ABSTRACT

Chromium can be conveniently electroplated from fused chloride electrolytes. The deposition from LiCl-KCl (eutectic)-CrCl₂ melts is known to produce large crystal grains. Large grain size and other problems encountered in the electrodeposition of microcrystalline chromium from fused salt are discussed. The results indicate that combined use of forced electrolyte convection and a nucleating pulse in conjunction with a periodic reverse pulse produces fine-grained deposits.

INTRODUCTION

Chromium metal has been shown to offer good corrosion resistance in sulfur/polysulfide environments and, therefore, constitutes a suitable material for use as a protective coating in sodium/sulfur batteries (1). The protective action of chromium can be fully utilized only if such coatings are coherent, have good adhesion, and provide a thorough coverage of the substrate. Chromium electrodeposition from aqueous solutions produces deposits which may have microcracks and incorporate hydrogen during plating. Hence, coatings thusly derived have not fully utilized the protective action of chromium (2).

In principle, the use of molten salt electrolytes (e.g., chlorides, fluorides) represents an attractive alternative for the production of chromium electrodeposits. Such electrolytes are oxygen-free, hydrogen-free, highly conductive media by which it is possible to deposit the pure metal at high current efficiencies. The electrodeposition of chromium from fluorides has received some attention, and the production of coherent, well-adhered deposits has been successfully demonstrated (3-6). However, the disadvantage of fluorides is that the systems are generally considered to be toxic and corrosive, and their utilization implies the use of relatively high temperatures (800-1000°C) (4). Chloride melts are a more suitable alternative for the following reasons: they can be operated
at relatively low temperatures (400-600°C), they offer high conductivity, and they are not considered too toxic or corrosive. In this work chromium was electrodeposited from (LiCl-KCl) eutectic-CrCl$_2$ melts. This melt is an adequate refining media for chromium, which can be obtained with total impurity contents of less than 70 ppm at average current efficiencies of 96% \(^{(7)}\). Under single galvanostatic/potentiostatic conditions, the electrodeposition of chromium from (LiCl-KCl) eutectic-CrCl$_2$ melts usually resulted in the production of highly dendritic or crystallized noncoherent coatings \(^{(8)}\). Clearly, a different approach was needed.

**APPROACH**

A notable improvement in the morphology of chromium electrodeposits obtained from these melts has been achieved by introducing an initial nucleation pulse \(^{(8)}\) followed by periodic reverse current. These steps enable the production of coherent, crack-free, well-adhered, and fine-grained deposits. Further work related to the characterization and understanding of the chromium electrocrystallization mechanism was undertaken, and the result was better control of the grain size of the deposits.

**EXPERIMENTAL**

The experiments were conducted in a helium-purified glove box (Sherman Reynolds Model B5935) which has two cylindrical furnace wells (each with a 7-cm dia and a 40-cm length). The furnace wells, which are provided with removable sealed tops, can be evacuated by a Duo Seal Vacuum Pump Model 1397. The electrochemical cell is placed in one of the wells. The heat is provided by a Marshall tubular furnace, and the temperature is controlled by a West S.C.R. stepless control unit. The melt is contained in a 80-mL Pyrex beaker that is placed within a 6.5-cm-dia by 17-cm-long stainless steel protective container resting on the bottom of the well. The cell is capped by a three-inlet glass head, which provides a centered stable base for the electrodes and enables their quick interchange. The preparation and weighing of the different salt mixtures were done within the same glove box, which is equipped with a Sartorius balance.

To generate the different potential and current programs needed for the tests, a Princeton Applied Research Model 273 Potentiostat/ Galvanostat and a PAR Model 175 Universal Programmer were used. The output signals (current/voltage transients) were recorded on a Tektronik Model R5103N Oscilloscope and on a Hewlett Packard 7044A X-Y Recorder or a Hewlett Packard 7100B Strip Chart Recorder. Coulometric measurements were done using the PAR Model 379 Digital Coulometer.
A conventional three-electrode system was used: the reference and the counter electrodes were made of chromium pieces (purified, carbon-free, fused) from Fisher Scientific Co. and were spot-welded to platinum wire for electrical contact. The chromium-melt contact areas were approximately 2 cm² and 0.5 cm², respectively. The working electrodes were Type 304 stainless steel (SS) coupons made of 0.5-mm thick plate spot-welded to 1.6-mm-dia Type 308 SS rods for electrical contact (1-2 cm² melt-substrate area). In some experiments, the working electrodes were held in a motor-driven stirrer, with variable speed in the range of 20–300 rpm. The SS electrodes were anodically cleaned before use in a H₂SO₄ solution (0.53 specific gravity) at 6 V for 1 min, according to a procedure recommended for improved deposit-substrate adherence (9). The morphology of surfaces and sections of the electrodeposits on steel substrate were examined by scanning electron microscopy (SEM).

The electrolyte consisted of LiCl-KCl (41.5–58.5 mol %, purified, Li contacted) eutectic from Anderson Physics Laboratories and chromium (II) chloride (98%, anhydrous) from Alfa Products. The working temperature was 450°C.

RESULTS AND DISCUSSIONS

Characterization of the System

Figure 1 shows some typical cyclic voltammograms obtained with the (LiCl-KCl) eutectic-CrCl₂ system. Two reversible waves are observed when scanning on tungsten electrode (curve a). A small pair of waves are on the anodic side at approximately +0.2 V, and a large pair are on the cathodic side at approximately -0.7 V. These potentials correspond to the reduction of Cr(III) to Cr(II) and Cr(II) to Cr(0), respectively. Studies of similar cyclic voltammograms obtained in the LiCl-KCl-CrCl₃ system at 500°C confirmed the number of electrons associated with each wave (10). The Cr(III)/Cr(0) wave does not appear in the cyclic voltammograms for tungsten or Type 304 SS (curve b). This is precluded by the early wave related to the anodic dissolution of the substrate. The waves corresponding to the Cr(II)/Cr(0) pair are observed in both substrates, and they exhibit the typical shape associated with a deposition/dissolution process on an inert substrate (11-13). Instead of increasing smoothly with the overpotential change, the current on the cathodic branch rises abruptly (curve a, Fig. 1) resulting in a sharp cathodic peak. An equally sharp fall in current occurs after the anodic peak; this is consistent with the stripping of a finite quantity of metallic deposit from the electrode surface. The rising part of the cathodic wave is cathodically displaced with respect to the equilibrium potential (E°) for Cr(II)/Cr(0). This delay in starting the cathodic process is related to the initial
resistance involved in the formation of the new chromium phase on a foreign substrate. This process requires the application of an extra overpotential related to the extra work necessary for the initial creation of critical chromium nuclei.

The chromium electrodeposition for low-concentration melts (0.931 mol dm\(^{-3}\)) has been observed to be controlled by mass transfer (9). Several facts suggest that, at very high CrCl\(_2\) concentrations, the chromium electrodeposition process in this melt is controlled, to a large extent, by ohmic resistance in the melt. Figure 2 shows cyclic voltammograms obtained on Type 304 SS at 2.12 mol dm\(^{-3}\) concentration. The rising cathodic branch shows a practically linear current-voltage relation for the case of still and rotated electrodes. The rotation of the electrode introduced only a slight increase in the current-voltage slope, indicating a slight degree of mass transfer control. Previous work on electrorefining chromium from similar melts reported a decrease of the conductivity of the electrolyte with an increase in the CrCl\(_2\) concentration (7).

**Chromium Electrodeposits**

Chromium deposits were obtained by different controlled-potential techniques at various CrCl\(_2\) concentrations. The most-frequent deposition technique used at this stage is the initial nucleation pulse (INP) technique, shown in Fig. 3. In this technique, the deposition process is started with a high, short overpotential pulse, where a large number of isolated chromium nuclei are formed to secure a thorough initial coverage of the substrate. The deposit is then grown at a low overpotential, precluding the growth of dendrites and ensuring the development of a coherent morphology.\(^ {14}\)

Figures 4 and 5 show the dramatic influence of CrCl\(_2\) concentration on the morphology of chromic electrodeposits produced by the INP technique. At the highest concentration 2.12 mol dm\(^{-3}\), Fig. 4), the deposit consists of large crystals that have not merged into a continuous layer, leaving large spaces between them. Between the large crystals, a lower layer of small crystals were formed during the initial nucleation stage these do not fully cover the substrate. At the low concentration (1.5 mol dm\(^{-3}\), Fig. 5), the deposits obtained show a noticeable decrease of the grain size and a very compact structure (deposits of this kind already show some metallic shine on their surface). The coatings were found to be well adhered to surface, as shown by optical microscopy of the chromium-substrate interface. Also, no microcracks were observed.

The observed morphological changes with CrCl\(_2\) concentration can be explained mainly based on the cyclic voltammograms. With the CrCl\(_2\) concentration variation from high to low, there is a
displacement in the electrodeposition-controlling mechanism from ohmic control in the melt toward mass-transfer control given by the diffusion of active species toward the electrode surface. This effect is also shown (Fig. 6) by the observed I vs. \( \eta \) plots for tungsten electrodes that were rotated at two different speeds. When the electrogrowth occurs under ohmic control, the formation and growth of nuclei involve the simultaneous development of large deactivating zones around each nuclei. These originate in the potential drop arising in the melt around growing centers\(^\text{15} \) and preclude the formation of a large number of nuclei and the development of a compact structure. This effect explains the morphological characteristics observed in deposits obtained at very high concentrations. The decrease in CrCl\(_2\) concentration reduces the effect of the ohmic control. This results in the initial formation of larger nuclei numbers and development of compact structures, provided that the development of dendritic structures is precluded by growing at overpotentials sufficiently low.

The application of both higher rotational speeds and a continuous potentiostatic pulse contributes to further reduction of the grain size. The results are shown in Fig. 7.

CONCLUSIONS

The electrodeposition of chromium from (LiCl-KCl)eutectic-CrCl\(_2\) melts using the INP technique enabled the production of coherent well-adhered as chromium coatings on Type 304 SS probes. The resultant morphology in the deposits seems to be the product of a delicate balance between the different mechanisms that control the electrocrystallization mechanism at different stages. These mechanisms are very dependent on the CrCl\(_2\) concentration present in the melt. The choice of very high CrCl\(_2\) concentrations, which would be, in principle, desirable with regard to the use of higher deposition currents, is restricted in practice by the decrease in the melt conductivity, which has deleterious effects on the electrogrowth process. On the other hand, the choice of very low CrCl\(_2\) concentrations is also not advisable because the mass transfer then becomes too important, resulting in the production of very crystallized deposits and enhanced dendritic growth. The experimental results obtained so far suggest 0.9-1.5 mol dm\(^{-3}\) as a convenient working range at 450°C.

The current state of the art enabled us to produce a set of chromium-plated Type 304 SS probes. A melt with 1.5 mol dm\(^{-3}\) CrCl\(_2\) concentration produced the most-coherent deposits with small grain size.
Further work will focus on the electrodeposition of chromium using forced mass-transfer conditions and more-complex pulsing current/voltage regimes and will be reported later. The desired result is to reach a more accurate control on the grain size distribution and morphology of the deposit.

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Figure 1. Cyclic Voltammogram for the (LiCl-KCl) eut-CrCl$_2$ System. 
C: 0.931 mol dm$^{-3}$, V: 0.1 s$^{-1}$. a: on Tungsten, b: on 304 SS.

Figure 2. Cyclic Voltammogram for the CrCl$_2$ on 304 SS. C: 2.12 mol dm$^{-3}$, V: 0.1 V s$^{-1}$. a: Still Electrode, b: Rotated Electrode (24 rpm).

Figure 3. Initial Nucleation Pulse Method; $\eta_N$: Nucleation Over-Potential, $\eta_G$: Growth Over-Potential, $t_N$: Nucleation Pulse Width, $t_G$: Growth Time.
Figure 4. SEM of Chromium Electrodeposited on 304 SS. C: 2.12 mol dm$^{-3}$, $\eta_N$: -0.6V, $t_N$: 2 s, $\eta_G$: -0.05V, $i_G$: 0.025 A cm$^{-2}$, l:~40 $\mu$m.

Figure 5. SEM of Chromium Electrodeposited on 304 SS. C: 1.5 mol dm$^{-3}$, $\eta_N$: -1.0V, $t_N$: 1 s, $\eta_G$: -0.09V, $i_G$: 0.07 A cm$^{-2}$, l:~25 $\mu$m.

Figure 6. I vs. $\eta$ Plot for Chromium Deposition at Different Rotation Rates for Tungsten Disc Electrode (Area = 0.0707 cm$^2$, C=1.0 M/cm$^3$).
Figure 7. SEM of Chromium Electrodeposit on Substrate of type 304 SS. C=1.0 M/dm³, 3-mm-dia Rod Electrode, Total Area 1 cm² (disc area 0.0707 cm²), 2500 rpm; Pulse B; η₅=−0.9 V, t₅=20 ms, η₆=−0.1 V, t₆=25 s, T₆=20 s; Surface (A) and Cross Sections [(B) and (C)] Etched for Different Times.