Effect of Microstructure of Ferrous Substrate On Porosity of Electroless Nickel Coating

By L. Das, D.-T. Chin, R.L. Zeller and G.L. Evarts

The corrosion resistance of electroless nickel (EN) coatings on ferrous substrates is affected by coating porosity. Carbon and iron carbide are present in the microstructure of ferrous alloys. If the sites of carbon and iron carbide are not as catalytically active to EN deposition as the rest of substrate surface, there is a possibility of pore formation on these sites. In the present study, the rate of EN deposition on carbon, iron carbide and steel surfaces was individually measured. The locations of EN deposits on the microstructure of a ferrous alloy were mapped with the SEM/EDS technique and compared to the locations of carbon on the original substrate surface. This paper summarizes the results of these investigations.

Electroless nickel (EN) deposition from hypophosphitecontaining baths has been used for providing corrosion protection to ferrous alloys.¹ EN coating functions as a barrier against corrosive chemicals. The presence of pits and pores on the coating is detrimental to its corrosion resistance. Many studies have been conducted to examine the effects of bath composition,²⁻⁴ operating conditions,⁵⁻⁷ deposit composition and post treatment procedures⁷ on the corrosion performance of EN. The role of ferrous alloy microstructure in the initiation of porosity on EN coatings has been overlooked. A substrate that has passive metallurgical inclusions, adsorbed poisons or is not homogeneously reactive to EN deposition on its surface, is likely to generate defects during the EN plating process, including porosity, poor adhesion, and stresses on the deposit.⁷

Low-carbon steel substrates contain 0.1 to 0.95 percent carbon, some of which is present in the form of iron carbide. The carbon and its compounds may act as inhibitors to the EN deposition process. The present investigation was undertaken to study the effect of substrate microstructure of ferrous alloys on the porosity of EN deposits. The EN plating rate on carbon and iron carbide was measured and compared to that on steel. A specially configured half iron/half graphite substrate was used to examine the spreading of EN deposits from iron to a non-catalytic carbon surface. EN coating on gray cast iron containing a high percentage of graphite flakes on its microstructure, was analyzed with the SEM/EDS element mapping technique to determine the locations where the EN deposit did or did not form. A non-destructive electrochemical porosity measurement technique was used to determine the porosity of the EN deposits. An electrochemical polarization technique was used to examine the catalytic activity of iron and carbon for the EN deposition reaction.

Experimental Procedure

EN Deposition on Steel, Carbon, Iron Carbide and Half Iron-Half Carbon Substrates

Electroless nickel deposition was carried out in a bath composed of 44 g/L of nickel sulfate hexahydrate, 10 g/L of sodium hypophosphite, 42 g/L of aminoacetic acid and 10 g/ L of acetic acid at 88 °C and pH 4.5. Four types of substrates were used: (1) AISI 1010 carbon steel coupons; (2) carbon substrates in the form of a graphite sheet, carbon disks and glassy carbon rods; (3) iron carbide; and (4) half iron/half carbon substrates.

The iron carbide substrates were prepared by applying a paste of iron carbide powder, methyl cellulose and water on a fiberglass disk support, which was then dried in an oven at 60 °C. Three configurations of half iron/half carbon substrates were used; they are schematically shown in Fig. 1. Configuration #1 (Fig. 1a) was prepared by electrodeposition of an iron coating 10 μ m in thickness on half of a graphite coupon. Configurations #2 (Fig. 1b) and #3 (Fig. 1c) were prepared by galvanically coupling a steel and a graphite coupon with a conducting wire outside the EN bath. In configuration #2, the steel and graphite coupons in the bath were 19 mm apart. In configuration #3, a TeflonTM sheet of known thickness was inserted between the steel and graphite coupons to reduce their separation to 1.6 - 12.7 mm.

Prior to EN plating, the steel substrates were polished with 1- μ m α -alumina powder, rinsed in water, anodically electrocleaned in sodium hydroxide solution and activated by dipping in 37-percent HCl. The carbon substrates were washed with water. The half iron/half graphite substrates were rinsed in water and dipped in 37-percent HCl to activate the iron portion of the substrates. The iron carbide substrates were washed with hot water to remove methyl cellulose on the outer surface of the fiberglass support disk. The iron carbide substrates were then dried and plated with EN.

The EN plating rate on all substrates was measured by the weight-gain method. A video camera was occasionally used to record the plating process and hydrogen evolution on the substrate surface through the side walls of a glass bath container.

SEM/EDS Analysis

After plating, the morphology of the EN coating on various substrate surfaces was examined under a scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) was used to analyze the nickel and phosphorus contents of the coating.

To study the effect of carbon inclusions in the microstructure of ferrous substrates on the EN plating process, a gray cast-iron coupon was polished with 1- μ m α -alumina powder and etched in a solution containing 95 mL of methanol, 5 mL of water and 3 mL of nitric acid.⁸ The sample was marked with a reference scratch line and examined under the SEM to determine the locations of graphite flakes on its surface. After EN plating, the sample was examined again under the SEM, and the EDS analysis was used to map the locations of Fe, C, Ni, and P on the sample surface.

Coating Porosity Measurements

A non-destructive electrochemical technique was used to determine the porosity of EN deposits. The tests were based on the principle that a two-phase metal surface (partly coating and partly substrate surface exposed by pores on the coating) exhibits a galvanic corrosion potential on exposure to a



Fig. 1—Three configurations of a half iron-half graphite substrate for EN plating: (a) graphite coupon electroplated with iron on part of its surface; (b) a graphite and an iron coupon galvanically connected with a conducting wire outside the EN bath; (c) galvanically connected graphite and iron coupons with Teflon[™] sheet between them to reduce separation distance.

corroding electrolyte. The corrosion potential depends on the area fraction of pores on the coating and the degree of polarization on the exposed substrate surface. For a metal substrate coated with a noble metallic coating with low porosity, there is a linear relationship between the corrosion potential and the logarithm of the area fraction of pores.^{9,10} In this study, a calibration plot of corrosion potential vs. area fraction of pores was prepared, using an EN-iron couple and a saturated calomel reference electrode in an electrolyte containing 3 percent NaCl (by wt) and 1.5 percent H₂O₂ (by vol). The corrosion potential of EN-coated AISI 1010 carbon steel and gray cast-iron coupons were subsequently measured in this electrolyte as a function of coating thickness, and the porosity of the EN coatings corresponding to the measured corrosion potential was read from the calibration chart.

Polarization Measurements

Individual anodic and cathodic polarization curves of the EN deposition reaction were measured with a potentiodynamic technique. The half-cell reaction for the reduction of nickel ions was studied in a half EN bath where no hypophosphite was added. Similarly, the half-cell reaction for the oxidation of hypophosphite ion was examined in a half bath not containing any nickel ions. A rotating disk made of AISI 1010 carbon steel, or EN, or glassy carbon, was used as the working electrode. The counter-electrode was platinum and a saturated calomel electrode (SCE) was used as the reference electrode. The anodic and cathodic polarization curves were measured with a computer-interfaced potentiostat at a potential scan rate of 10 mV/sec and a rotational speed of 750 rpm. The experiments were carried out at 85 °C and pH 3.8.

Results and Discussion

Rate of EN Deposition on Steel, Carbon & Iron Carbide

Figure 2 shows the rates of EN deposition on carbon steel, carbon and iron carbide substrates as a function of bath pH at 88 °C. The EN plating rate on iron carbide was comparable to that on steel, while the plating rate on carbon was zero. It was noticed that the EN deposition reaction was always accompanied by a parallel hydrogen evolution reaction on the substrate surface. There was instantaneous evolution of hydrogen upon immersion of steel and iron carbide substrates in the EN bath; no hydrogen evolution was observed for all carbon substrates, including carbon disks, graphite sheets, and glassy carbon rods. The SEM/EDS analysis of the samples



Fig. 2—Rate of EN deposition on AISI 1010 carbon steel, iron carbide and graphite substrates as a function of bath pH at 88 $^{\circ}{\rm C}.$

after EN plating revealed the presence of a nickel-phosphorus deposit on the steel and iron carbide and none on carbon surfaces.

EN Deposition on Half Iron/Half Carbon Substrates Video recording of the EN plating process was carried out for the configuration #1 half iron/half carbon substrates prepared by electroplating iron on the top half of a graphite sheet, as shown in Fig. 1a. Because hydrogen bubbles were formed on the surface sites where EN was deposited, tracing the movement of hydrogen bubbles with a video camera would give an idea about the spreading of the EN coating on substrate surface.

Figure 3 is a schematic representation of the hydrogen bubble movement process during EN plating on a half iron/ half graphite substrate. At the beginning of the plating process, evolution of hydrogen bubbles occurred only on the iron half of the substrate, as shown in Fig. 3b. After five min immersion in the EN bath, hydrogen bubbles began to spread across the iron-graphite border and evolved on the graphite half of the substrate, as shown in Fig. 3c. The number of hydrogen bubbles on the graphite increased with time and ultimately the entire graphite surface was covered with them (Fig. 3d). These results indicate that on a half iron/half carbon surface EN deposition was initiated only on the iron portion of the surface. The EN deposition moved to the carbon portion of the surface by a galvanic action between the carbon and iron (or EN which had deposited on the iron) in the bath.¹¹ The galvanic activation of carbon first occurred in the immediate neighborhood of the carbon-iron (or carbon-EN) border, then gradually spread across the graphite surface. After



Fig. 3—Schematic representation of EN deposition process on a half iron/half graphite substrate: (a) prior to EN plating: (b) at 1 min immersion, hydrogen bubbles evolved only on the iron portion of the substrate; (c) after 5 min immersion, hydrogen bubble evolution sites spread toward graphite surface; (d) after 30 min immersion, both iron and graphite surfaces completely covered by hydrogen bubbles.



Fig. 4—SEM photomicrograph and EDS spectra of a half iron/half graphite substrate: (a) prior to EN plating; (b) after 5 min EN plating; (c) after 15 min EN plating.

30 min, the entire graphite portion of the substrate was covered by an EN coating.

Figure 4a is a SEM photomicrograph of the half iron/half graphite substrate prior to EN plating. The accompanying EDS spectrum indicates that there was only C on the carbon portion and Fe on the iron portion of the surface. Figure 4b is a SEM photomicrograph of the substrate surface after 5 min of EN plating; the accompanying X-ray spectrum revealed that there was a nickel-phosphorus deposit on the iron portion and very little nickel on the graphite portion of the substrate. Figure 4c is a SEM photomicrograph of the substrate surface after 15 min of EN plating; the accompanying EDS spectrum revealed that there was a nickel-phosphorus deposit on both iron and graphite portions of the substrate. These results were



Fig. 5—X-ray map of individual element on surface of gray cast iron after 2 min EN plating: (a) gray image of substrate surface prior to plating; (b) gray image of EN coating; (c) map of Fe; d) map of C; (e) map of Ni; (f) map of P.



Fig. 6—X-ray map of individual element on the surface of gray cast iron after 5 min EN plating: (a) gray image of substrate surface prior to plating; (b) gray image of EN coating; (c) map of Fe; (d) map of C; (e) map of Ni; (f) map of P.

repeatable and were also observed on pelletized carbon disks that were in contact with a steel coupon in the EN bath. Although EN deposition did not occur spontaneously on carbon, the carbon surface could be activated by galvanic contact with an active metal, such as iron, nickel and EN, to permit EN plating to occur on the carbon surface.

To examine the effect of separation distance on the galvanic initiation of EN deposition on a carbon surface, two other configurations of half iron/half carbon substrates were used. In configuration #2 (Fig. 1b), a steel and a graphite coupon were positioned 19 mm apart in an EN bath. They were galvanically connected with an external conductor and were immersed in the EN bath for one hr. The EDS and weight-gain analyses after the plating revealed that there was an EN deposit on the steel surface, but none on the graphite surface. In configuration #3, the distance between the steel and the graphite was made smaller by inserting a Teflon sheet (1.6 to 12.7 mm in thickness) between them as shown in Figure 1c. EN deposition, along with hydrogen evolution, was observed on both the graphite and steel surfaces. The EN deposition rate on the graphite surface decreased, however,





Fig. 8—Anodic and cathodic polarization curves for EN deposition reaction on rotating disk electrode made of: (a) AISI 1010 carbon steel; (b) glassy carbon (750 rpm, pH 3.8, 85 °C).

Fig. 7—Porosity of EN coatings on AISI 1010 carbon steel and gray cast iron as a function of coating thickness. Carbon content in substrates was: 0.1 wt % for carbon steel and 2.95 wt % for gray cast iron.

with an increase in the separation distance, as shown in the table.

When the external conducting wire in configuration #3 was removed, no EN deposit was observed on the graphite for all the separation distances in the table. This indicates that it was necessary for the graphite to be in galvanic contact with steel in order to be active to EN deposition reaction. The data also suggest that some sort of active soluble species diffuses from the steel to the graphite, causing EN deposition to occur.

Carbon Inclusions in Substrate Microstructure & EN Deposition Process

To study the effect of carbon in ferrous alloys on EN deposition, gray cast iron was chosen as the substrate because it has a high percentage of graphite flakes in its microstructure. Several gray cast-iron coupons were polished, anodically electrocleaned, etched, and marked with a reference scratch line. They were individually examined under the SEM to record the locations of graphite flakes on their surfaces. Afterward, they were cleaned and simultaneously immersed in a common EN bath. The coupons were withdrawn from the EN bath at different plating times to permit the build-up of different thicknesses of EN. The coupons were re-examined under the SEM, and the locations of individual elements, such as Fe, C, Ni, and P, on the coupon surface were mapped by EDS analysis.

Figure 5a shows the SEM photomicrograph of a gray cast-iron coupon prior to plating. The light areas represent the iron portion of the surface and the graphite flakes are represented by dark streaks. This coupon was EN-plated for two min and had an average EN thickness of $0.4 \,\mu$ m. Figure 5b is the SEM photomicrograph of the coating on the same area of the substrate. The EN coating was so thin that the dark graphite flakes were still visible under the coating. The X-ray element maps showing the presence of Fe, C, Ni, and P on the same sample area are given in Figs. 5c, d, e, and f, respectively. The light color in a particular location of the map shows the presence of an identified element in that location. A comparison of Figs. 5c - f shows that Ni and P were present in the same locations as iron, and that there was no Ni or P in the locations where carbon was present.

Figure 6a is the photomicrograph of another gray cast-iron coupon prior to EN plating. This coupon was immersed in the EN bath for five min and was coated with a layer of EN 1.2 μ m in thickness. Figure 6b is the photomicrograph of the coating, which shows that most of the substrate surface was



The above results indicate that at the initial state of the EN plating process, EN deposition initiated only on the iron portion of the substrate and there was no EN deposition on the graphite portion of the microstructure. With increasing time, EN deposition occurred on the graphite because of the galvanic contact between the iron and graphite in the substrate. The coating thickness on the graphite locations was thinner, however, than that on the iron portion of the substrate. For a thin EN coating on a ferrous substrate, there was a possibility of pore formation on the spots where graphite was present on the surface.

covered with EN, including the locations where graphite was

present in the microstructure. Figures 6c, d, e and f show the

The effect of carbon content in ferrous substrates on the porosity of EN coating is shown in Fig. 7, where the measured coating porosity is plotted against coating thickness for an AISI 1010 carbon steel and a gray cast-iron substrate. The carbon content of the substrates was 0.1 wt percent for the carbon steel and 2.95 wt percent for the gray cast iron. The porosity of an EN coating is seen to decrease linearly with increase in coating thickness. For the same thickness, the EN coating on the gray cast iron had a higher porosity than on the carbon steel, resulting from a higher carbon content in the microstructure of gray cast iron.

Polarization Curves

To examine why spontaneous EN deposition reaction does not occur on a carbon surface, polarization measurements

Plating Rate on Graphite and Steel As a Function of the Separation Between Them

	Plating Rate (μm/hr)			
Separation	Electrically		Electrically	
Distance	Connected		Isolated	
(mm)	Steel	Graphite	Steel	Graphite
1.6	9.2	8.2	9.1	0
3.2	9.1	5.5	9.2	0
6.4	9.1	3.2	9.2	0
12.7	9.2	1.6	9.1	0

with half EN baths were performed with EN, steel, and glassy carbon rotating disk electrodes (RDE). Electroless nickel and steel exhibited similar polarization characteristics in the anodic half-bath that did not contain nickel ions as well as in the cathodic half-bath not containing hypophosphite ions. Figure 8a shows the anodic polarization curve on AISI 1010 carbon steel for the oxidation of hypophosphite in the anodic half-bath and the cathodic polarization curve for the reduction of nickel in the cathodic half-bath. The two polarization curves intersected at a mixed potential of -0.74 V vs. SCE, and the deposition current at the mixed potential was 2.65 mA/cm² corresponding to an EN deposition rate of $3.7 \,\mu$ m/hr. This value was in reasonable agreement with an EN deposition rate of 4.1 μ m/hr for a carbon steel rotating disk in a full EN bath under the same experimental conditions (750 RPM, pH 3.8, and 85 °C).

Figure 8b shows the anodic and cathodic polarization curves obtained with the glassy carbon RDE. The cathodic polarization curve shows that reduction of nickel ions took place on the carbon electrode at a lower rate than on the steel electrode. The anodic polarization curve on the glassy carbon electrode occurred at a more positive potential of -0.1 V vs. SCE. This potential did not correspond to the oxidation of the hypophosphite in acidic media, which should occur at -0.75 V vs. SCE. The anodic and cathodic polarization curves on the glassy carbon electrode did not intersect to exhibit a mixed potential as shown in Figure 7b. Accordingly, the reason for no spontaneous EN deposition on the carbon surface was that carbon did not catalyze the oxidation reaction of hypophosphite ions.

Conclusions

A study has been made of the effect of carbon and iron carbide inclusions in the microstructure of ferrous substrates on the EN deposition process. The results indicate that spontaneous EN deposition reaction did not occur on the carbon surface. This was because carbon did not catalyze the oxidation reaction of hypophosphite ions. When carbon was in galvanic contact with a catalytically active metal, however, such as iron, EN deposition occurred on the carbon surface. Studies with a half iron-half carbon substrate and EDS element mapping of EN coating on gray cast iron revealed that EN deposition first occurred on the iron surface and then gradually spread to the carbon surface as a result of galvanic activation of carbon for the EN deposition process. Given sufficient time, EN deposits ultimately covered the entire carbon area. On the carbon surface, however, the induction time for EN deposition was longer and deposit thickness was thinner than for the iron portion of the substrate surface. The results indicate that carbon inclusions on substrate microstructure served as potential sites for the formation of pores on EN coatings. The porosity of EN coatings increased with increasing carbon content of ferrous alloys.

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About the Authors



Leena Das is a doctoral candidate in the Dept. of Chemical Engineering, Clarkson University, Box 5705, Potsdam, NY 13699-5705. She received a B. Tech in chemical engineering from the Indian Institute of Technology, Kharagpur, and an MS from Clarkson University.

Dr. Der-Tau Chin is professor of chemi-

cal engineering, Clarkson University. He has more than 20 years' research experience in electroplating, corrosion, electrochemical energy conversion, and industrial electrolytic processes. Prior to joining Clarkson, he was a senior research engineer in the Electrochemistry Department of General Motors Research Laboratories. Dr. Chin received his PhD from the University of Pennsylvania.

Dr. Robert L. Zeller III, P.E., is the technical team leader for specialty chemicals at Occidental Chemical Corp., Niagara Plant. He holds a BS and MS in chemical engineering from the University of Akron and a PhD in chemical engineering from Case Western Reserve University. He was recently recognized by OxyChem as a 1994 Inventor of the Year for a patented process to produce hypophosphorous acid by electrodialysis.

Gerald L. Evarts, CEF, is a technologist at the Occidental Chemical Corp. Technology Center, Grand Island, NY. He has been involved in the coatings industry for more than 25 years in various research and technical service positions. He has published several papers and holds five patents in the field of protective coating.