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Substrate roughness, deposit thickness and the corrosion of electroless nickel coatings

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The affect of substrate roughness and coating thickness on the corrosion resistance of electroless nickel coatings on mild steel in a 0.99M Na_2SO_4 + 0.01M H_2SO_4 + 0.05M NaCl solution has been investigated using electrochemical techniques. The coating was electrochemically more active than pure nickel. The anodic polarization, corrosion potential, and corrosion current depend on the substrate roughness and coating thickness. The substrate roughness decreased for finishes in the order, as-ground, 240 grit, 600 grit, and 1 μm diamond polish, but the corrosion current on relatively thin coatings decreased in the order 240 grit, as-ground, 600 grit, and 1 μm diamond finish. The corrosion potential and the corrosion current of coatings more than about 10 μm thick were independent of the surface roughness and similar to those observed with pure nickel. The fraction porosity was estimated to be about 0.005 in a coating about 5 μm thick on a 600 SiC grit substrate.

1. Introduction

Electroless nickel coatings are widely used to protect the surfaces of engineering components from degradation by corrosion and wear. It is generally considered that the corrosion resistance of electroless nickel coatings is superior to that of electrodeposited nickel. Early work supporting this position has been summarized by Gawrilov [1], and the same claim has been made recently by Duncan [2]. The performance, however, of electroless nickel coatings have frequently been poor in solutions containing chloride [3, 4], and several commercial electroless nickel coatings exposed for long periods in simulated mine waters containing chloride, showed that there were substantial differences in the pitting and corrosion behaviour of the various coatings [4].

Porosity is an important factor that promotes the pitting and corrosion of electroless nickel coatings [1, 4, 5]. The pre-treatment degreasing and pickling conditions [6] and the surface roughness due to mechanical preparations of the surface [7], have a direct effect on the porosity of the coating, and recent work has indicated clearly the presence of porosity associated with the lay of the mechanically ground substrate [5]. Coating thickness is also important in determining the effect of porosity on the corrosion behaviour. Thicker coatings generally have fewer pores that penetrate the coating and hence provide an increase in the corrosion resistance [1, 4, 5].

Thus in addition to the inherent corrosion resistance of the electroless nickel alloy itself, the performance of the electroless nickel coating depends on the surface roughness of the substrate, and on the porosity and thickness of the deposit. These are related, and in the present work the effect of surface roughness of a mild steel substrate and deposit thickness on the corrosion behaviour of a commercial electroless nickel coating was investigated. Profilometry, electron microscopy, and electrochemical techniques, were used to characterize the surface roughness of the substrate and the coating, examine the microstructure, and measure the corrosion behaviour of the coating, respectively. The complexity of electroless nickel coatings frequently makes their corrosion behaviour irreproducible and in order to assess the reproducibility of the measuring technique and to provide a basis for comparison, a commercially pure nickel was also briefly tested.

2. Experimental details

A commercial electroless nickel system containing about 11% phosphorus was used*, and samples about 2 cm^2 were plated in the laboratory. The substrate was cut from cold-drawn bars of mild steel (specification EN3b), and samples were prepared in the as-ground, 240 SiC grit, 600 SiC grit, and 1 μm diamond polish conditions. Microscopical details and the roughness parameters of the surfaces are shown in Fig. 1 and given in Table I respectively. For comparison, a commercially pure (nominally 99.8%) nickel, Ni200†, was also examined. Analar reagents and distilled water was used to make the solutions. The solution 0.99M Na_2SO_4 + 0.01M H_2SO_4 + 0.05M NaCl had a pH of 2.5

Corrosion testing using a potentiostat and a ramp generator followed a standardized procedure. In outline, the solution was deaerated for 30 min using nitrogen before the specimen (exposed area 100 mm^2) was immersed. The corrosion potential was measured shortly after immersion and after 30 min under open

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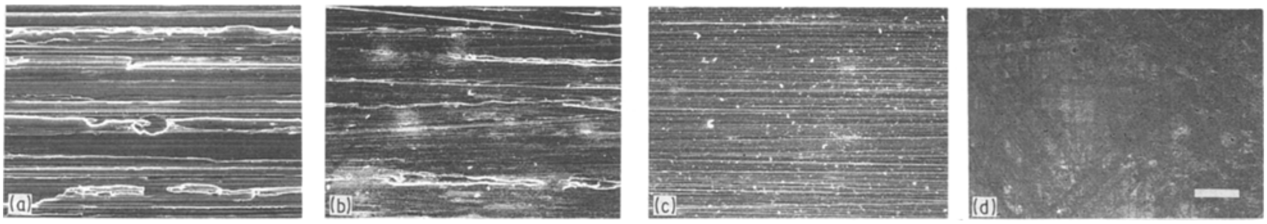

Figure 1 Steel substrate in the (a) as-ground, (b) 240 SiC grit finish, (c) 600 SiC grit finish, and (d) 1 μm diamond polish, conditions. SEM marker 20 μm.

circuit conditions (the initial and final values respectively in Tables II and III). Magnetic stirring and deaeration continued throughout the test. The linear polarization resistance was then measured [8], before the specimen was anodically ramped at 1 mV sec^{-1} to 1.5 V (SCE), held for 5 min, and then reversed back to the corrosion potential.

A microcomputer controlled Talysurf was used to characterize the surface roughness of the substrate (Table I) in terms of the centre line average (Ra), vertical distance between the highest peak and the lowest valley (Rt), and the shape parameters, skewness (Sk), and kurkosis (Ku). Standard metallographic techniques were used to examine the specimens.

3. Results

Typical polarization curves are shown in Fig. 2, and details from all the results for pure nickel are given in Table II. Results for the duplicate tests using the zero chloride solution were almost identical. As the amount of chloride in solution increased the passivation was reduced [9]. Oxygen evolution followed the equation

$$E(\mathrm{SCE}) = 0.0225 \lg (i/\mathrm{A\,m^{-2}}) + 1.10\,\mathrm{V}$$

and increased the thickness of the passive film so that on the reverse scan i_{pass} was reduced to a value less than 0.01 A m^{-2} (Table II). Chloride above 0.01M affected the reverse sweep, and it was on this basis that the solution used to test the coatings contained 0.05M chloride, insomuch, that it was hoped that the solution would be suitably aggressive to provide an accelerated test, without the possibility of simply creating a limiting current density that would swamp the electrochemical details of the coating.

An anodic polarization curve for an electroless nickel coating deposited for 30 min is included in Fig. 2, and corrosion parameters from all the results are given in Table III. Some results for the mild steel substrate are also included in Table III. All the coatings showed an active corrosion loop to a greater or lesser extent and a tendency to passivate. The coatings were anodically more active than pure nickel (Fig. 2). On open circuit, however, the coatings deposited for 60 min had a slightly higher corrosion potential and a similar corrosion current, cf E_{corr} for the 60 min coatings (−268, −268, −269, and −265 V) and for the nickel (−320 V), and I_{corr} for the 60 min coatings (3, 3, 2, and 4 μA) and for the nickel (8 μA) in Table II. Substrate roughness and deposit thickness clearly affects the corrosion (Table III and Figs 3 and 4). In general, for a given surface finish, E_{corr} increases and I_{corr} decreases for coatings on substrates with finishes in the order 240, AsG, 600 and 1 μm, rather than, as might be expected from the surface roughnesses (Table I), in the order AsG, 240, 600 and 1 μm. For coatings deposited for 60 min (coatings more than about 10 μm thick), the corrosion potential and the corrosion rate was independent of the surface roughness.

TABLE I Surface characteristics of mild steel substrate

Code	Condition	Roughness parameters			
		Ra (μm)	Rt (μm)	Sk	Ku
AsG	As-ground	0.53	4.71	−1.0	4.5
240	240 SiC grit	0.40	2.47	0.1	2.4
600	600 SiC grit	0.18	1.02	−0.7	2.4
600	600 SiC grit	0.22	1.10	−0.9	2.5
600	600 SiC grit	0.19	0.96	−0.8	2.4
1 μm	1 μm diamond finish	0.02	0.12	−0.5	3.4

Maximum hardness is usually obtained by heat treating at 400° C [5], and two tests were conducted by heat treating samples sealed under vacuum in silica ampoules for 1 h at 400 and at 600° C (over-aged). Small changes occurred in the polarization curves (not

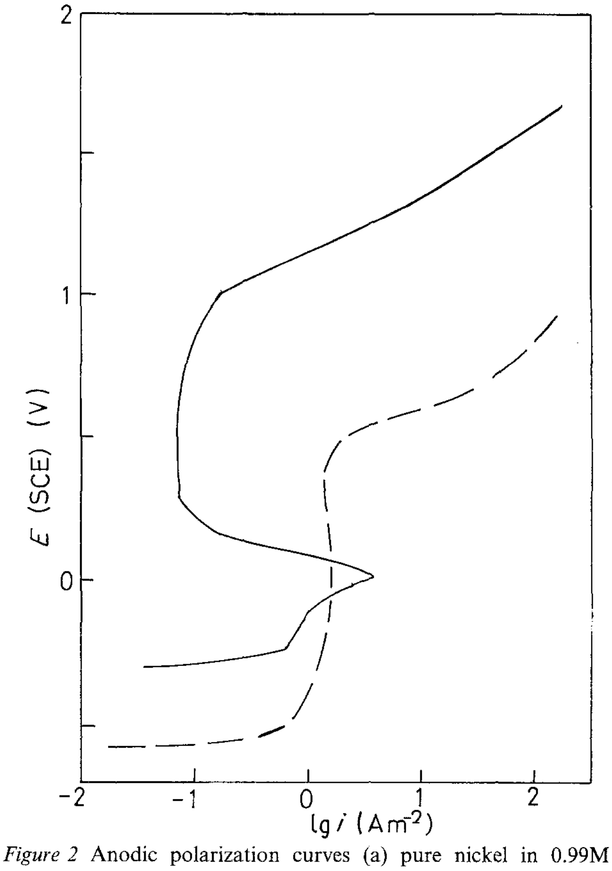

Figure 2 Anodic polarization curves (a) pure nickel in 0.99M Na_2SO_4 + 0.01M H_2SO_4 solution (——), and (b) electroless nickel deposited for 30 min on a 240 SiC ground substrate in 0.99M Na_2SO_4 + 0.01M H_2SO_4 + 0.05M NaCl solution (– – –).

TABLE II Corrosion parameters of pure nickel with a 600 SiC grit finish polarized in 0.99M Na_2SO_4 + 0.01M H_2SO_4 containing various amounts of sodium chloride

Concentration Cl^- ($mol\,dm^{-3}$)	E_{corr}*			Active loop peak		Minimum passivation		Minimum repassivation
	Initial (mV)	Final (mV)	Change (mV)	E_{pk} (mV)	i_{pk} ($A\,m^{-2}$)	E_{pass} (mV)	i_{pass} ($A\,m^{-2}$)	i_{rep} ($A\,m^{-2}$)
zero	−300	−260	+40	20	3.3	400	0.07	< 0.01
zero	−360	−325	+35	10	2.9	300	0.08	< 0.01
0.01	−346	−321	+25	20	4.1	350	0.07	< 0.01
0.05	−300	−320	−20	0	6.0	260	0.11	0.09
0.07	−280	−310	−30	20	6.0	240	0.19	0.52
0.10	−280	−302	−22	30	9.2	–	–	–

*With respect to the S.C.E. The change = E_{corr}(final) − E_{corr}(initial).

illustrated) but the corrosion currents were unaffected (Table III).

4. Discussion

When considering the corrosion of electroless nickel coatings it is important to keep two things in mind. Firstly, electroless nickel coatings are a nickel–11% phosphorus alloy with a complex microstructure, including porosity [5]. Secondly, corrosion depends on the solution and the testing method, and the presently used method is an accelerated test both in terms of the polarization technique and the aggressive nature of the chloride solution. The results on pure nickel are important because they confirm the validity of the testing method, and enabled a suitable solution to be used which was not so aggressive as to eliminate passivation but would act to promote corrosion at any flaws or porosity in the coating. In addition, they provide a basis for comparing the corrosion behaviour of the Ni–P coatings.

The general anodic polarization behaviour of the electroless nickel coating with the enhanced dissolution rate is similar to that observed by Flis and Duquette [10]. In the present case, with the thinner coatings there is the added influence of the active iron substrate. As the thickness of the coating increases, the corrosion behaviour approaches that of the Ni–P alloy (Figs 3 and 4). Heat treatment affects the polarization behaviour but it has no affect on I_{corr}.

Roughness of the substrate clearly has a substantial and systematic effect on the corrosion behaviour of relatively thin coatings (Figs 3 and 4). Except for the ground surface, the trend is to follow the surface roughness. Grinding produces a thin (about 1.0 μm), hard, white layer, on the machined surface which is in residual compression (about 600 MPa) and resists corrosion [11], and we suggest that the white layer on the ground specimen is the cause of the corrosion current decreasing in the order 240, AsG, 600, and 1 μm, rather than in the order AsG, 240, 600, and 1 μm, that might have been expected on the basis of the roughness (Table I).

TABLE III Corrosion parameters of electroless nickel coatings of various thicknesses (deposit times) formed on mild steel of various surface roughnesses polarized in 0.99M Na_2SO_4 + 0.01M H_2SO_4 + 0.05M NaCl

Substrate finish	Coating time* (min)	E_{corr}†			Active loop peak		Minimum passivation		I_{corr}‡ (μA)
		Initial (mV)	Final (mV)	Change (mV)	E_{pk} (mV)	i_{pk} ($A\,m^{-2}$)	E_{pass} (mV)	i_{pass} ($A\,m^{-2}$)	
AsG	5	−561	−653	−92	−240	63.1	350	35.5	102
240	5	−565	−660	−95	−260	47.3	400	20.5	117
600	5	−560	−645	−85	−240	51.6	400	19.4	81
1 μm	5	−290	−585	−295	100	4.6	–	–	41
AsG	30	−480	−560	−80	0	1.6	–	–	25
240	30	−312	−582	−270	75	1.6	350	1.3	33
600	30	−250	−534	−285	–	–	–	–	18
1 μm	30	−340	−395	−65	–	–	–	–	3
AsG	60	−347	−268	+79	–	–	–	–	3
240	60	−343	−268	+75	0	4.7	300	4.0	3
600	60	−304	−269	+35	–	–	–	–	2
1 μm	60	−337	−265	+72	60	6.1	320	1.2	4
1 μm 400° C	30	−210	−250	−40	−140	0.3	−40	0.2	4
1 μm 600° C	30	−170	−494	−324	20	5.2	80	0.9	3
AsG	Steel§	–	−628	–	–	–	–	–	104
240	Steel	–	−638	–	–	–	–	–	196
600	Steel	–	−637	–	–	–	–	–	171
1 μm	Steel	–	−628	–	–	–	–	–	45
600	Nickel§	−300	−320	−20	0	6.0	260	0.1	8

*The coatings deposited for 60 minutes had an average thickness of 10 to 12 μm, calculated from the weight and the density.
§With respect to SCE. The change = E_{corr}(final) − E_{corr}(initial).
‡For nominal surface area 100 mm^2.
§Mild steel substrate and pure nickel (see Table II) for comparison.

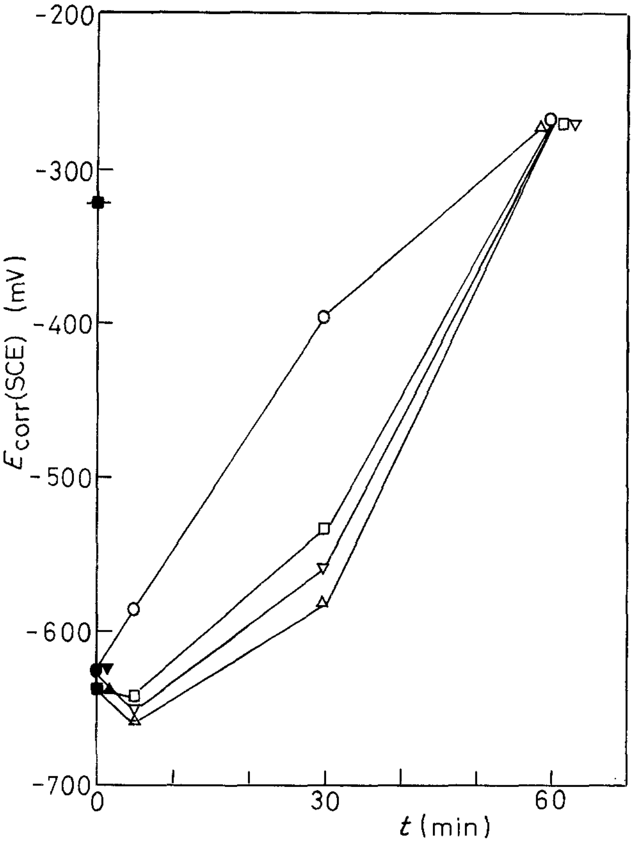

Figure 3 Corrosion potential E_{corr} as a function of substrate roughness and electroless nickel deposition time t. Symbols: substrate finish (a) 1 μm (○), (b) 600 SiC (□), (c) 240 SiC (△), and (d) as-ground (▽). Closed symbols steel substrate, and -■- pure nickel.

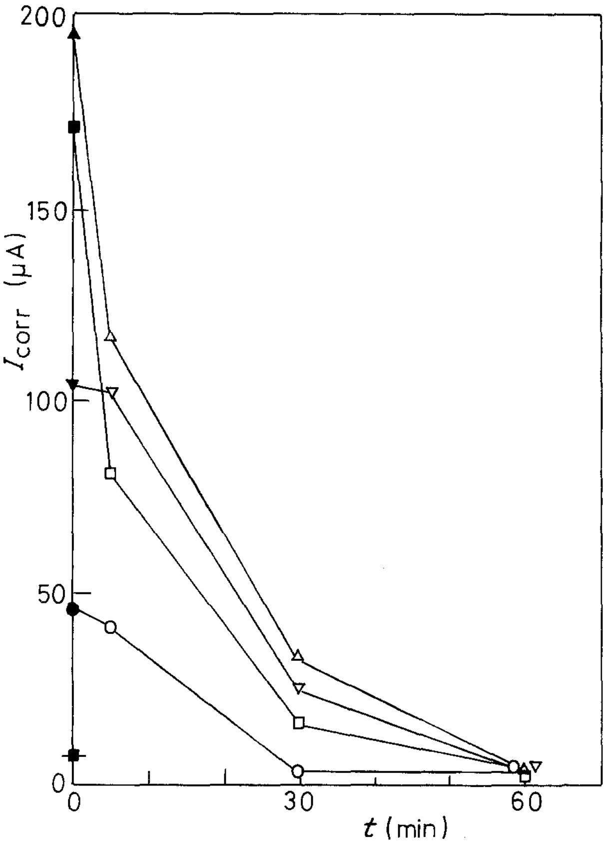

Figure 4 Corrosion current I_{corr} as a function of substrate roughness and electroless nickel deposition time t. Symbols: substrate finish (a) 1 μm (○), (b) 600 SiC (□), (c) 240 SiC (△), and (d) as-ground (▽). Closed symbols steel substrate, and -■- pure nickel.

The porosity in electroless nickel coatings tends to be associated with the lay of the surface finish [5]. If we assume for a porous coating that

$$I_{tot} = f_{Fe} I_{Fe} + f_{Ni} I_{Ni}$$

where f_{Fe} is the fraction of the surface that is iron. For the 600 SiC grit finish and 30 min deposition, $I_{corr} = 18\,\mu$A at -534 V (Table III). A separate measurement showed that at -534 V I_{Fe} was approximately 3500 μA. Hence assuming $I_{Ni} = 3\,\mu$A (Table III) we calculate $f_{Fe} \approx 0.005$. In practice, I_{Ni} will be less than 3 mA at -534 V but the change in f_{Fe} will be negligible.

5. Conclusions

From the present work on the effect of substrate roughness and coating thickness on the corrosion of electroless nickel coatings in a 0.99M Na_2SO_4 + 0.01M H_2SO_4 + 0.05M NaCl solution we conclude the following

1. The surface roughness of the mild steel substrate decreases for finishes in the order: as-ground, 240 SiC grit, 600 SiC grit, and 1 μm diamond polish.

2. The anodic polarization behaviour of the coatings showed that they had only a small tendency to passivate and that they were more active than pure nickel.

3. For a given substrate roughness, the corrosion potential of the coatings increased and the corrosion current decreased as the thickness of the coatings increased.

4. For a given coating thickness, the corrosion potential and the corrosion current depended on the surface finish but they were not a simple function of the surface roughness. The corrosion potential was the lowest and the corrosion current the highest on coatings deposited on a 240 SiC grit finish, and the corrosion potential increased and the corrosion current decreased for coatings deposited on substrates with finishes in the order: 240 SiC grit, as-ground, 600 SiC grit, and 1 μm diamond polish.

5. The corrosion potential and the corrosion current of coatings deposited for 60 min, was independent of surface roughness, and similar to those of pure nickel.

6. Heat treatment at 400 and 600° C did not affect the corrosion current.

7. The fraction porosity was estimated to be about 0.005 in the coating formed on a 600 grit surface for 30 min (approximately 5 μm thick).

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