

Influence of pulse parameters on electrocodeposition of Cr–Al₂O₃ nanocomposite coatings from trivalent chromium bath

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Cr and Cr–Al₂O₃ coatings were electrodeposited from Cr(III) bath with both pulsating and direct current onto copper substrates. Pulsating current resulted in homogeneous films of higher Al₂O₃ content and lower particle agglomeration than the direct current. Differences were more tangible at shorter duty cycles and pulse frequencies. Pulsating current improved both microhardness and corrosion resistance. The presence of alumina nanoparticles resulted in greater current efficiency, higher film microhardness and better corrosion resistance. Maximum current efficiency, highest microhardness and densest electrodeposited coatings were achieved at current density of 20 A dm⁻², duty cycle of 40% and pulse frequency of 10 Hz.

Keywords: Nanocomposites, Pulse plating, Trivalent chromium, Codeposition, Corrosion resistant, Microhardness

Introduction

Electrodeposition from Cr(VI) baths has traditionally been used for decoration, surface hardening and corrosion resistance enhancement for more than a century.^{1,2} Tanks of Cr(VI) used for electroplating and anodising are large sources of highly toxic and carcinogenic emissions in the USA.³ Hence, electroplating from Cr(VI) baths needs to be substituted with safer methods.⁴ Owing to the fact that Cr(VI) containing compounds are powerful epithelial irritants and human carcinogens, the United States Environmental Protection Agency has classified materials containing leachable chromium as hazardous waste except when they are proved other than Cr(VI). Exposure to Cr(VI) causes hyperaemia, ulceration and inflammation of mucous lining of the respiratory tract and its ingestion can cause irritation or ulcers in the stomach and intestines.⁵ USA, European Union, Japan and China have passed regulations restricting hazardous substances like Cr(VI) from use in many industries. The issue of hexavalent chromium bath has resulted in widespread attention to trivalent baths⁶ which are non-carcinogenic due to their inability to pass through transporters residing within the cell membrane. The main advantage of trivalent chromium plating bath is thus its non-toxic behaviour.

Deposition of thick Cr from Cr(III) bath is cumbersome and thin Cr does not have enough wear resistance.⁶ A metal matrix composite seems to be a solution.^{7,8} Codeposition of ultrafine metal, oxide,

carbide and polymer particles on metallic matrices has successfully been done before.^{9,10} Hence, production of Cr–Al₂O₃ nanocomposite from Cr(III) bath appears a feasible way for improvement of wear resistance, hardness, lubricity and high temperature resistance of the deposited layer.¹¹ Microstructure and morphology of Cr layers are substantially affected by electroplating pulse conditions.¹ There is no general agreement on quantitative details of this effect, however.

From codeposition results of other systems,⁸ it is expected that pulsating current will yield a better Cr–Al₂O₃ layer than direct current. Effects of current density, the imposed current type, nanoparticle addition, pulse frequency and duty cycle of pulsating current on current efficiency, microstructure, microhardness and corrosion resistance of the deposited Cr–Al₂O₃ layer are scrutinised in this paper.

Experimental

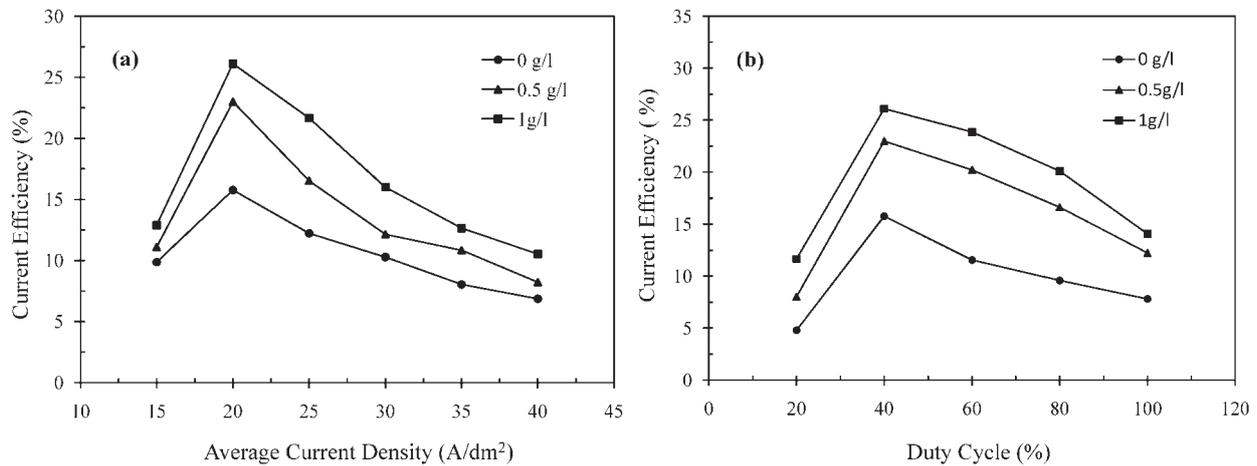
Alpha-Al₂O₃ powder of ~50 nm diameter (Nanostructured & Amorphous Materials Inc.) was ultrasonically dispersed into a trivalent chromium bath that was mixed at 200 rev min⁻¹ for 1 h by a magnetic stirrer which prevented particle sedimentation. Pure Cr and Cr–Al₂O₃ were then electroplated from the bath onto carefully cleaned copper plates. The distance between anode and cathode was 2 cm and the ratio of the anode to cathode areas is ~2:1.

Before electrodeposition, the Cu plates were mechanically polished to obtain 0.05–0.1 μm surface roughness. They were sequentially cleaned in ethanol and distilled water activated in 5 wt-%HCl for 20 s and washed in distilled water before immersion into the Cr(III) bath.

A galvanostatic power supply was used in the experiments for deposition of coatings by direct current.

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1 Variation in current efficiency at different nanoparticle contents with *a* average current density at $dc=40\%$ and *b* duty cycle at $I_a=20 \text{ A dm}^{-2}$

A pulse plating unit was designed to generate various duty cycles and pulse frequencies of up to 8 A amplitude. Duty cycles of 1–100% and pulse frequencies of up to 50 kHz were applied with the assembled unit. Bath composition and operating conditions were given in Table 1.

The electrochemical experiments were performed in a three electrode electrochemical cell using a potentiostat/galvanostat AUTOLAB model PGSTAT302N. The polarisation curves were measured at a sweep rate of 1 mV s^{-1} in 0.5 M NaCl solution at room temperature.

The surface morphology of the nanocomposite coatings was observed using a Hitachi model HIT-S4160 operated at 15 kV field emission scanning electron microscopy and the percentage of the codeposited Al₂O₃ particles was evaluated by using energy dispersive X-ray spectroscopy unit. All chemical compositions were the average of at least five measurements quoted in weight percentage. Hardness of the coatings was measured by a Vickers microhardness (HV) indenter applying 25 g load for 10 s. An average of five readings was quoted for each hardness number.

Table 1 Bath composition and electrodeposition parameters used in this research

Electrolyte	M L ⁻¹
CrCl ₃ .6H ₂ O	0.4
Glycine	0.5
H ₃ BO ₃	0.5
NaCl	0.5
NH ₄ Cl	0.5
NH ₄ Br	0.2
AlCl ₃ .6H ₂ O	0.01
Process	Amount/type
Temperature	$30 \pm 1^\circ\text{C}$
Plating time	20 min
Anode	Platinum
Cathode	Copper
pH	2.7
Agitation	Magnetic stirring (200 rev min ⁻¹)
Average current density	20 A dm^{-2}
Current	Direct or pulsating
Duty cycle	20, 40, 60 and 80%
Frequency	1–1000 Hz

Results and discussion

Current efficiency

Inserting pulse plating parameters into Faraday equation, current efficiency η (%) of the system is obtained

$$\eta = \frac{mZF(T_{\text{on}} + T_{\text{off}})}{MI_p T_{\text{on}} A t} \quad (1)$$

where m is mass of deposit (wt-%Cr), Z is valance, F is Faraday constant, T_{on} and T_{off} are on/off durations of the pulse, M is molar mass, I_p is peak current density, A is area of coating and t is the electrodeposition time. Average current density I_a , duty cycle (dc) and frequency f are defined as

$$I_a = \frac{I_p T_{\text{on}}}{T_{\text{on}} + T_{\text{off}}} \quad (2)$$

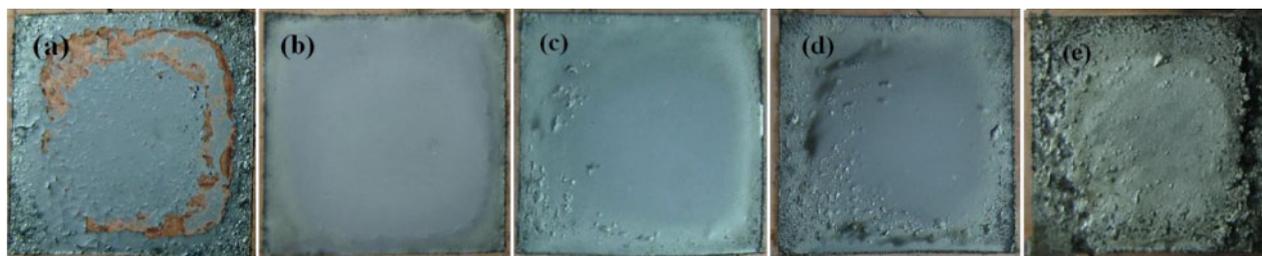
$$dc = \frac{T_{\text{on}}}{T_{\text{on}} + T_{\text{off}}} \times 100 \quad (3)$$

$$f = \frac{1}{T_{\text{on}} + T_{\text{off}}} \quad (4)$$

Figure 1 illustrates the effects of average current density and content of nanoparticles on η . At $I_a < 15 \text{ A dm}^{-2}$, due to extremely slow plating rate, no results are recorded (Fig. 1a). Above 15 A dm^{-2} , η increases with current density. $I_a = 20 \text{ A dm}^{-2}$ is a critical current density also observed by previous authors for chromium deposition from Cr^{3+} bath without alumina nanoparticles.¹² Optimum electroplating with high quality coating occurs at this I_a . Above 20 A dm^{-2} , η decreases with I_a and Cr layer becomes porous. The influence of I_a in reducing η above 20 A dm^{-2} has two reasons:

- the small rate of transfer of Cr^{3+} containing complex towards cathode⁶ which results in lowering of Cr^{3+} concentration beside the cathode surface and reduction in η
- the decomposition of water which causes hydrogen evolution and increases current loss.¹³

Figure 1b illustrates the variation in η with dc and Al₂O₃ nanoparticle content C_{np} . It is seen that η increases with dc up to $dc=40\%$. Afterwards, η decreases to as low as 7.8% for pure chromium ($C_{\text{np}}=0$) and 14.1% for Cr having 1 g L^{-1} Al₂O₃. With $dc=20\%$, because of small



a 1 Hz; b 10 Hz; c 50 Hz; d 100 Hz; e 1000 Hz

2 Macrographs of layers electrodeposited at pulse frequency

on time intervals, the deposition rate is lower than $dc=40\%$. Above $dc=40\%$, η decreases with dc due to smaller peak currents which are unable to deposit as much Cr–Al₂O₃.

Enhancement of η with C_{np} is attributed to:

- (i) formation of a metallic ion film around each alumina nanoparticle immersed in the electrolyte^{14,15} which results in their facilitated transfer towards the cathode and their faster reduction¹⁴
- (ii) attachment of alumina nanoparticles to the cathode surface increases nucleation sites and facilitates chromium deposition.^{7,14} This raises the current efficiency of the process.

It is, therefore, concluded that for optimum deposition rate, $I_a=20 \text{ A dm}^{-2}$ and $dc=40\%$ are preferable.

The effect of pulse frequency on macroscopic appearance of the coating surfaces produced by electrodeposition is illustrated in Fig. 2. The best quality seems to be achieved at 10 Hz. At a low frequency of 1 Hz, the coating fails to have enough adhesiveness and spalls easily because of long interruption of the off time cycle.

By increasing the frequency to 50 Hz and higher, coatings become more porous, less adhesive and darker in colour. Significant weight increase in the deposit is also observed as a result of hydration of chromium on the substrate. Optimum frequency is, hence, considered to be 10 Hz.

Nanoparticle incorporation

Effects of duty cycle, pulse frequency and Al₂O₃ contents on incorporation of Al₂O₃ nanoparticles onto the Cr deposited film are shown in Fig. 3. It is seen that the pulsating current with lower duty cycle results in higher Al₂O₃ incorporation. At lower duty cycles, the off time is longer which results in higher wt-% of Al₂O₃. Figure 3b indicates a decrease in nanoparticle incorporation with increasing frequency. At lower frequencies, pulse cycles are lower and the off time is longer. This gives more chance for Al₂O₃ nanoparticles to reach the cathode surfaces. More alumina is, hence, incorporated onto the chromium layer and a harder coating is thus deposited.

Figure 4 indicates the higher uniformity of coating produced by pulsating current instead of direct current. This observation confirms previous authors' remarks on Ni–SiC deposition¹⁶ and seems to be due to homogeneous Al₂O₃ dispersion. Uniform distribution of elements like Al and Cr, as illustrated in Fig. 5, indicates homogeneous dispersal of Al₂O₃ particles due to pulse current throughout the electrodeposited layer.

From many mechanisms proposed for codeposition of ceramic particles, Celis and Buelens¹⁵ have considered five steps for the development of their model:

- (i) formation of adsorbed ion layers which surround the particles
- (ii) convective transfer of the particles to hydrodynamic boundary layer
- (iii) arrival of the particles to the cathode surface by diffusion
- (iv) reduction of both free and adsorbed ions onto the cathode
- (v) incorporation of the particles with the Cr layer after reduction of a fraction of the ions originally adsorbed onto the particles.

Celis' model is compatible with systems containing very small solid particles like the one used in this research.^{15,17} Under pulsating current, mass transfer continuously occurs due to bath turbulence. Charge transfer, on the other hand, is discontinuous. Al₂O₃ reaches the cathode surface carrying adsorbed ions at both on and off time of the pulses. Charge transfer happens, however, only during the pulse on time. Free ions move faster than the adsorbed ions. The numbers of free ions that reduce at the cathode are more than those adsorbed on the particles. Hence, the amount of incorporated particles is reduced at higher duty cycles and pulse frequencies.

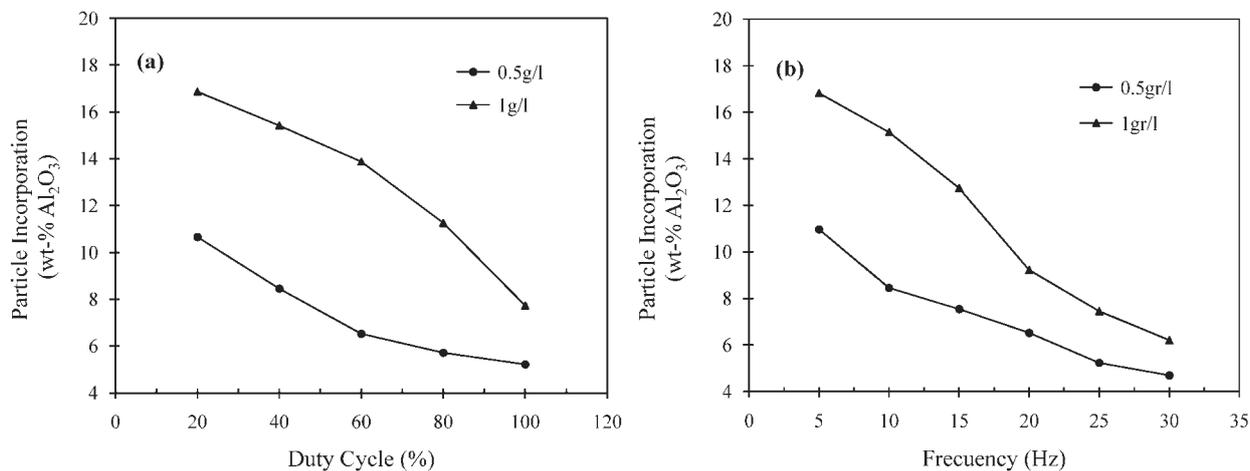
During the off time which increases with the decreasing duty cycle and the pulse frequency, there is no electrochemical reaction. Particles reach and crowd around the cathode surfaces while having their adsorbed ions at their exterior. Hence, at pulse on times, too many particles with their adsorbed ions join to the Cr deposit.

Hardness improvement

The effect of duty cycle and frequency on microhardness of pure chromium and Cr–Al₂O₃ nanocomposite coatings is shown in Fig. 6. As observed, composite coatings exhibit higher hardness than pure chromium coatings in all duty cycles and frequencies due to incorporation of nanoparticles.

Microhardness results shown in Fig. 6a indicate that the hardest coating is at $dc=40\%$. The densest deposit with lowest porosity forms at this dc due to adequate relaxation time of the bath during pulse off time. Figure 1b indicates that this same dc value corresponds to the highest current efficiency, too. At $dc=20\%$, due to high I_p , the deposit is powdery and burnt with poor adhesion and low hardness. At $dc>40\%$, lower residence time results in porosity increase and hardness decrease.

As can be seen from Fig. 6a, the hardness of the deposit depends on the amount of both duty cycle and nanoparticles. The influence of duty cycle on microhardness of the deposit is, however, more determinant than alumina percentage. Zimmerman *et al.*¹⁸ have observed similar results for Ni–SiC deposit. Hence, the



3 Variation in nanoparticle incorporation at different Al₂O₃ contents with *a* pulse duty cycle at $f=10$ Hz and *b* pulse frequency at $dc=40\%$: $I_a=20$ A dm⁻²

positive influence of dc on layer hardness due to metal matrix structural change is of great interest.

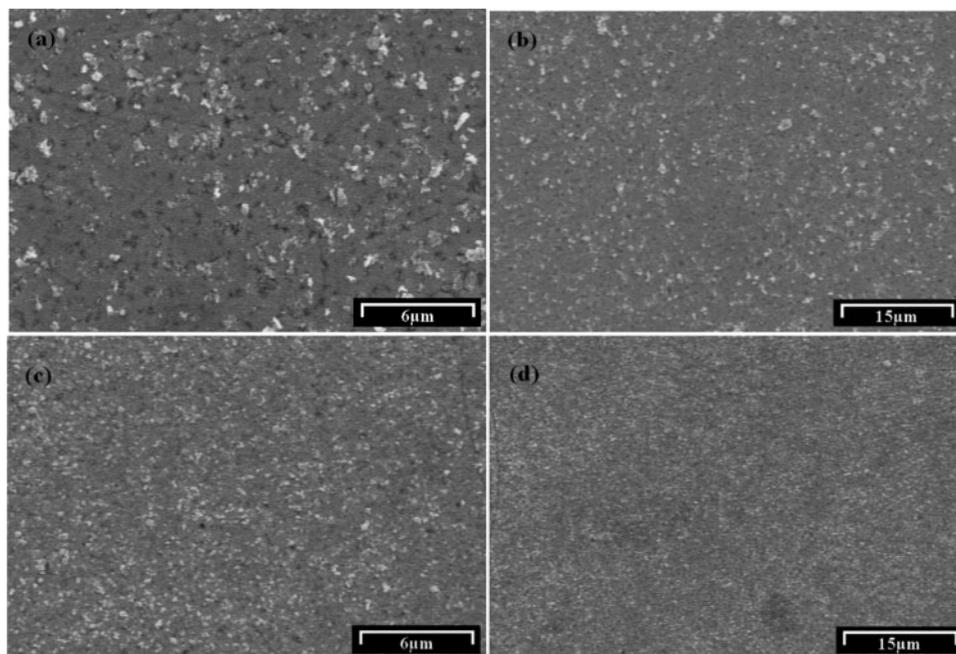
According to Fig. 6b, higher hardness values are obtained at lower pulse frequencies. This result is consistent with the coating surface observations shown in Fig. 2. As aforementioned, lower pulse frequency also results in greater incorporation of nanoparticles. Pulse frequency decrease and nanoparticle percentage increase both result in changing of the hardness of the Cr–Al₂O₃ composite layer. The influence of percentage of nanoparticles on hardness is, however, much greater than the influence of the pulse frequency decrease.

Corrosion improvement

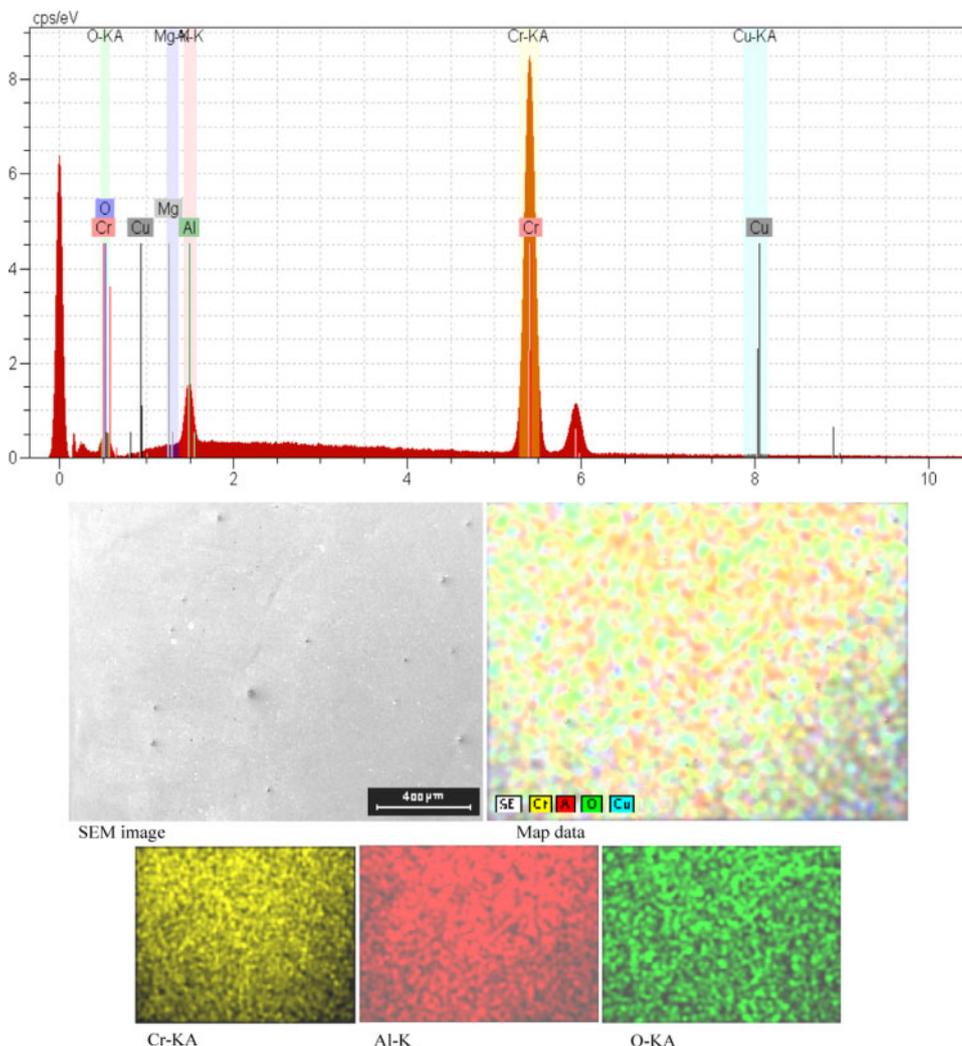
Potentiodynamic polarisation curves of pulsed and direct current Cr and Cr–Al₂O₃ nanocomposite coatings tested with 0.5M L⁻¹ NaCl solution are illustrated in Fig. 7. The values of the corrosion potential and the

current density were determined from the intersection of the cathodic and anodic Tafel curves using the Tafel extrapolation method. Figure 7 indicates that for pure chromium electrodeposition, pulse current results in lower corrosion current density i_{corr} and higher corrosion potential E_{corr} than the direct current. It also indicates that the anodic Tafel slope of pure chromium electrodeposition is higher for pulse current than for the direct current, showing better resistance for the case of pulsed chromium coating.¹⁹ Corrosion characteristics of both pure Cr and composite Cr–Al₂O₃ coatings produced by direct and pulsed currents are summarised in Table 2.

A significant decrease in corrosion current density and increase in corrosion potential (~ 130 mV) of the pulsed current polarisation curve of the composite coating occurs with respect to pure Cr deposition. This surplus corrosion potential is a thermodynamic quantity



4 Images (SEM) of Cr–Al₂O₃ composites electrodeposited with average current density of 20 A dm⁻² from Cr(III) bath containing 1 g L⁻¹ alumina with *a* direct current at lower magnification, *b* direct current at higher magnification, *c* pulse current with $dc=40\%$ and $f=10$ Hz at lower magnification and *d* pulse current with $dc=40\%$ and $f=10$ Hz at higher magnification

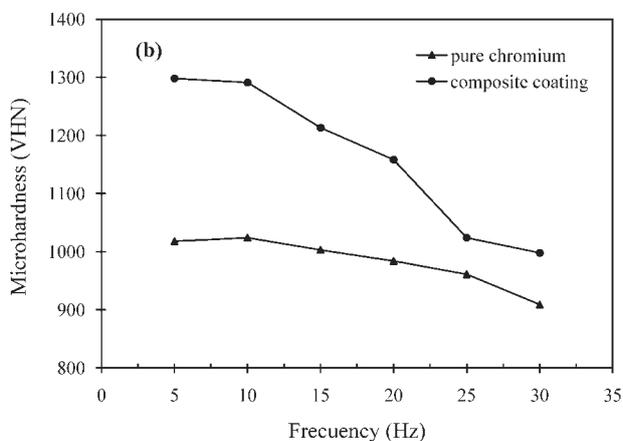
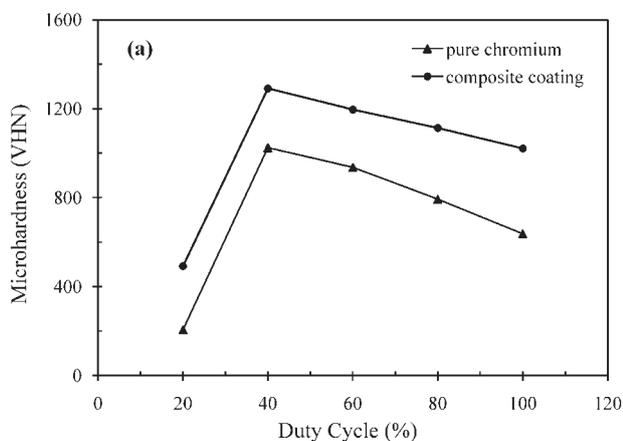


5 Results of X-ray chemical analysis showing distribution of elements on Cr–Al₂O₃ composite electrodeposited by pulse current at dc=40% and f=10 Hz

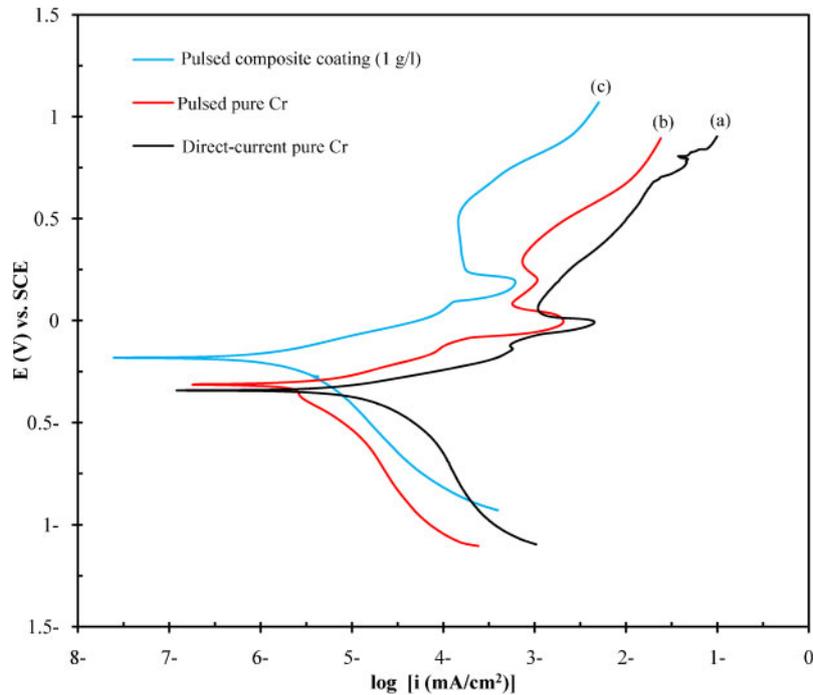
resulted from the increase in the chemical resistance of the surface¹⁹ of the composite coating. The anodic Tafel curve of the pulsed composite coating shows a passive area with the potential amplitude of 275 mV in current density of about 160 μA cm⁻². In spite of the relatively high current density, the produced passive film has

competitive stability up to the breaking potential of 520 mV.

The polarisation resistance R_p relates to the corrosion behaviour of the coating which corrodes homogeneously and uniformly. By assuming that under the experimental conditions, the polarisation resistance is equal to the



6 Microhardness of pure Cr and Cr–Al₂O₃ films electrodeposited from Cr bath containing 1 g L⁻¹ alumina against a duty cycle and b frequency



7 Polarisation curves of *a* pure chromium coating deposited from Cr(III) bath containing 0.5M L⁻¹ NaCl using direct current, *b* pure chromium coating deposited from Cr(III) bath containing 0.5M L⁻¹ NaCl from pulsed current and *c* chromium–alumina nanocomposite deposited from Cr(III) bath containing 0.5M L⁻¹ NaCl and 1 g L⁻¹ alumina using pulsed current

charge transfer resistance R_{ct} , the R_p of coatings was calculated from the Stern–Geary equation (5)¹⁹ and the results were given in Table 2

$$\frac{1}{R_p} = 2.303i_{Corr} \left(\frac{1}{\beta_B} + \frac{1}{\beta_C} \right) \quad (5)$$

As observed in Table 2, the corrosion rate (corrosion current density) of the pulsed pure chromium and direct current pure chromium are 2.5 and 10 times higher than the corrosion rate of the pulsed composite coating respectively. These results indicate that the usage of pulse current and incorporation of nanoparticle Al₂O₃ in the chromium matrix results in an improvement of the corrosion resistance of the nanocomposite coatings. Enhancement of corrosion resistance of pulsed Cr–Al₂O₃ nanocomposite coating is attributed to:

- (i) decrease in crevices, gaps and micrometre holes of the chromium matrix by embedded Al₂O₃ nanoparticles. In addition, they function as inert physical barriers to initiation and development of corrosion at defects.
- (ii) decrease in residual stress due to the use of pulse current during composite electroplating

- (iii) using pulse current contributes to more particle incorporation and higher uniformity of particle distribution in chromium matrix
- (iv) covering a fraction of surface by Al₂O₃ nanoparticles which have more chemical stability in comparison with chromium.

Conclusions

Effects of current density, duty cycle and pulse frequency on current efficiency, amount of alumina deposition, product hardness and corrosion resistance of Cr and Cr–Al₂O₃ nanocomposite films electrodeposited from Cr(III) bath were determined. Nanoparticle percentage, current density and duty cycle all significantly affected the electroplating process:

1. Presence of alumina nanoparticles in the bath increased electrodeposition current efficiency.
2. Decreasing duty cycle and pulse frequency resulted in higher Al₂O₃ percentage.
3. Cr–Al₂O₃ electrodeposition with pulse current resulted in lower particle agglomeration than with direct current.
4. Maximum current efficiency and hardness were obtained at dc=40% and $f=10$ Hz.

Table 2 Corrosion parameters obtained from polarisation studies with 0.5M L⁻¹ NaCl electrolyte

Sample	Current	E_{corr}/mV	$\beta_a/mV/decade$	$\beta_c/mV/decade$	$i_{corr}/\mu A cm^{-2}$	$R_p/k\Omega cm^2$
Cr–Al ₂ O ₃ composite	Pulsed	-183	228	-76	1.23	21.04
Pure Cr	Pulsed	-313	301	-62	3.07	7.52
Pure Cr	Direct current	-343	174	-96	12.13	2.39

5. Pulsating current and presence of alumina nanoparticles in the chromium coating resulted in improvement of corrosion resistance.

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