Studies on nickel electrodeposits on dc magnetron sputtered copper substrates

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Investigations into nickel electrodeposits on dc magnetron sputtered copper substrates are reported. Thin layers of copper were deposited by dc magnetron sputtering on mild steel substrates. Onto these sputtered copper surface, layers of nickel were electrodeposited using a Watt's bath. The coatings were vacuum annealed at 200°C for 120 min. The growth of the deposit is discussed in terms of structural and microstructural analysis by X-ray diffraction (XRD), SEM and atomic force microscopy (AFM). The orientation along (111), (200) and (220) was observed for the vacuum annealed $Cu_{3\cdot8}Ni$ alloy deposits. Uniform and pinhole free morphology was observed from SEM. AFM images reveal that these coatings have a granular morphology. The corrosion behaviour of these samples in a 3·5 wt-%NaCl solution was examined. A decrease in I_{corr} and high charge transfer resistance indicated the improved corrosion resistant behaviour of the nickel sample plated over a sputtered copper base.

Keywords: Magnetron sputtering, PVD, Electroplating, Metallic coating, Electrochemical impedance spectroscopy, Morphology, Characterisation methods, SEM, AFM, X- ray diffraction, Corrosion, Cu–Ni alloy, Corrosion resistance, Potentiodynamic polarisation studies, Nyquist plot, Metals and alloys

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Introduction

In the past two decades, there has been growing interest in metal multilayers. Compositionally modulated multilayers (CMM) consisting of alternating layers of two different metals or alloys seem to possess unusual and enhanced mechanical and magnetic characteristics, such as improved strength, wear and corrosion resistance.[1–6] Cu–Ni based giant magnetoresistance (GMR)[7–8] has been the prime focus of many researchers because of its potential application in magnetic sensors and storage devices. These multilayers are generally prepared by vacuum deposition techniques such as evaporation, sputtering and molecular beam epitaxy. The practicalities are that, while physical vapour deposition (PVD) and chemical vapour deposition (CVD) processes are feasible for these coatings, electrodeposition is likely to be economic in the long term.

Electrodeposition is a well established industrial process which operates at a lower temperature, so the risk of interdiffusion between the different layers is low. It offers a greater choice of shape and size of substrate. Higher production rates are also obtained. A combination of electrodeposition and PVD is impractical from a commercial standpoint. However, if the virtue of such a combination is proved, commercial pressures will soon ensure a way forward. Copper is used as a preplate for improved adhesion of subsequent layers. Copper and nickel are fcc metals, and they form a continuous series of solid solutions.[9] The preferred orientation (texture) of the crystalline grains of polycrystalline metals influences their physical, chemical and mechanical properties.[10] In the present work, plated Ni electrodeposits in combination with dc magnetron sputtered copper were analysed for corrosion resistance.

Experimental

Mild steel substrates 75×25 mm were mechanically polished and degreased with trichloroethylene (TCE). The substrates were then electrocleaned in alkali solution containing sodium hydroxide and sodium carbonate for 2 min at 70°C, followed by rinsing with distilled water. The substrates were finally cleaned ultrasonically in acetone and then placed in the vacuum chamber of the sputtering system AVS 114D. The chamber was evacuated to a vacuum level of 1×10^{-5} mbar by means of a diffusion pump backed by a rotary pump. The operating pressure was 6×10^{-3} mbar. The distance between the cathode (target) and the substrate was found to be optimum at 60 mm. A high purity (99·99%) argon was fed into the vacuum chamber up to a pressure of 3×10^{-1} mbar. A bias voltage of 450 V was given. The duration of deposition was varied at 10, 20 and 30 min. A high purity >99·99%Cu target 10 cm in diameter was used as the cathode. The deposition parameters for sputtering are summarised in Table 1.

Nickel was deposited on these dc magnetron sputtered Cu substrates by electroplating using a Watt's bath. The composition of the bath and the operating parameters for nickel plating are listed in Table 2. The deposited films were analysed for crystallographic structure with a

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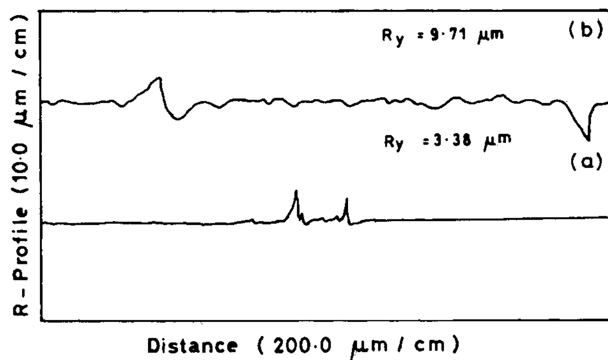
Published by Maney on behalf of the Institute
Received 10 September 2004; accepted 6 October 2004
DOI 10.1179/174329405X40858



a sputtered Cu on MS; *b* Ni plated over sputtered copper sample
1 Roughness profile

JEOL JDX 803a X-ray diffractometer using a Cu K_α line. The microstructure of these coatings was examined using a Hitachi S 3000H scanning electron microscope and a molecular imaging atomic force microscope. The The surface hardness values of the coated samples were measured on a microhardness tester (Leco DM 400 model) using a Vickers indenter at a load of 25 g. The surface roughness of the coating was measured using Mitutyo profilometer. The composition of the coatings was analysed on a HORIBA X ray analytical microscope XGT 2000. The optical characterisation of these coatings on glass substrates was carried out using a CARY 5E UV-Vis-NIR spectrophotometer in the 400–2500 nm wavelength region. Potentiodynamic polarisation experiments and ac impedance investigations were done using a BAS IM6 electrochemical analyser.

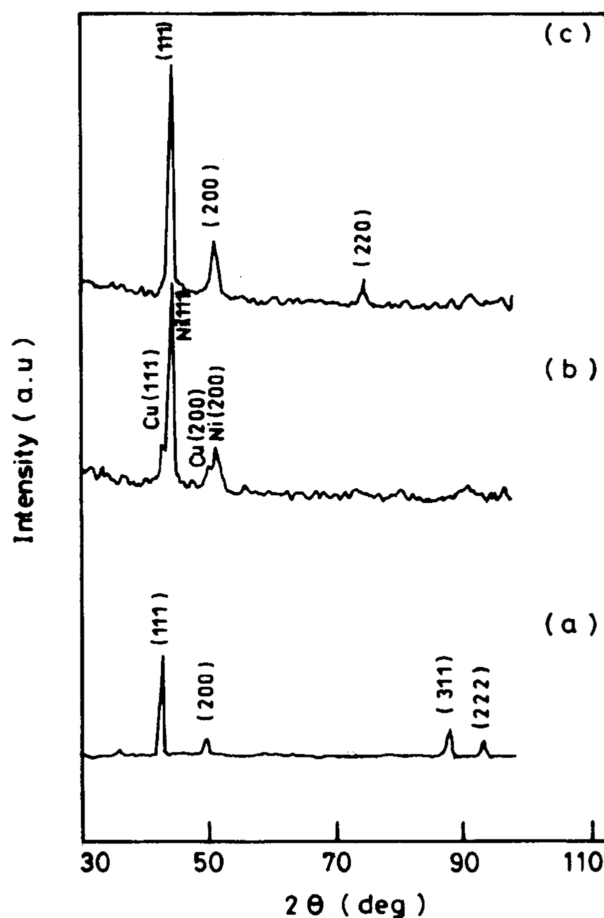
Results and discussion

Thin copper coatings were prepared by dc magnetron sputtering on mild steel substrates. The typical pink colour of copper was obtained at ⩾20 min. Nickel plating was done on these dc magnetron sputtered copper substrates for 45 min.

The nickel plated samples with the sputtered copper undercoat were bent through an angle of 180° repeatedly, as required by BS 54110 standards, and no lifting or peeling was found, which showed good adhesion to the substrates. Microhardness values of ~170–190 HV(25 g) were measured on the plated nickel on a sputtered copper base.

Roughness and profilometric thickness

A profilometer was used to measure the surface roughness profile of the coated samples. However, it can be used to measure the step height between a base substrate and the adjacent coating. A stylus made of stainless steel with a diamond tip is drawn across the step from the substrate to the coating, and both the vertical and horizontal motion of the stylus are amplified and recorded. A region of the substrate was masked before depositing the elements. The uniform nature of the coatings is observed in Fig. 1*a*, *b* for the sputtered Cu and plated Ni overcoat. Thickness values of 3·38 μm for the sputtered Cu and 9·71 μm for the plated Ni overcoat and underlying Cu were obtained.



a sputtered Cu; *b* as plated Ni over sputtered Cu; *c* vacuum annealed Ni plated over sputtered copper sample
2 X-ray diffraction

X-ray diffraction and composition analysis

Figure 2*a–c* shows the X-ray diffraction patterns obtained for a dc magnetron sputtered copper thin coating, plated Ni over sputtered Cu substrate and a vacuum annealed Ni+Cu sample, respectively. A good polycrystalline nature of the coating with fcc structure was observed. The comparison of *d* values calculated from the observed XRD pattern and standard *d* values from JCPDS files are shown in Table 3. It was found

Table 1 Deposition parameters for Cu sputtering

Parameter	Value
Ultimate vacuum	1×10^{-5} mbar
Operating vacuum	5×10^{-3} mbar
Ar gas pressure	2–3 kg cm^{-2}
Ar gas flow rate	12 cm^3 min^{-1}
Substrate biasing	450 V
Power	32 W
Distance between target and substrate	60 mm

Table 2 Composition of Ni plating bath

Parameter	Value
Nickel sulphate	240 g L^{-1}
Nickel chloride	40 g L^{-1}
Boric acid	30 g L^{-1}
Temperature	60°C
pH	4
Current density	3 A dm^{-2}
Duration	45 min

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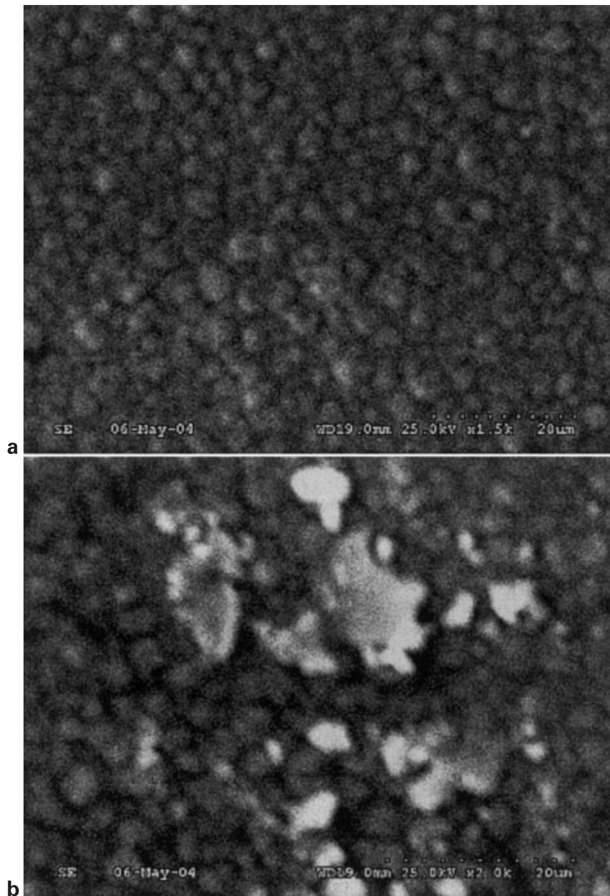


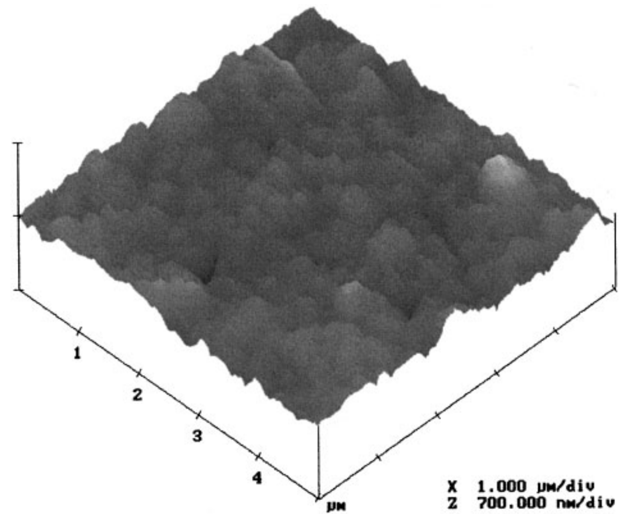
a as plated; *b* vacuum annealed Ni plated over sputtered copper

3 Scanning electron micrographs of samples

that there is a very good agreement in *d* values. Figure 2*c* indicates the $Cu_{3.8}Ni$ alloy formation of the sample vacuum annealed at 200°C for 120 min. Sequential evaporation of Cu and Ni and the subsequent annealing at 200°C yielded a Cu–Ni alloy.[11] The composition of the coatings obtained from X-ray fluorescence (XRF) is shown in Table 4. The presence of Mn and Fe is due to the substrate, and indicates the thin nature of the coating. As the thickness of the plated nickel increases, the nickel content is found to be higher for the electroplated Ni over sputtered Cu sample. The vacuum annealed sample showed a change in composition which may be due to the formation of Cu–Ni alloy. During heat treatment, diffusion of

Table 3 Comparison of *d* values from the observed XRD pattern

Samples	d_{obs}, nm	d_{std}, nm	*hkl*	Phase
(a) Sputtered Cu on mild steel	2·090	2·088	111	Cu
	1·819	1·803	200	Cu
	1·093	1·091	311	Cu
	1·046	1·042	222	Cu
(b) Plated Ni over sputtered Cu base	2·097	2·088	111	Cu
	2·043	2·037	111	Ni
	1·809	1·808	200	Cu
	1·770	1·764	200	Ni
(c) Annealed sample (b)	2·078	2·083	111	$Cu_{3.8}Ni$
	1·793	1·796	200	$Cu_{3.8}Ni$
	1·276	1·270	220	$Cu_{3.8}Ni$



4 AFM image of representative vacuum annealed Ni plated over sputtered copper sample

copper atoms into nickel lattice forms $Cu_{3.8}Ni$ alloy. The theoretical mass percentage ratio of Cu and Ni present in $Cu_{3.8}Ni$ alloy is 78·2 : 21·8. This is in close agreement with the experimentally found ratio of 74·08 : 25·92 for Cu and Ni, respectively.

Surface morphology

The surface morphology of the as deposited and vacuum annealed Cu–Ni coatings is shown in Fig. 3*a* and *b* The surface structure of as deposited Cu–Ni showed a spherical nodular structure, and the grains are very coarse. A similar structure with few clusters was seen for the vacuum annealed sample, and the cluster formation may be due to alloy formation. Uniform coverage of the surface without pinholes is seen on the surface of the as prepared and annealed coatings.

Figure 4 shows the region of vacuum annealed Ni plated over the sputtered copper base sample. AFM images reveal that these coatings have a granular morphology. They also show the presence of hills on top of a homogeneous granular background surface. The density and the height of the hills increase with the thickness of the deposit. The growth of the Ni coating on a sputtered copper base by electroplating is associated with the formation of three-dimensional grains in a perpendicular direction without lateral diffusion of adatoms on the surface parallel to the base. This is attributed to the preferentially oriented crystalline nature of the sputtered copper base over which Ni is deposited. The presence of pits on the surface of the annealed sample may be due to localised pitting during heat treatment of the precorrosion tested samples.

Table 4 Composition analysis obtained from XRF

Sample	Elements	Wt-%
(a) Dc magnetron sputtered Cu	Mn	1·15
	Fe	39·58
	Cu	59·27
(b) Electroplated Ni over sputtered Cu base	Fe	0·70
	Cu	56·09
	Ni	44·21
(c)Vacuum annealed sample (b)	Cu	74·08
	Ni	25·92

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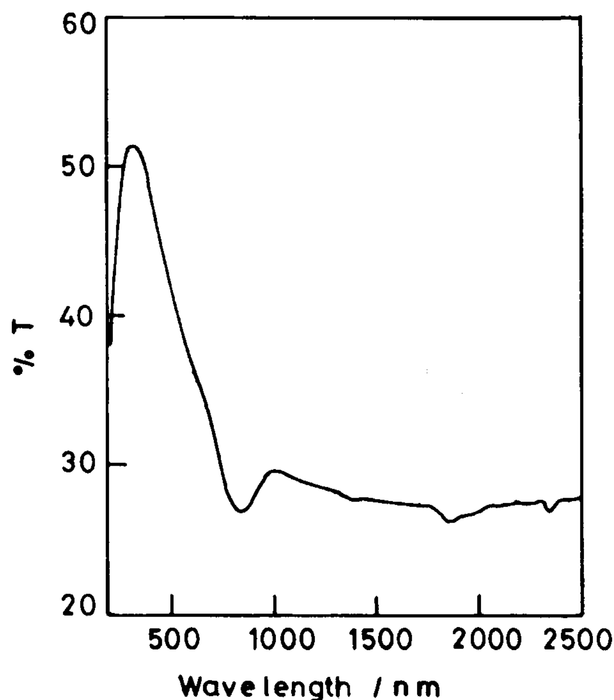

5 Optical transmittance spectrum for vacuum annealed Ni plated over sputtered copper sample

Optical transmittance and electrical resistivity measurement

The substrates used for optical transmittance and electrical resistivity measurement were ordinary microscope slides 1 mm thick. The substrates were cleaned with acetone, alcohol, a hot detergent solution, distilled water and finally dried with lint free paper. Figure 5 shows the optical transmittance spectrum obtained for the thin Ni plated sample $\sim$1 μm thick over sputtered Cu substrates 0·4 μm thick. A high transmittance in the visible and low transmittance in the IR region indicate that these coatings are suitable in a window system if good heat insulating properties are required.

Electrical resistivity measurements of these coatings on glass substrates were performed using the four probe method at room temperature. In this technique, four sharp probes are placed on a flat surface of the Cu–Ni as deposited and vacuum annealed samples, a current is passed through the two outer electrodes, and the floating potential is measured across the inner pair. A nominal value of probe spacing, which has been found satisfactory, is an equal distance of 1·5 mm between adjacent probes.

Resistivity was found to be 32 μΩ cm for the plated Ni on sputtered copper and 40 μΩ cm for the vacuum annealed coatings. These values are in good agreement with the resistivity values reported earlier by Ishikawa *et al.*[12] for hybrid films of electroless Cu–Ni films and multilayered Cu/Ni films.

Potentiodynamic polarisation and ac impedance spectroscopy

Corrosion resistance measurements were performed using a three electrode assembly. The samples were masked with lacquer to expose an area of 1 cm^2 on one side of working electrode. A platinum foil and saturated calomel electrode were employed as auxiliary and reference electrodes, respectively. Polarisation studies were carried out in 3·5 wt-% neutral sodium chloride solutions. Typical polarisation curves obtained for the corrosion behaviour of the samples are shown in Fig. 6. Table 5 includes the values of the corrosion potential E_{corr}, the corrosion current density I_{corr}, the anodic and cathodic Tafel slopes during polarisation in 3·5 wt-%NaCl and the corrosion rate. The observed positive shift in E_{corr} for the Ni plated samples from E_{corr} values of sputtered copper base and mild steel panel is indicative of an increasing corrosion resis tance with Ni overcoat samples. The observed decrease in I_{corr} for the Ni plated onto a sputtered copper base confirms the improved corrosion resistant behaviour of Ni topcoat samples. This will also be due to a reduction in porosity at the increased coating thickness.

The same three electrode cell assembly that was used for the potentiodynamic polarisation experiments was employed for the ac impedance investigations. Impedance measurements using a Nyquist plot were made at open circuit potential (OCP) applying an ac signal of 10 mV in the frequency range 10 Hz–1 MHz. Figure 7*a–c* shows the corrosion behaviour of a 1 cm^2 area of pure mild steel, sputtered copper on mild steel and Ni plated on a sputtered copper base.

Table 6 gives the values of OCP, charge transfer resistance R_{ct} and the double layer capacitance C_{dl}. In the case of the Ni plated sample, the OCP is the most positive, which suggests that the deposit should be the most resistant to corrosion. The measured R_{ct} of this sample was the highest at 2·79 KΩ and, consequently, the double layer capacitance would be at a minimum for this deposit, and it was found to be $5{\cdot}70\times10^{-7}\ \Omega^{-1}$.

Table 6 Corrosion parameters obtained from impedance measurements

Sample	OCP *v.* SCE, mV	R_{ct}, Ω	C_{dl}, Ω^{-1}
Mild steel panel	−515	540	$1{\cdot}58\times10^{-4}$
Sputtered Cu on mild steel	−363	910	$5{\cdot}56\times10^{-5}$
Plated Ni over sputtered Cu	−216	2790	$5{\cdot}70\times10^{-7}$

Table 5 Corrosion parameters obtained from polorisation studies in 3·5 wt-%NaCl

		Tafel slope			
Sample	E_{corr} *v.* SCE mV	b_a, mV decade^{-1}	b_c mV decade^{-1}	I_{corr} cathodic, μA cm^{-2}	Corrosion rate, mil year$^{-1}\times10^{-3}$
Pure mild steel	−695	29·2	−28·6	9·26	11·926
Sputtered Cu on mild steel	−394	25·4	−65·4	2·96	3·812
Plated Ni on sputtered Cu	−214	30·8	−52·6	0·71	0·914

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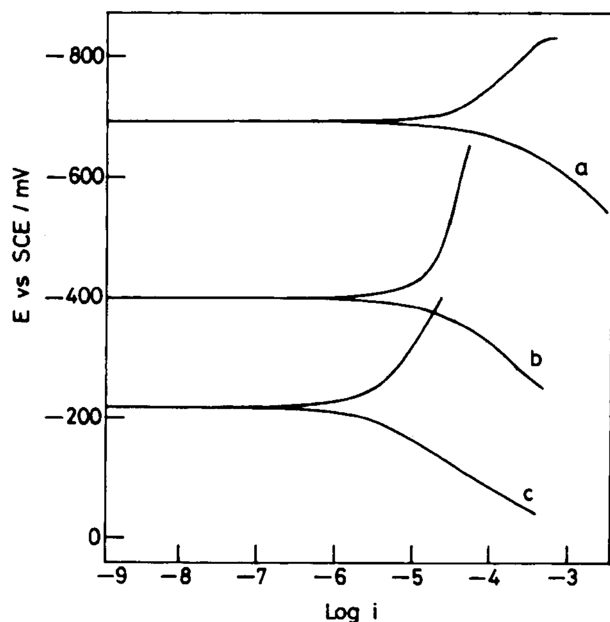
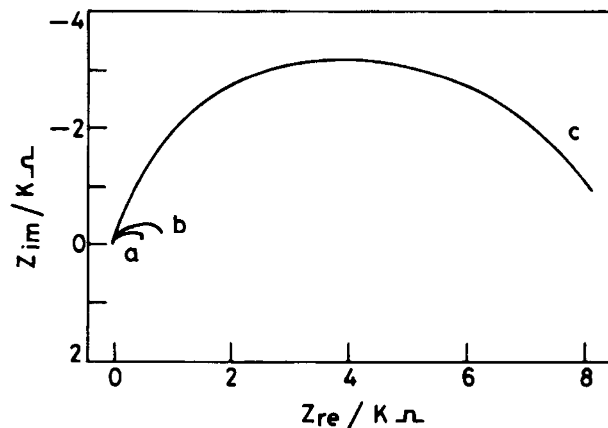


a pure mild steel; *b* sputtered copper over mild steel; *c* Ni plated over sputtered copper base in 3·5 wt-%NaCl

6 Polarisation studies

Conclusion

As deposited and vacuum annealed Ni electrodeposits over dc magnetron sputtered copper base were studied in detail. The uniform nature of the coatings was observed from profilometric roughness measurement and microstructure analysis. A good polycrystalline nature with a fcc structure was observed for the Ni and Cu coatings. Vacuum annealing at a lower termperature of 200°C for 120 min showed $Cu_{3\cdot8}Ni$ alloy formation as confirmed by XRD and composition analyses. Low electrical resistivity was observed for this hybrid Cu–Ni coatings. A low transmittance in the IR region indicated that these coatings are suitable in a window system. The positive shift in E_{corr} and decrease in I_{corr} values for the Ni electrodeposits over a sputtered copper base showed its highly corrosion resistant nature. The most positive OCP



a pure mild steel; *b* sputtered copper over mild steel; *c* Ni plated over sputtered copper base

7 Nyquist plots for corrosion

value and the highest charge transfer resistance confirmed the Ni electrodeposits over a sputtered copper base were the most resistant to corrosion.

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