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Preparation and characterization of chromium deposits obtained from molten salts using pulsed currents

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Abstract

The electroplating of chromium from fused chloride electrolytes was investigated. The experimental conditions were defined taking into account the mechanisms of the electrochemical reduction of $CrCl_2$ and of the chromium nucleation and electrocrystallization phenomena. Chromium was plated on various substrates from concentrated LiCl–KCl–$CrCl_2$ (600 to 800 mol m^{-3} $CrCl_2$) electrolyte. Direct or pulsed current electrolysis were carried out under a dry argon atmosphere in the 400 to 440 °C temperature range. The shape of the current signals was chosen, taking into account the chromium electrocrystallization phenomena onto a foreign substrate, so as to obtain well-defined structures for the chromium layers. The chromium deposits were characterized by SEM and EDX analysis, and by microhardness determination. Uniform chromium electroplates of high purity, high adherence with no cracks, were obtained by using pulsed current: signals with cathodic pulses and open-circuit periods preceded by cathodic pre-pulses. With this current shape, the mean rate of the chromium electroplating process remained lower than 10 μm h^{-1}. However, using a repeated of periodic cathodic pre-pulse/cathodic pulse/anodic pulse/open circuit sequences, the growth rate of compact chromium layers increased to 100 μm h^{-1} or more.

1. Introduction

Molten electrolytes are employed for the electrowinning of the less electronegative metals such as Mg, Ca, Li, Na and Al, which cannot be obtained from aqueous electrolytes. The electroplating of refractory metals has been achieved from molten fluoride electrolytes [1, 2], and processes have been employed at an industrial level (W, Hf). The electroplating of refractory metals from molten fluorides has not been developed on a large scale, due to the high operating temperature required with these media. Low-melting electrolytes are needed to develop electroplating processes of refractory metals from molten salts.

The chromium electroplating processes which have been used up to now involve aqueous electrolytes. In such conditions, chromium electrodeposition is always accompanied by hydrogen evolution. Moreover, these processes produce polluting wastes with significant amounts of chromium(VI) species. Molten salt electrolytes are a way of avoiding hydrogen evolution, as well as formation of chromium(VI) polluting species.

Electrochemical studies of various molten halides or oxide mixtures with added chromium salts have been carried out; and chromium coatings have been obtained [3–11] in such media. A few authors [5, 8] have previously designed chromium plating procedures that involve pulsed current electrolysis and take into account the electrochemical properties of the system. But discrepancies remain concerning the electrochemical properties of chromium in molten chlorides. The Cr(II)/Cr exchange has been claimed to be slow [3, 12] or Nernstian [4], coupled [3, 7] or not coupled [4, 13] to Cr(II) species adsorption; the chromium nucleation has been shown to be instantaneous or progressive [4, 5, 7]. White et al. [4] have found that instantaneous nucleation occurred on gold, platinum and nickel substrates, with no adsorption phenomena interference, whereas Inman et al. [5] assumed that progressive nucleation took place on a tungsten substrate.

The present authors [9, 10] recently reexamined both the electrochemical behaviour of the Cr(II)/Cr couple and the chromium electrocrystallization phenomena, in molten $CrCl_2$–LiCl–KCl electrolyte. They found that the kinetic parameters of the Cr(II)/Cr electron exchange, the occurrence of the Cr(II) species adsorption and the kinetics of chromium nucleation on a foreign substrate, were related to the nature of the substrate, and also depended on whether equilibrium of the substrate–electrolyte interface was achieved or not. For instance, in agreement with the findings of White et al. [4], they did not find any Cr(II) species adsorption on freshly immersed gold. But they observed adsorption of the Cr(II) species on a gold electrode previously immersed for a few hours in the molten electrolyte. They showed that nucleation occurred [9, 10] during reduction of Cr(II) ions even on a fresh chromium substrate.

In this paper the effects of the nature of the substrate, the electrolysis current parameters and the temperature, on the chromium deposits obtained in molten LiCl–KCl–$CrCl_2$, are analysed. The authors have designed a chromium plating procedure that involves pulsed current electrolysis fitted to the electrochemical properties of chromium in the molten chloride mixtures, and to the characteristics of chromium nucleation onto a foreign substrate. In a few cases, the electrolysis current modulation took into account the chromium nucleation onto the freshly deposited chromium layer.

2. Experimental details

The experimental set-up was described previously [9, 10]. The molten LiCl–KCl (STREM Chemicals) solvent was contained in a graphite crucible inserted in an airtight Pyrex glass cell. The solvent was dehydrated by heating under vacuum to the melting temperature, and, once molten, maintained under a purified argon flow containing less than 1 ppm O_2 and H_2O. This treatment was effective, since the resulting melts were the same as those obtained by bubbling HCl for half an hour and then flushing purified argon through the melt [14]. The $CrCl_2$ (STREM Chemicals) solute was introduced as pellets through an airlock. High purity chromium chips placed at the bottom of the graphite crucible acted as a soluble anode.

The reference electrode was Ag/0.75 molar AgCl, LiCl–KCl placed inside a thin Pyrex glass bulb. Iron, molybdenum, nickel and steel 304L, 10 mm × 20 mm × 1 mm, plates were used as cathodes. The surfaces were prepared as follows: (i) mechanical polishing; (ii) chemical polishing, by immersing the pieces first in a 2 M NaOH aqueous solution maintained at room temperature and then in a 12 M HCl aqueous solution; and rinsing with distilled water, then ethyl alcohol.

The chromium electroplating experiments involved direct or pulsed current electrolysis regimes. The current density was set to the highest possible values compatible with smooth chromium, and the electrolysis duration was calculated to obtain 30 μm thick chromium coatings.

The working temperatures were between 400 and 440 °C, because several authors [5, 11] had observed that low operating temperatures favoured good electrode surface coverage by the deposits. The chromium electroplating experiments were performed using concentrated $CrCl_2$ electrolytes, to minimize dendritic growth of the chromium deposits.

Previous authors [3, 15] generally assumed that oxygen and moisture must be avoided to prevent the formation and inclusion of Cr_2O_3 during the chromium electrocrystallization. However Benslimane [11] pointed out that the chromium layer structure was improved when the electrocrystallization process was run under an oxygen atmosphere.

Although the beneficial influence of an addition of fluoride ions to the electrolyte on refractory metal electrocrystallization is generally admitted, no significant effect on the chromium crystallization phenomena has been observed when fluoride ions were introduced in the electrolyte. Therefore, the experiments reported here were carried out using a fluoride-free electrolyte maintained under a dry argon atmosphere.

The deposits were allowed to drain over the melt before being removed from the cell under argon atmosphere. They were washed with hot distilled water, rinsed with acetone in an ultrasonic bath then dried and stored.

The deposits were examined by X-ray diffraction techniques and optical and scanning electron microscopy (SEM). Lattice parameter **a** was evaluated by means of Bragg's law based on $2\theta_{hkl}$ values associated with the main $(h\ k\ l)$ Cr diffraction peaks.

Classification of the chromium layers according to their crystallization characteristics was made from analysis of the XRD peak. Two parameters A and B were defined: A is the ratio of the peak height of a given line to that of the strongest line ($I = 100$) of the same sample; B is the ratio, calculated for a given line, of this line intensity in a given sample to that of the strongest intensity of the same line, observed among a series of samples. The A values allow a comparison with the relative peak intensities values given in ASTM cards, whereas B values are used to compare various specimens having different degrees of crystallization.

The surface roughness of the deposits, their micro hardness, compactness and homogeneity were also examined.

3. Results

A series of chromium plates were first obtained using direct current electrolysis. Efforts were made to improve the chromium layers properties, by using a series of cathodic current pre-pulses to increase the initial number of chromium nuclei formed on the surface of the substrate, or by using open-circuit periods alternatively with cathodic pulses of current to ensure regular growth of the chromium layer. Both were combined with a view to increasing the chromium plating rate. Then the electrolysis current modulation was modified to take into account the chromium nucleation that occurs on the freshly just deposited chromium layer.

Finally, the chromium layers were characterized.

3.1. *Chromium electroplating with direct current*

Figure 1 illustrates the variation with time of the potential of a nickel cathode subjected to d.c. chromium electroplating. The electrode potential started very cathodic, due to a large electrocrystallization overpotential, and slowly reached the Cr(II)/Cr(O) equilibrium potential (−0.8 V) after 20 min, and then remained constant as the chromium electroplating continued. Qualitatively similar observations were made in the case of the other substrates investigated.

Figures 2 and 3 show chromium surface micrographs of the deposits, for the same charge, with two different values of the current density. The deposit shown in Figure 2, obtained with a low current density, was adherent, uniform and smooth. This homogeneous chromium layer consisted of crystals with a mean size of 20/25 μm. The other deposit, Figure 3, obtained at a larger current density, was dendritic, with branching apparent. Chromium electroplated by direct current electrolysis became increasingly dendritic as the current density was increased.

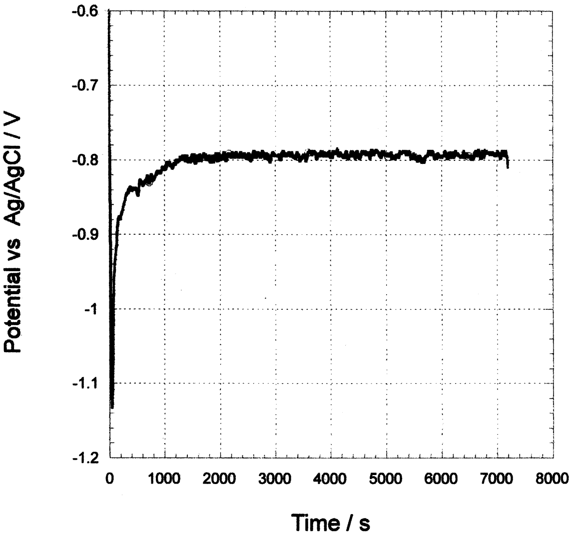

Fig. 1. Nucleation overpotential associated to the chromium nucleation onto a nickel substrate. Electrolyte: solution of $CrCl_2$ (176 mol m^{-3}) in the LiCl–KCl eutectic; cathodic current density: 150 A m^{-2}, temperature: 410 °C.

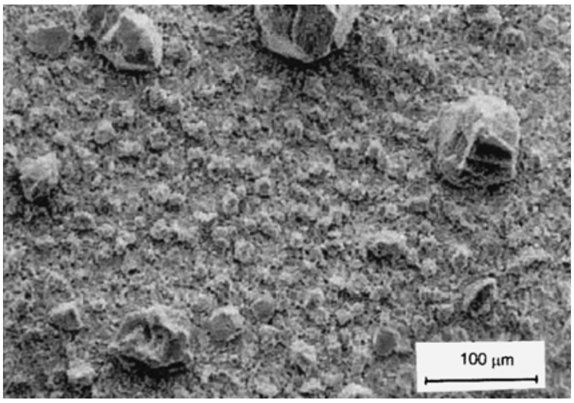

Fig. 2. SEM of a chromium deposit obtained on a steel substrate during a direct current electrolysis. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; cathodic current density: 40 A m^{-2}, temperature: 420 °C, electrolysis duration: 46 800 s.

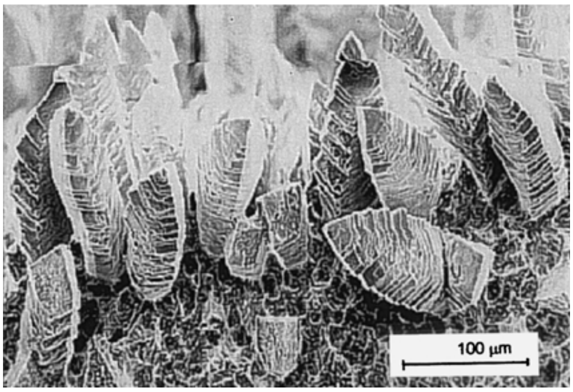

Fig. 3. SEM of a chromium deposit obtained on a steel substrate during a direct current electrolysis. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; cathodic current density: 150 A m^{-2}, temperature: 420 °C, electrolysis duration: 10 800 s.

3.2. *Investigation of modulated current to improve chromium electroplating*

3.2.1. *Direct current electrolysis preceded by a cathodic pre-pulse*

Vargas [5] has obtained promising results for chromium electroplating from molten LiCl–KCl–$CrCl_2$ electrolyte by using a high overpotential pulse/low overpotential electrolysis sequence. In the present work similar conditions were considered but voltage pulses were replaced by current pulses [4] in view of industrial applications. The idea is to promote a high initial coverage of the substrate by starting the chromium electroplating process by a short and high initial galvanostatic cathodic pulse to increase the number of chromium nuclei on the surface of the substrate, and growing the deposit with a lower direct current density to avoid the formation of dendrites (see the corresponding current profile Figure 4(a)).

It was observed that the use of a high initial cathodic current pre-pulse followed by a lower intensity direct current electrolysis did improve the morphological characteristics of the chromium layers. But when the direct current density value was set higher than 40 A m^{-2}, again dendritic growth of the deposit was observed, as in the case of d.c. plating. Since the objective was that the deposit could be obtained at high current densities, new current wave forms involving pulses were investigated. The current wave forms could involve cathodic pulses that allow chromium nucleation followed by growth of the deposit, anodic pulses to promote the redissolution of the protuberances of the deposit, and an interruption open circuit (o.c.) time to allow the diffusion layer to relax, when the adsorption and the bulk concentration homogeneity would be restored. Once again the pulsed electrolysis regime

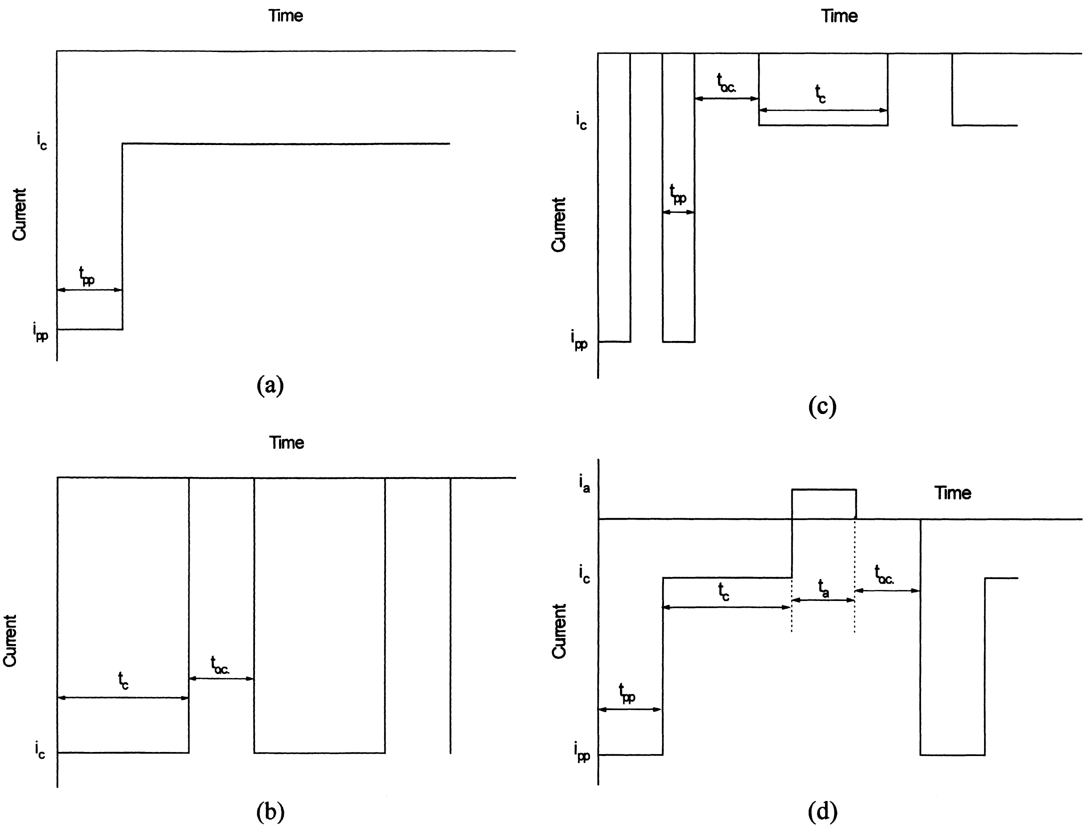

Fig. 4. Current electrolysis profiles. (a) High initial current pre-pulse followed by d.c. electrolysis. (b) General shape of a cathodic pulse–o.c.period current profile (c) General shape of a cathodic pulse–o.c. period current profile preceded by cathodic prepulses (d) repeated cathodic prepulse–cathodic pulse–anodic pulse–o.c.period sequences.

could be combined with a high level initial cathodic prepulse to promote a high concentration of chromium nuclei on the substrate surface.

3.2.2. *Pulsed current electroplating*

(a) *Sequences of cathodic pulses and open circuit periods.* Chromium deposits were first prepared using repeated sequences of a cathodic pulse and an o.c. period, as shown on Figure 4(b). The SEM micrograph of a deposit obtained at low cathodic current (Figure 5) shows the smoothness of the surface and the good coverage of the substrate by the deposit. But, as in the case of direct current electrolysis, where high quality chromium deposits were obtained when a low cathodic current density was employed, the chromium surface became more and more dendritic as the cathodic pulse current density was increased.

(b) *Cathodic pre-pulses followed by cathodic pulses and o.c. periods.* To improve the characteristics of the plated chromium layers, a few cathodic pre-pulses were applied, prior to the main cathodic current pulse/o.c. sequence (Figure 4(c)): after the initial pre-pulses, the cathodic current pulses were set to lower values (between 50 and 450 A m^{-2}), and the electrolysis run for the time needed to obtain the target thickness. It was observed that the deposit structures were finer and more homogeneous when five to seven initial current prepulses pulses were applied.

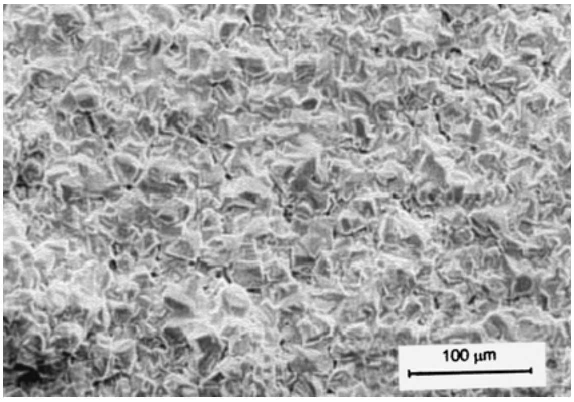

Fig. 5. SEM of a chromium deposit obtained on a steel substrate during a pulsed current electrolysis by cathodic current pulse–o.c. period sequences. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic at 426 °C; cathodic current pulse: $i_c = 50$ A m^{-2}, $t_c = 60$ s; o.c.time: 240 s; electrolysis duration: 16 000 s.

A series of operating conditions for chromium electroplating experiments is summarized in Table 1, and the scanning electron micrographs of the surface of the corresponding deposits reported in Figures 6, 7 and 8. The deposits obtained using high initial pulses followed by cathodic current pulse/o.c. period sequences with moderate cathodic pulse current density are smooth and uniform. Moreover, the nature of the substrate influences the morphological characteristics of the deposits:

Table 1. Three examples of operating conditions used for chromium layers electroplatting on steel substrates by using cathodic pulse/o.c.period sequences preceeded by five pre-pulses

	Example 1	Example 2	Example 3
Pre-pulses:			
Current density	2300 A m^{-2}	2300 A m^{-2}	2300 A m^{-2}
Duration	0.07 s	0.07 s	0.07 s
Cathodic pulse:			
Current density	50 A m^{-2}	150 A m^{-2}	450 A m^{-2}
Duration	30 s	30 s	30 s
o.c.period	200 s	200 s	200 s

Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in molten LiCl–KCl eutectic. temperature: 426–436 °C.

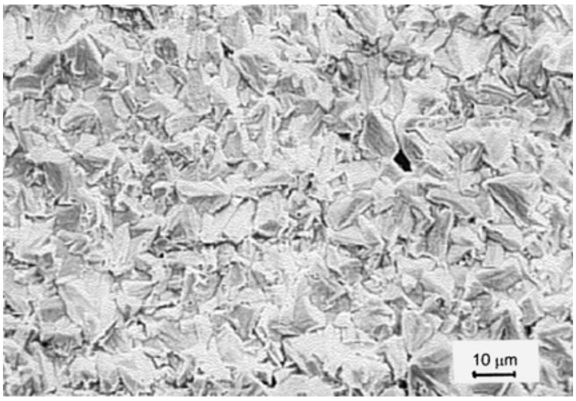

Fig. 6. SEM of a chromium deposit obtained on a steel substrate during a pulsed current electrolysis preceded by five high intensity current pre-pulses. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; pre-pulse: $i_{pp} = 2300$ A m^{-2}, t_{pp}: 0.07 s; cathodic current pulse: $i_c = 50$ A m^{-2}, $t_c = 30$ s; o.c.time: 200 s; temperature: 426 °C; electrolysis duration: 16 200 s.

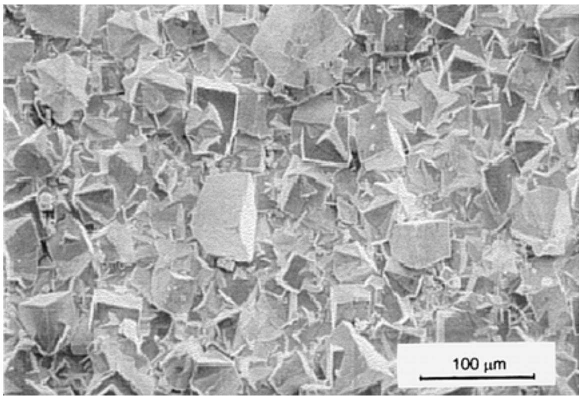

Fig. 7. SEM of a chromium deposit obtained on a steel substrate during a pulsed current electrolysis preceded by five high intensity current pre-pulses. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; pre-pulse: $i_{pp} = 2300$ A m^{-2}, t_{pp}: 0.07 s; cathodic current pulse: $i_c = 150$ A m^{-2}, $t_c = 30$ s; o.c.time: 200 s; temperature: 426 °C; electrolysis duration: 10 800 s.

square, polyhedric, rectangular and prismatic crystals were respectively obtained on nickel, molybdenum and steel substrates. One can observe that a prismatic morphology favors the formation of large chromium crystals (sides up to 30 μm) and the growing of adherent and uniform chromium layers.

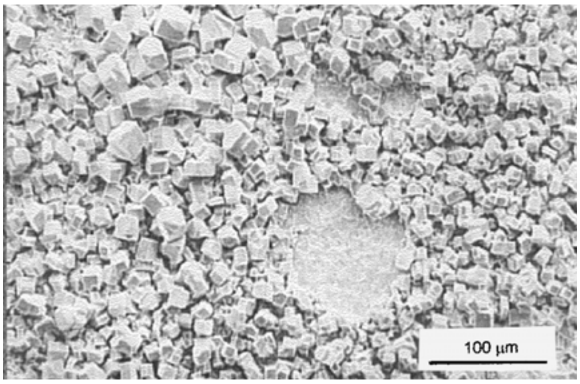

Fig. 8. SEM of a chromium deposit obtained on a steel substrate during a pulsed current electrolysis preceded by five high intensity current pre-pulses. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; pre-pulse: $i_{pp} = 2300$ A m^{-2}, t_{pp}: 0.07 s; cathodic current pulse: $i_c = 450$ A m^{-2}, $t_c = 30$ s; o.c. time: 200 s; temperature: 426 °C; electrolysis duration: 3600 s.

The maximum rates of growth to obtain satisfactory deposits, typically 10 μm h^{-1} still remains too low for industrial applications. The periodic repetition of a wave form that includes a cathodic prepulse, a cathodic growth pulse followed by an anodic pulse and an o.c. relaxation period should improve the situation, as investigated in Section 3.4., since this scheme takes into account the chromium nucleation step onto each freshly deposited chromium layer.

3.3. *Characterisation of the chromium layers*

The characteristics of a series of chromium deposits are reported in Table 2. The microhardness measurements were performed on cross sections of the chromium layers. The values obtained were in the range 390/450 HV, which is much lower than those obtained for chromium electrodeposits from aqueous solution (850/1000 HV [16]), but higher than those obtained (130/280 HV [5]) through potentiostatic electrolysis in the same electrolyte as in this study. These values could be related to the higher chromium purity obtained from molten chloride electrolytes as compared to aqueous electrolytes.

In the case of a molybdenum substrate, investigations by SEM and EDAX (energy dispersive X-ray analysis) of the specimen cross section revealed a sharp interface

Table 2. Properties of a series of chromium layers deposits obtained by using current pre-pulse(s) followed by cathodic pulse/o.c.period sequences

Substrate	Nickel	Molybdenum	304L Steel	304L Steel	304L Steel
Electroplating rate/μm h^{-1}	3.20	1.28	0.89	2.67	8.01
Microhardness	435 HV	405 HV	402 HV	447 HV	390 HV
Adhesion (interface structure)	poor	good	good	fairly good	poor
Grain size and morphology	10 μm prismatic, (bottom) 10 μm squared (top)	30/40 μm polyhedral facetted	20/25 μm polyhedral and rectangular cracks	25/30 μm prismatic	5/10 μm (bottom) 20 μm (top) prismatic

Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in molten LiCl–KCl eutectic.

and a good adherence proved by the lack of delamination, exfoliation or blistering zones. The chromium layer was uniform but some pores and cracks occurred on top of this layer. The CrK_α X-ray distribution map (Figure 9) confirmed the compactness, homogeneity and uniformity of this layer whereas the maps for CrK_α and MoL_α exhibited interdiffusion of these elements (chromium in substrate and molybdenum in layer) over small depths

In the case of the steel substrates, good adhesion was obtained only if the chromium electroplating was carried out under moderate cathodic pulse current density ($i_c \leqslant 150$ A m^{-2}). Although the top layer surface was very rough, as is usually the case for many chromium layers deposited on steel substrates, the interface between the chromium layer and steel was found to be very smooth (Figure 10). In summary, in the case of steel substrates, the microhardness decreased at a low ($\sim$1 μm h^{-1}) or a high ($\sim$8 μm h^{-1}) electroplating rate.

The adhesion appears good for various substrates at moderate electroplating rates between 1 and 3 μm h^{-1}. Increasing the electroplating rate led to various crystal grain morphologies in the top and bottom regions of the chromium deposits.

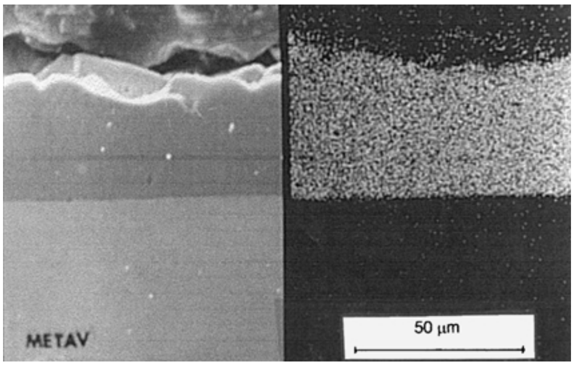

Fig. 9. SEM image and X-ray CrK_α map of a chromium deposit obtained on a molybdenum substrate during a pulsed current electrolysis preceded by five high intensity current pre-pulses. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; pre-pulse: $i_{pp} = 1700$ A m^{-2}, t_{pp}: 0.07 s; cathodic current pulse: $i_c = 72$ A m^{-2}, $t_c = 30$ s; o.c.time: 200 s; temperature: 426 °C; electrolysis duration: 4500 s.

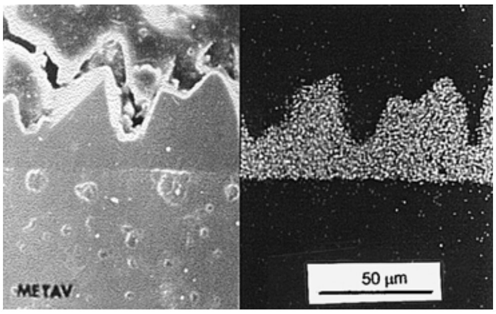

Fig. 10. SEM image and X-ray CrK_α map of a chromium deposit obtained on a steel substrate during a pulsed current electrolysis preceded by five high intensity current pre-pulses. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; pre-pulse: $i_{pp} = 1700$ A m^{-2}, t_{pp}: 0.07 s; cathodic current pulse: $i_c = 150$ A m^{-2}, $t_c = 30$ s; o.c.time: 200 s; temperature: 426 °C; electrolysis duration: 10 800 s.

The X-ray diffraction data related to the main chromium peaks were recorded for plated chromium layers samples. As an example, the main diffraction peaks (0 1 1) are shown in Figure 11 for three chromium layers plated on steel substrates. Sharper peaks were obtained when cathodic pulses were applied and the best results were obtained for a current density of 150 A m^{-2}. In Table 3, some physical parameters (the full width B_{hkl} at half maximum height of the ($h\ k\ l$) peak, A and B values, lattice and crystallinity parameters a and L_c) were estimated for the main chromium peaks. $L_c = k\lambda / B_{hkl} \cos\theta$ was computed only from the data of the (0 1 1) and (0 0 2) peaks, because the (1 1 2) peaks were too broad.

The lines characteristic of α-Fe (from the substrate) are visible in the X-ray pattern related to the deposits obtained by d.c. electrolysis, though they are missing in the spectra related to the deposits obtained by pulsed electrolysis, which indicate incomplete coverage in the case of direct current electrolysis.

The mean crystallite size of the chromium layers, measured by the crystallinity parameter L_c, was found to vary in the range 250–450 Å, the highest values corresponding to an initial application of cathodic prepulses.

The value of the lattice parameter, a, measured for the chromium deposits, was generally lower than the

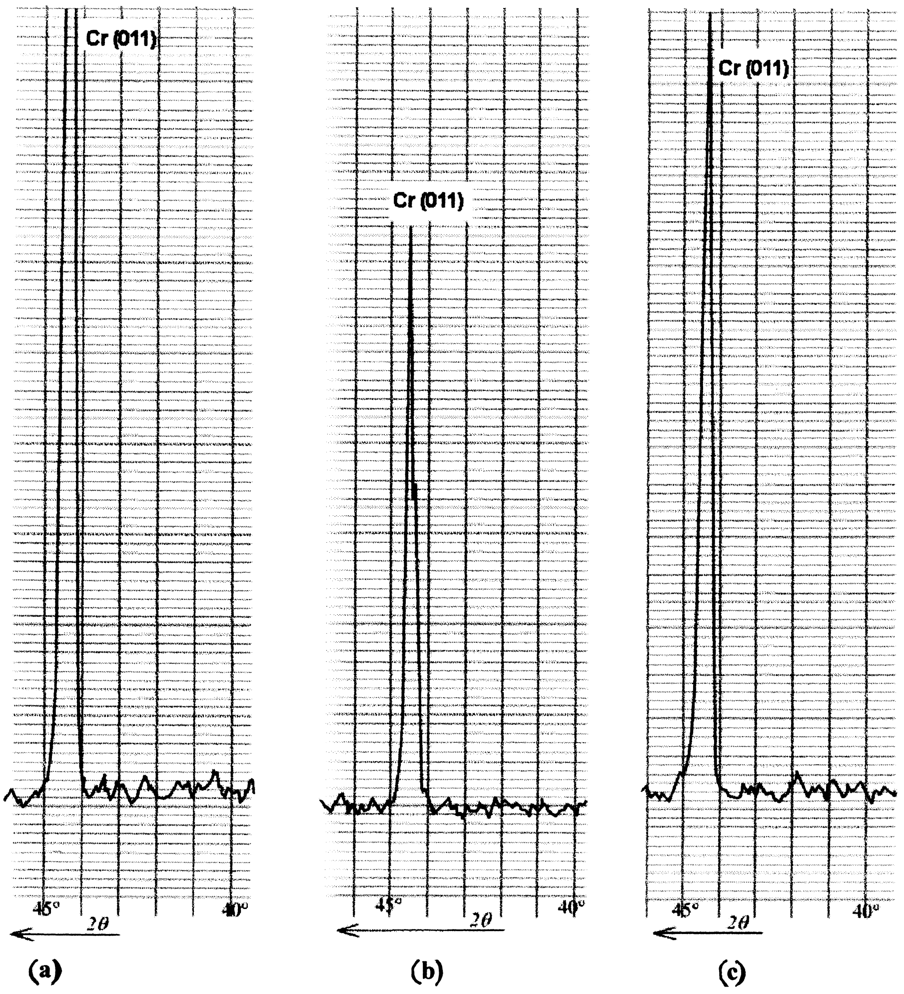

Fig. 11. Cr (0 1 1) line for a series of chromium layers plated on steel substrates: (a) 50 A m^{-2}; without high initial current pulses; (b) 50 A m^{-2}; five high initial current pulses; (c) 150 A m^{-2}; five high initial current pulses.

Table 3. X-ray diffraction data related to the (0 1 1) chromium line for a series of chromium layers plated on steel substrates from $CrCl_2$–LiCl–KCl molten electrolyte

Current profile	(0 1 1) peak			(0 0 2) peak			(1 1 2) peak	a/Å
	B_{011} (0)	L_c /Å	A, B	B_{002} (0)	L_c /Å	A, B	A, B	
Direct current *(cf. SEM photo Figure 3)*	0.23			0.41				2.880
Direct current *(i_c = 80 A m^{-2} SEM is not reported)*	0.35			0.23				2.875
Cathodic pulse/o.c.period sequences *(cf. SEM Figure 5)*	0.35	273	100,100	0.31	337	10,33	59,100	2.888
Cathodic pulse/o.c.period sequences preceded by cathodic pre-pulses *(cf. SEM Figure 6)*	0.29	330	100,73	0.23	454	43,100	43,78	2.882
Cathodic pulse/o.c.period sequences preceded by cathodic pre-pulses *(cf. SEM Figure 7)*	0.23	415	100,92	0.23	454	26,78	26,78	2.883

theoretical value (a = 2.885 Å) but values of this order have been measured for the best crystallized chromium layers (pulsed current). In the case of the less crystallized chromium deposits, a slight compression of the chromium elementary cell parameter (up to 0.3%) was found.

The analysis of the XRD peak relative intensities on the basis of *A* and *B* parameters (defined in the Experimental Section and estimated in Table 3 for different chromium peaks and for a series of crystallized chromium layers) was used for a tentative classification of the chromium deposits according to their crystallization characteristics.

The *A* values are compared to the theoretical values of the relative intensities associated with the (0 1 1), (0 0 2), (1 1 2) peaks (100/20/30 according to the ASTM cards). Although a good agreement could be seen, there was also a relatively strong (1 1 2) texture (line 3 in Table 3) and high values registered for (0 0 2) and (1 1 2) lines (line 4 in Table 3). Therefore, no special texture effects were observed in chromium deposits on steel substrates in the case of the application of cathodic pre-pulses and $i_c = 150$ A m^{-2}.

The *B* values allowed the chromium layers to be classified into well and poorly crystallized deposits. The best crystallized layers appeared to be obtained with pulsed current electrolysis since the *B* values for the main chromium peaks were greater in the case of cathodic pre-pulse treatment.

3.4. *Modified pulses regime to increase the deposition rate*

The pulse sequence was modified by introducing an anodic current pulse between the cathodic pulse and the o.c. relaxation period. The whole sequence was then periodically repeated, to allow the growth of a regular chromium layer.

The corresponding electrolysis current profile, (Figure 4(d)), was designed to have the following effects: formation of numerous chromium nuclei by the current pre-pulse; growing of the nuclei in the subsequent cathodic current pulse; dissolution of the protuberances by the anodic current pulse; and bulk electrolyte concentration relaxation during the o.c. period.

An optimal set of parameters for the pulsed current sequences has not been fully achieved in the present work, but it is shown, using the parameters reported in Table 4, that the growth rate on a steel substrate may be increased by a factor of 10 or more while preserving the qualities of the deposits (see the SEM micrograph of such a deposit in Figure 12).

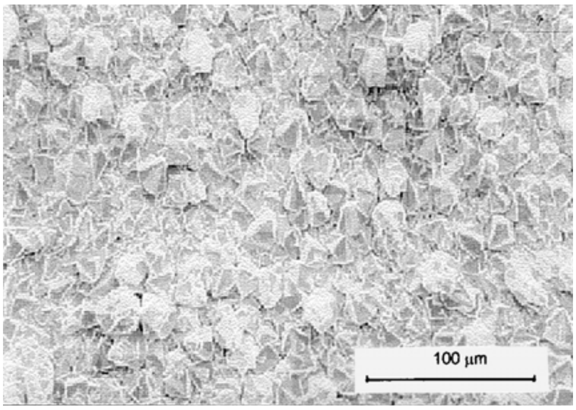

Fig. 12. SEM image of a chromium deposit obtained on a steel substrate at high deposition rate. Electrolyte: solution of $CrCl_2$ (770 mol m^{-3}) in the LiCl–KCl eutectic; pre-pulse: $i_{pp} = 2300$ A m^{-2}, t_{pp}: 0.03 s; cathodic current pulse: $i_c = 460$ A m^{-2}, $t_c = 29$ s; anodic pulse $i_a = 96$ A m^{-2}, $t_a = 0.15$ s; o.c. time: 0.8 s; temperature: 416 °C; electrolysis duration: 1800 s.

4. Conclusion

Uniform adherent well-crystallized chromium deposits can be obtained on various substrates by molten salt electrolysis. This necessitated a prior surface treatment and application of pulsed currents. On steel substrates of industrial interest, 25 μm thick deposits were obtained with a growth rate of 10 μm h^{-1}.

On the basis of estimation of the crystallinity parameter L_c a grain size between 250 and 450 Å was found in chromium deposits with the highest values arising after an initial application of cathodic pre-pulses. An evaluation of peak relative intensities was used for a tentative classification of the chromium layers based on their degree of crystallization. Some of the better crystallized chromium layers exhibited a (0 0 2) and (1 1 2) texture but no special texturing effects were observed for medium current density and initial current pre-pulses. When the pulse regime was matched with the electrocrystallization mechanism, this growth rate could be increased by a factor of 10 or more. The final pulse sequence, periodically repeated, was composed of a cathodic pre-pulse for nucleation, a cathodic pulse for crystal growth, an anodic pulse to dissolve irregularities and an o.c. period to allow the system to relax. These improvements have been demonstrated on a few samples, although the values of the pulses parameters are not yet fully optimized.

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Table 4. Convenient parameters for sucessfully increasing the deposition rate

Electrolysis current sequences	Current density	Duration of the step
Pre-pulses of current	2300 A m^{-2}	0.03 s
Cathodic pulse of current	300/500 A m^{-2} range	2 to 30 s range
Anodic pulse of current	96 A m^{-2}	0.03 to 0.15 s range
Open circuit period		0.3 to 1 s range

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