Corrosion studies on pulsed and direct current chromium deposits

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SUMMARY – Chromium was deposited on steel substrates using direct current pulsed high frequency and pulsed low frequency plating methods. The samples obtained from the different plating techniques were later exposed to a corrosive NaCl solution. The time of exposure was varied, for 0, 80 and 140 hours and later the samples were subjected to impedance measurements. In the present study an attempt has been made to characterise the best plating method using impedance data analysis.

INTRODUCTION

Electrolytic deposition of chromium is characterised by a low current efficiency (ϕ) in the traditional sulphate catalysed chromium bath. The current efficiency is $12 - 20\%$, but it has been observed that it increases up to 38% under low and high frequency pulse current electroplating. Pulse plating is a method of depositing a metal on a substrate using interrupted direct current. The pulses often applied at a rate of 10-10,000 per second provide advantages which include increased plating speeds, improved distribution, refined grain structure, increased ductility of deposit, increased cathodic current efficiency and reduced hydrogen embrittlement. In pulse plating, the pulse current density, the on-time and off-time, can be varied independently over a very broad range. Hence, very high instantaneous current densities and very high negative potentials can be attained. An high overpotential greatly influences the nucleation rate which contributes to high efficiency in the case of pulse plating[1].

Moreover in the case of conventional D.C. plating the metal ions become depleted near the cathode and thicker deposits are formed at the edges due to polarisation effects[2]. In the case of pulse current plating, the metal ions are deposited on the cathode during the on-time and later during the off-time the equilibrium of the solution is re-established, thus restricting the development of cathode concentration gradients. Further, in the case of pulse current plating the polarisation effects are evenly distributed throughout the diffusion layer and are no longer concentrated on the edges of the cathode. These are the main reasons for improved efficiency in the case of pulse current plating. In this paper, the corrosion resistances of chromium plated samples by pulse plating are compared with those from direct current plating by using electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

Chromium was deposited on a steel substrate of area 4×4 cm^2 after mechanical polishing and pickling in an hydrochloric acid-ethanol-water mixture. The composition of the bath used at 45 ºC was: $CrO_3 - 250$ g dm^{-3}, $H_2SO_4 - 2.5$ g dm^{-3}. In pulse plating a rectangular pulsating current, fluctuating between zero and constant peak cathodic current was used to deposit chromium. The pulse conditions are given in Table I. The on/off pulsating was carried out in two parts – high frequency (short pulse cycle) and low frequency (long pulse cycle). Frequencies above 90 Hz were used for low-frequency plating and frequencies above 90 Hz were used for high frequency pulse plating. The plated samples were exposed to 3% NaCl solution for different exposure times and were subjected to impedance measurements using an Electrochemical Impedance Analyser Model BAS IM6 at frequencies from 10 mHz to 100 kHz.

RESULTS AND DISCUSSION

Figure 1 clearly shows Nyquist plots for D.C. plated samples under various hours of exposure in 3% w./v. NaCl solution. The semicircular region is more pronounced in the case of 0 hours of exposure indicating that samples which have not been exposed to NaCl have maximum corrosion resistance as observed from the high frequency region of the impedance spectra. The same trend is also observed in Figure 2 which is the Bode plot for pulse high frequency samples. The R_{ct} and C_{dl} values are clearly shown in Table II. It can be seen that there is a notable decrease in R_{ct} and R_s values as the hours of exposure in NaCl is increased.

When compared to the direct current plated sample, those plated with pulsed current possess very high resistance and low capacitance values. This shows that the pulse plated samples are highly corrosion resistant. The R_{ct} and R_s values are very high for low frequency pulse plated samples when compared to those of high frequency pulse plated samples and D.C. plated samples. This trend is clearly shown in Figures 3 and 4.

The phase angle plots for the samples plated by all three plating methods when subjected to 140 hours of exposure in NaCl solution are shown in Figure 5. There are
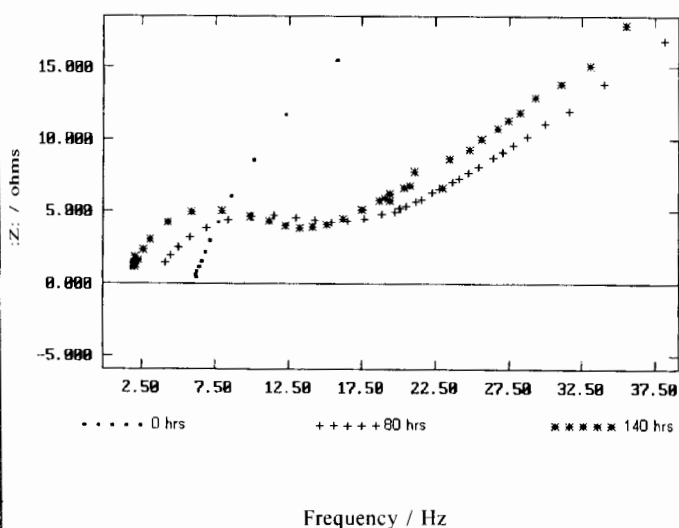
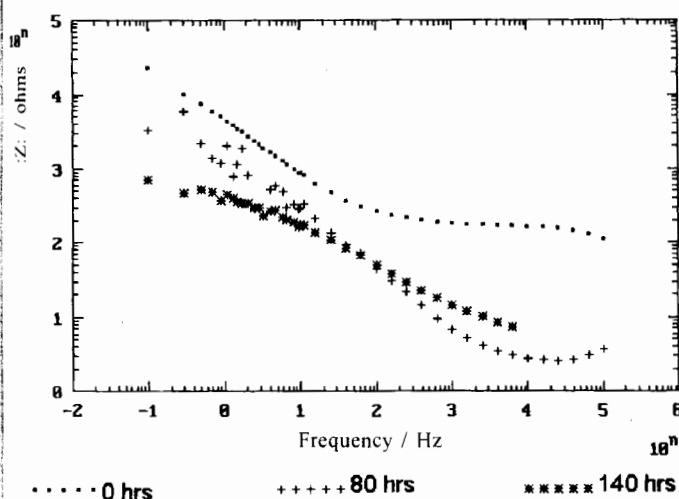**Figure 1** Nyquist plots for direct current plated samples with different hours of exposure in 3% NaCl.

Figure 2 Bode plots for pulse high plated samples with different hours of exposure in 3% NaCl.
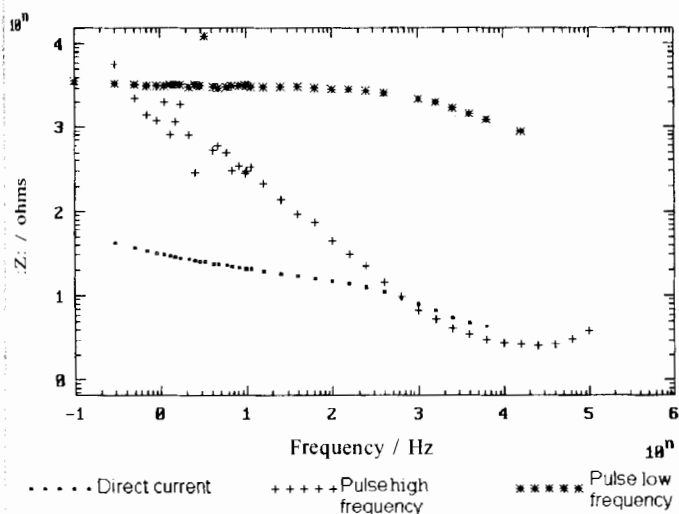
Figure 3 Bode plots for differently plated samples with 80 hours of exposure in 3% NaCl.
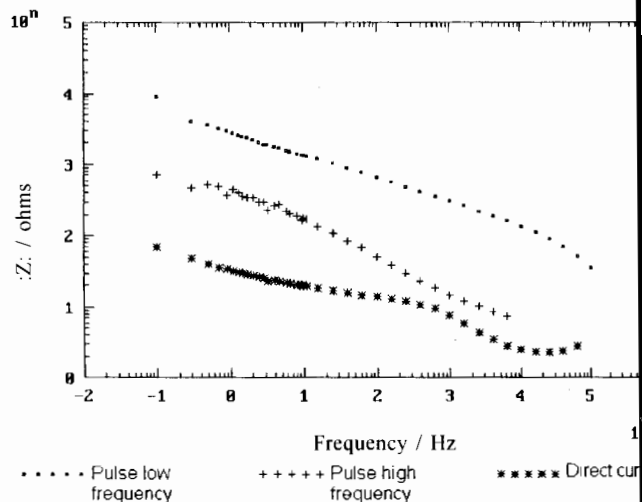
Figure 4 Bode plots for differently plated samples with 140 hours of exposure in 3% NaCl.
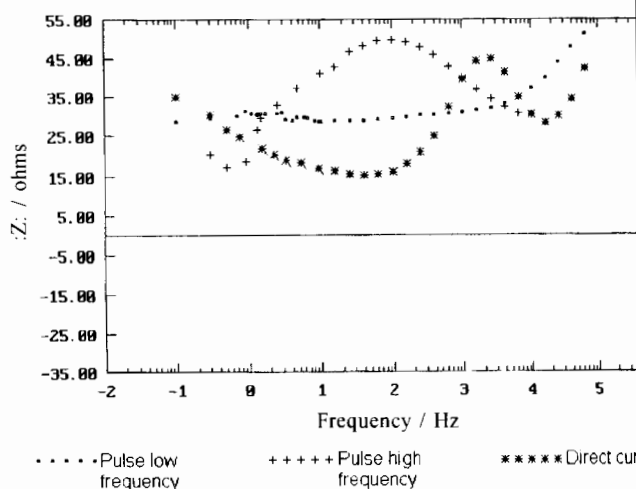
Figure 5 Phase angle plots for differently plated samples with 140 hours of exposure in 3% NaCl.
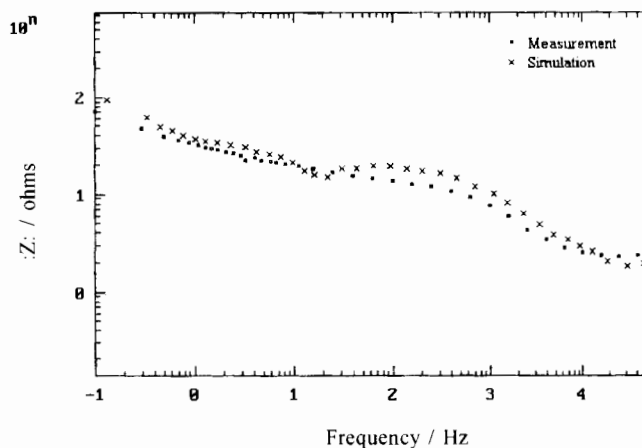
Figure 6 Simulated and experimental plots for direct current plated samples with 140 hours of exposure in 3% NaCl.

Table I.

Pulse Frequency / Hz Pulse on-off times / ms			
50	500	1111	2000
10-10	1-1	0.8-0.1	0.4-0.1
9-11	1.1-0.9	0.7-0.2	0.3-0.2
8-12	1.2-0.8	0.6-0.3	0.2-0.3

variations in phase angle for the high frequency pulse plated sample and almost no variation for a low frequency pulse plated sample. From the variations in the values of phase angle it can be predicted that the D.C. plated samples are more prone to corrosion and it can be concluded that the low frequency pulse plating method is superior and produces better results compared to the other two plating methods.

According to Miller and Pan[2], in the case of high frequency pulse plating, the increased interruptions make the surface topography of the samples an incoherent conglomerate of high peaks and deep cavities. The high frequency interruptions prevent the establishment of an oriented growth of the deposit and thus lead to large needle-like grains, poor adhesion and increased stress in the deposit. As a result, the hardness and the resistance values of the sample decreases[2]. These limitations are relieved in the case of low frequency pulsed electroplating which ultimately increases the hardness and the resistance offered to charge transfer also increases.

The D.C. plated chromium samples have lower corrosion resistance than the low frequency pulse plated samples and this may be due to low hydrogen content (3.2%) in the
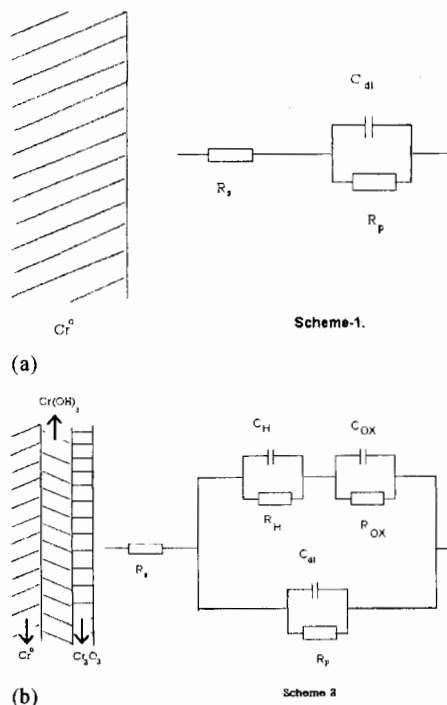

(a)

(b)

Figure 7 (a)Equivalent circuit diagram for D.C. chromium plated samples (b)Equivalent circuit diagram for low frequency and high frequency pulsed chromium deposits

case of D.C. plating compared to that of low frequency pulse plating (31.2% at f = 50 Hz)[3]. Moreover, the attack of the chloride ions is more facile on D.C. plated chromium samples since the surface compositions reported in Ref. 3 show only a layer of CrO whereas in the case of low frequency pulse plating the surface composition may be various layers of $Cr(OH)_3$, Cr_2O_3 and CrO. Even though these

layers are formed in the case of high frequency pulse plating the initial peaks and deep cavities formed due to the increased number of interruptions evidently reduce the corrosion resistance of such samples.

The effect of on-time and off-time is one of the major reasons for the difference in corrosion resistance of high and low frequency pulse chromium plating. As reported in[1] an increase in t_{off} leads to an increase in β-Cr in the chromium deposits. Thus, in the case of low frequency pulse plated samples the β-Cr content of the chromium deposit is greater than for high frequency pulse plated samples. Since β-Cr has been shown to be chromium hydride[4,5] it is reasonable to deduce that the hydride layer formed in the case of low frequency pulse plating offers considerable corrosion resistance whereas this hydride layer is not very significant for high frequency pulse chromium plating.

Based on the above explanations, equivalent circuits were deduced for all three chromium plated samples. In the case of D.C. plated samples, it is assumed that a very thin chromium oxide layer is formed over the CrO layer. Figure 6 shows the simulation for D.C. plated samples after 140 hours of exposure in NaCl solution based on the equivalent circuit shown in Figure 7 (a).

The equivalent circuit for the low frequency and high frequency pulse plated samples is shown in Figure 7 (b). Based on the above equivalent circuit, simulations were carried out for high frequency and low frequency plate samples and are shown in Figures 8 and 9, respectively.

The evaluation of diffusion coefficients for the plated samples gives a clear idea regarding the behaviour of the plated samples in the corrosive medium. The conventional method of estimating the diffusion coefficient is by using the following equation[9],

$$D = \frac{L^2}{3R_L C_L} \quad (1)$$

where L is the thickness of the diffusion layer, R_L and C_L are the series resistance and series capacitance of the diffusion layer, respectively. The value of the diffusion coefficients are given in Table III. It can be observed that in the case of the low frequency pulse plated samples the diffusion coefficient of the chloride ions is minimum when compared to that of the high pulse frequency and direct current plating. This trend clearly proves that compared to the other two techniques, low frequency pulse plating is superior. The resulting deposits are highly corrosion resistant.

Table II.

Hours of exposure	Plating method	Chromium		
		R_s / ohms	R_{ct} / ohms	C_{dl} / Farads
0	D.C.	5.770	76.17	2.068e-3
0	Pulse-High frequency	148.2	612.2	6.013e-5
0	Pulse-Low frequency	2.615k	2.302k	1.004e-10
80	D.C.	4.217	15.76	2.09e-2
80	Pulse-High frequency	38.18	609.6	2.83e-4
80	Pulse-Low frequency	598	2.090k	4.725e-5
140	D.C.	2.772	11.13	2.83e-3
140	Pulse-High frequency	5.369	57.09	1.43e-3
140	Pulse-Low frequency	35.13	179.9	1.869e-4

Table III.

Plating method	R_s / ohms	R_{ct} / ohms	Diffusion co-efficient / cm^2s^{-1}
D.C. plating	2.744	9.398e-3	8.08e-9
High frequency pulse plating	317	587.8e-6	1.12e-9
Low frequency pulse plating	2.099e3	85.06e-6	1.16e-9

CONCLUSIONS

D.C. plated samples were compared with pulse plated samples. All the chromium plated samples obtained by pulse plating had very high R_p and R_s values and proved to be more efficient compared to D.C. plating. For pulse plating, the low frequency pulse plated samples proved to be the best as they had very high corrosion resistance and very low double layer capacitance. This trend was further confirmed by the diffusion coefficient
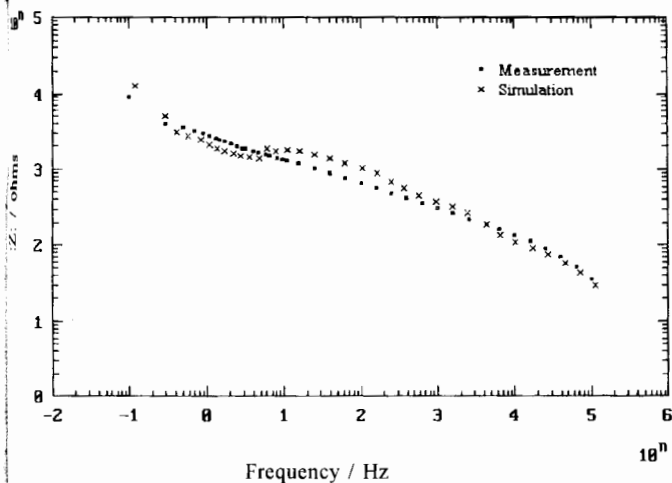
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Figure 8 Simulated and experimental plots for pulse low frequency plated samples with 140 hours of exposure in 3% NaCl.
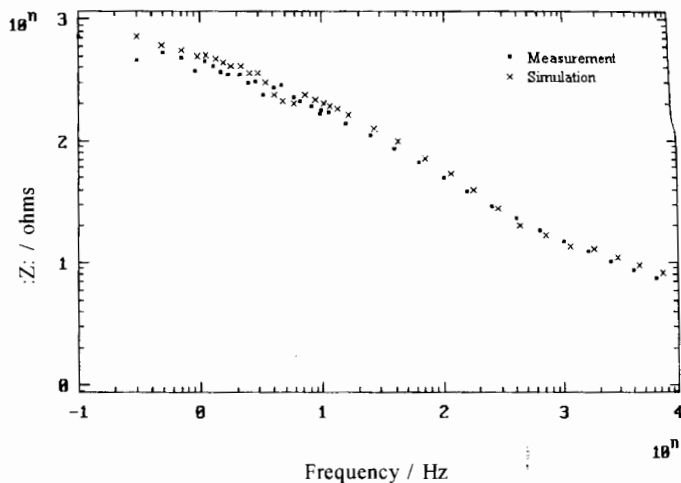

Figure 9 Simulated and experimental plots for pulse high frequency plated samples with 140 hours of exposure in 3% NaCl.

calculations wherein we obtained very low values of d only in the case of low frequency pulse plated samples.

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