hardness increase of the chrome layer deposited in the modified Sargent bath containing the organic compound, phase identification was carried out with an X-ray diffractometer. As is shown in Fig. 4a, a deposit without any annealing shows a broad feature, which corresponds to an amorphous structure. This amorphous structure is known to be related to the supersaturation of carbon [7, 9]. As the

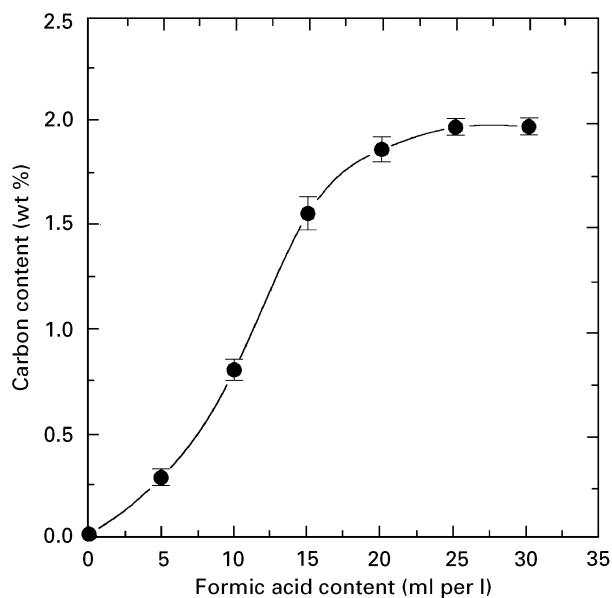


Figure 2 The average carbon concentration in the deposited chrome layer with the concentration of formic acid in the bath.

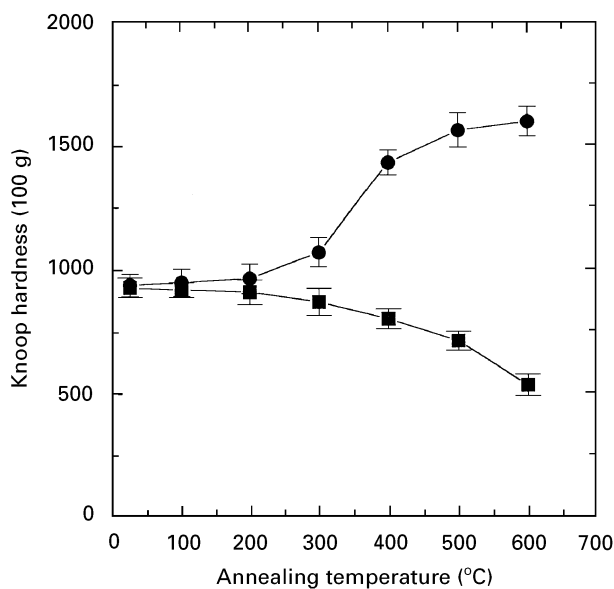


Figure 3 The hardness changes of the chrome layers with annealing temperature: annealed at 1.333×10^{-1} Pa for 1h. (●) amorphous chrome layer; (■) conventional chrome layer.

deposit was annealed up to 600 °C, peaks of metallic chromium and chromium carbide were observed in the X-ray diffraction pattern and the broad feature of the amorphous structure disappeared (Fig. 4b). Since chromium is a strong carbide former, chromium carbide can be produced during annealing in the layer supersaturated with carbon. Hence the precipitation of chromium carbide during annealing is related to the hardness improvement of the chrome layer deposited in the modified Sargent bath containing an organic compound.

The wear resistance of the chrome layer containing the carbide precipitate was determined by the Taber wear test. Fig. 5 shows the variation of wear factor with annealing temperature, where a higher Taber wear factor means a lower wear resistance. As is shown Fig. 5, the wear factor of the chrome deposited

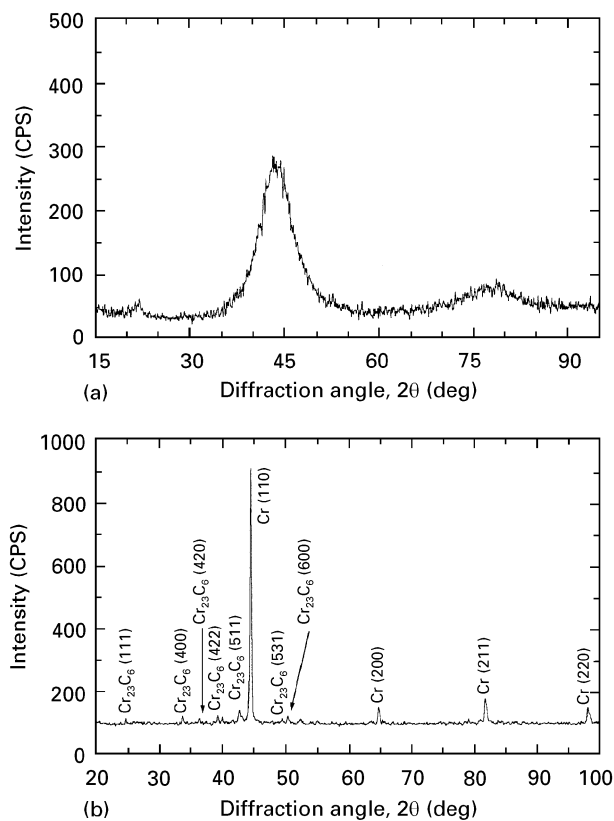


Figure 4 X-ray diffraction patterns of the chrome layers deposited in the modified Sargent bath containing the organic compound (a) as received (b) after vacuum annealing at 600 °C for 1h.

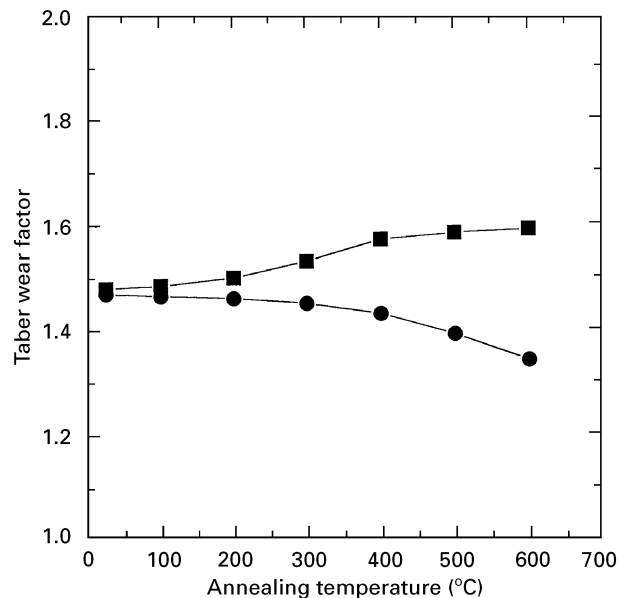


Figure 5 Taber wear factors of the chrome layers with annealing temperature. Higher Taber wear factor means a lower wear resistance: (●) amorphous chrome; (■) conventional chrome.

in the modified bath increases with annealing temperature, however, that of the chrome deposited in the bath containing formic acid slightly decreases with annealing temperature. The decreased wear resistance of the modified chrome results from softening after annealing. [2, 3] Fig. 6 (a and b) shows typical scanning electron micrographs of chrome layer before and

after the Taber wear test, where microcracks and nodules of as-received chrome surface are worn out after the Taber wear test. Net-like microcracks and debris are also observed on the wear damaged surface of the chrome layer. Considering the relatively weak interfacial bonding strength between metallic chrome and the chromium carbide and oxide particles, the small improvement of wear resistance for the chrome deposited in the bath containing the organic compound seems due to the combined effects of the precipitation hardening and the effective detachment of the carbide particles during the Taber wear test.

From a previous study on the electropolishing effect on the surface structure of steel, there is an optimum electropolishing time for a given solution. Fig. 7 (a–c) shows the effect of electropolishing time on a neutral salt fog spray test. Each sample was electropolished at 53 °C and a current density of 0.6 Acm^{-2} in a modified Sargent bath containing $300 \text{ gl}^{-1} \text{CrO}_3$. In the case of a modified Sargent bath, as is shown in Fig. 7, the sample electropolished for 3 min shows the highest corrosion resistance in a neutral salt fog spray environment. This result agrees with the observed optimum electropolishing time.

Fig. 8 (a–c) shows the effect of the electropolishing time in the modified Faust solution after 90 h in a neutral salt fog spray test. Each sample was electropolished in the solution at 53 °C and a current density of 0.6 Acm^{-2} . Electropolishing times for the samples were (a) 30 s, (b) 1 min and (c) 2 min. A reverse

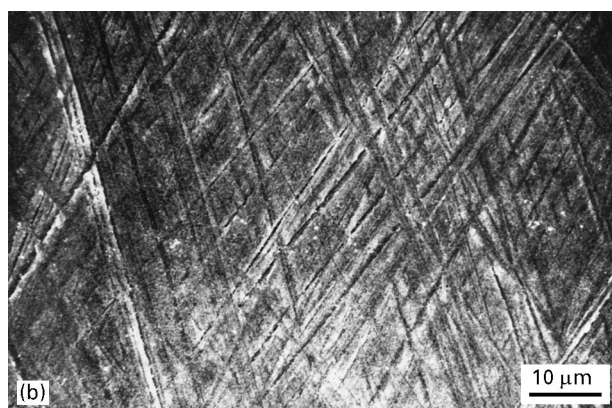
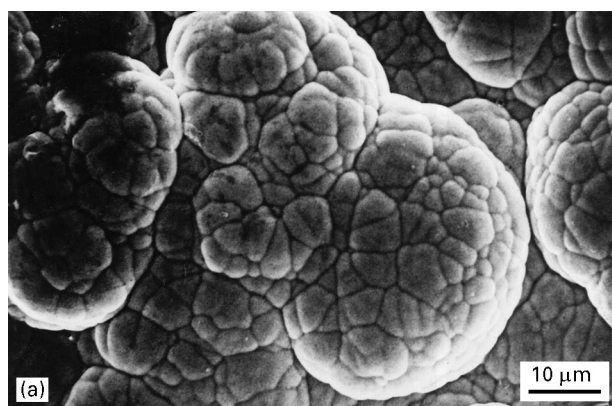


Figure 6 Scanning electron micrographs of the wear damaged chrome surface: (a) as received; (b) after 50 000 cycle rotation.

potential before the chrome plating was not applied to these samples. From Fig. 8, at least 1 min of electropolishing time in the Faust solution is required to improve corrosion resistance.

Fig. 9 (a and b) and 10 (a and b) show the chrome surfaces after 90 and 120 h neutral salt spray tests with different electropolishing solutions, respectively. The chrome thickness for both samples is about 0.08 mm.

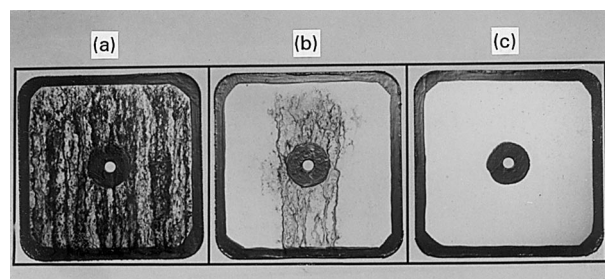


Figure 7 Chrome surface after 90 h neutral salt spray test. All samples were chrome plated at 53 °C and 0.6 Acm^{-2} after electropolishing in modified Sargent bath. (a) Electropolishing for 1 min, 0.078 mm thick. Cr layer: rust on Cr surface (b) Electropolishing for 2 min, 0.076 mm thick. Cr layer: rust on Cr surface (c) Electropolishing for 3 min, 0.078 mm thick. Cr Layer: no rust on Cr surface.

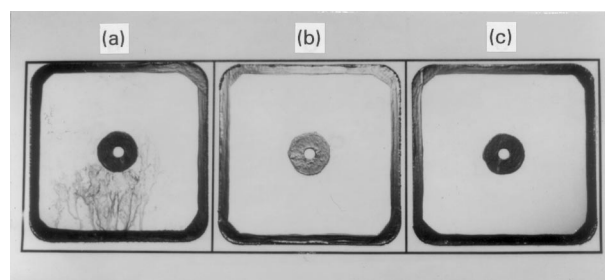


Figure 8 Chrome surface after 90 h neutral salt spray test. Each sample was chrome plated at 53 °C and a current density of 0.6 Acm^{-2} after electropolishing in the modified Faust solution. (a) Electropolishing for 30 s, 0.078 mm thick. Cr layer: rust on Cr surface. (b) Electropolishing for 1 min, 0.078 mm thick. Cr layer: no rust. (c) Electropolishing for 2 min, 0.078 mm thick. Cr: no rust.

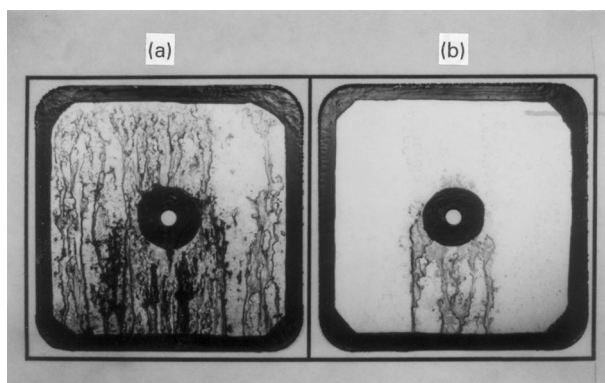


Figure 9 Chrome surface ($\times 0.37$) after 120 h neutral salt spray test. Each sample was chrome plated at 53 °C and a current density 0.6 Acm^{-2} . (a) Electropolishing for 2 min in a modified Sargent bath, 0.076 mm thick Cr.: rust is observed on the Cr surface. (b) Electropolishing for 1 min in a modified Faust solution followed by 30 s in a plating bath, 0.076 mm thick Cr.: less rust is formed on the Cr surface.

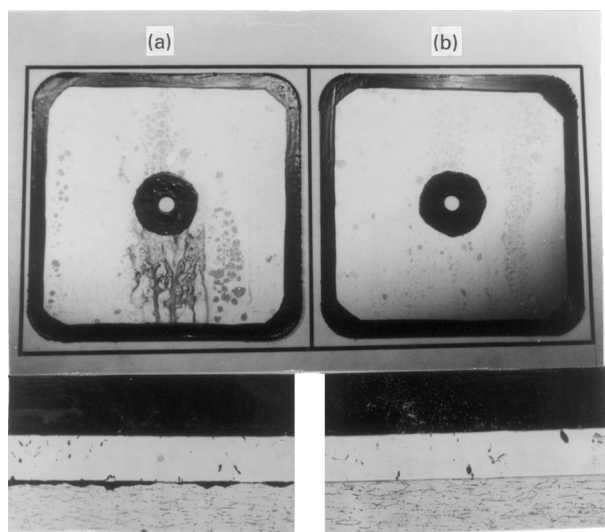
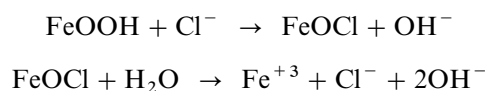


Figure 10 Chrome surface ($\times 0.36$) and microstructure ($\times 144$) after 90 hs neutral salt fog spray test. Each sample was chrome plated in the modified Sargent bath at 53°C and a current density of 0.6 Acm^{-2} . (a) Electropolishing for 2 min in a modified Sargent bath, 0.078 mm thick Cr: rust and corrosion pits are observed on the chrome surface and below the chrome layer, respectively. (b) Electropolishing for 2 min in the modified Faust solution, 0.078 mm thick Cr: no rust and pits.

The (a) series in Figs 9 and 10 are the chrome plated sample with the best corrosion resistance amongst the samples electropolished in the production bath. The (b) series in the figures are the samples electropolished in the Faust solution. As is shown in Figs 9b and 10b the samples electropolished in the Faust solution show a better neutral salt fog spray life than a sample treated in the production bath for a given plating condition.

In order to study the process of rust formation on a chrome layer during the neutral salt fog spray test, a cross-sectional observation of the chrome plated steel was carried out. Fig. 10 (a and b) shows the microstructure and chrome surfaces after the neutral salt fog spray test. As is shown in Fig. 10a, the chrome layer with rust has large corrosion pits between chrome layer and steel substrate. Although it is hard to find whether the defect structure is interconnected in the study, as is shown in Fig. 10a micro-cracks and voids were observed in the chrome layers. Fig. 11 is a schematic representation of the processes occurring at an actively growing pit in the steel substrate below the chrome deposit. During the neutral salt fog spray test, the salt fog penetrates into the steel substrate through defects in the chrome layer. It is known that chloride ions catalyse the liberation of Fe^{+3} by the displacement of the layer of the passive film by such reactions as;



where FeOCl approximates to the composition of the islands on the passive film [11].

Copious anodic production of positively charged Fe^{+2} also attracts negative anions like Cl^- to the

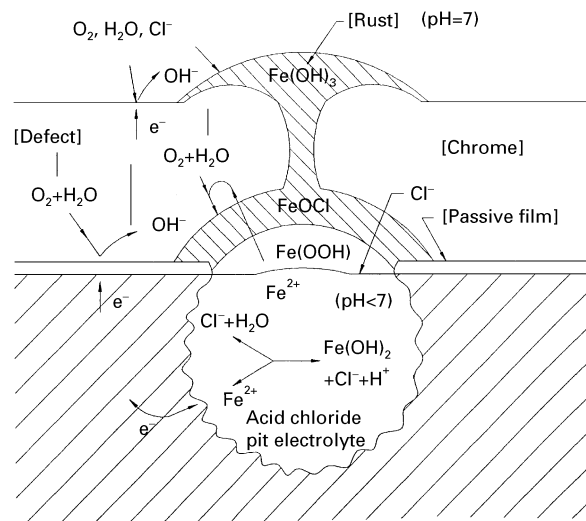


Figure 11 Schematic of processes occurring at an actively growing pit in the steel substrate below a chrome layer.

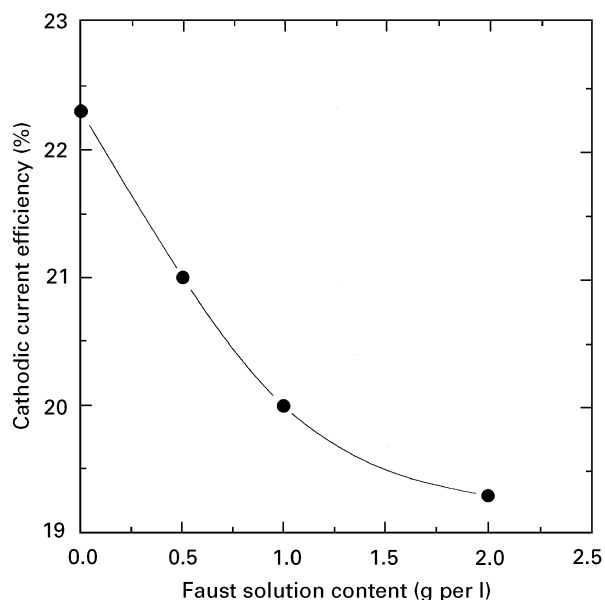


Figure 12 Cathode current efficiency change with the content of the modified Faust solution in a modified Sargent bath.

initiation of pit site. Hydrolysis by $\text{Fe}^{+2} + 2\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow \text{Fe}(\text{OH})_2 + 2\text{HCl}$ produces a local pH reduction at the initiation site. The result is an autocatalytic mechanism of pit growth. The acid chloride solution further accelerates anodic dissolution, which in turn further concentrates chloride in the pit. The insoluble corrosion products, such as $\text{Fe}(\text{OH})_3$, spout through the defects of the chrome layer and collect on the layer. Fe^{+2} diffuses out of the acid pit interior into the exterior of the chrome layer, where it is oxidized to Fe^{+3} and precipitates in the neutral bulk solution. Hence, rust was observed on the chrome deposit that had pits below the layer after the neutral salt fog spray test. However, it was difficult to observe pits at the steel substrate for the chrome layer that did not rust.

In order to understand the effect of the contamination of the production bath by the modified Faust solution on the cathode current efficiency, the current efficiency was determined with the Faust solution content in the modified Sargent bath. Fig. 12 shows the

cathode current efficiency change with the content of the modified Faust solution in the solution. The cathode current efficiency decreases with the amount of the Faust solution content. The efficiency drop at the plating condition of 53 °C and a current density of 0.6 Acm⁻² is about 5% when the amount of Faust solution is 0.5 gl⁻¹ in the modified bath.

4. Conclusions

1. The chrome electrodeposited in a modified Sargent bath containing formic acid has an about 2.0 wt% carbon content, which is higher than that from a modified Sargent bath.

2. The X-ray diffraction pattern of the chrome layer deposited in the modified Sargent bath containing formic acid shows a broad feature which corresponds to an amorphous structure. As the sample is annealed at temperatures up to 600 °C, peaks corresponding to metallic chrome and chromium carbide were observed in the X-ray diffraction patterns.

3. The hardness and wear resistance of the chrome deposited in the modified Sargent bath increased with annealing temperature up to 600 °C which resulted from a precipitation hardening effect due to the formation of chromium carbide.

4. A sample electropolished in the modified Sargent bath for 3 min has the longest neutral salt spray life amongst samples electroplated in the same solution.

5. Electropolishing in the modified Faust solution improves the neutral salt spray life of chrome plated steel to a greater extent than electropolishing in the production bath. A sample electropolished in the Faust solution for 2 min at a current density of 0.6 Acm⁻² and 53 °C shows the highest corrosion resistance among the samples prepared for this study.

6. The contamination of production bath with the modified Faust solution reduces the cathodic current efficiency. The efficiency drop is about 5% when the amount of the Faust solution increases from 0.0 to 0.5 gl⁻¹ in the modified Sargent bath.

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References

1. C. A. SNAVELY, *Trans. Electrochem. Soc.* **92** (1947) 537.
2. G. DUBPERNELL, "Modern Electroplating", 2nd Edn (Wiley, New York, 1963) p. 87.
3. R. M. BURNS and W. W. BRADLEY, "Protective Coating for Metals", 3rd Edn (Reinhold, New York, 1967) p. 38.
4. K. S. WILSON, *Plating* **59** (1972) 226.
5. H. FURUYA, T. MISAKA and Y. TANABE, *J. Metal Finishing Soc. Jpn.* **32** (1981) 631.
6. T. MORIKAWA and S. EGUCHI, Extended abstracts from the 70th Ann. Conf. of the Metal Finishing Society of Japan, (1984).
7. S. HOSHINO and H. A. LAITINEN, *Electrochem. Sci. and Tech.* **4** (1986) 681.
8. J. B. KUSHNER, "Electroplating Know How", 5th Edn (Kushner Electroplating School, Sunnyvale, CA., 1987).
9. B. HOFLUND, H. A. LAITINEN, and S. HOSHINO, *Appl Surf. Sci.* **28** (1987) 224.
10. T. LAYMAN, "Metals Handbook", 8th Edn (ASM, Metals Park, OH., 1973) p. 274.
11. D. A. JONES, "Corrosion Process", edited by R. N. Parkins, (Applied Science Engineering, NJ, 1982) p. 180.

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