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High-temperature electroplating of chromium from molten FLINAK

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Electroplating of chromium has been investigated in molten FLINAK (46.5 LiF–11.5 NaF–42.0 KF; mol %) over a temperature range of 600 to 1000° C. When Cr(III) is the electroactive species employed, a considerable amount of Cr(II) must be generated before chromium metal is deposited. Various parameters were tested to establish the optimum conditions for obtaining a smooth and thick chromium plating. Bath temperature was found to be a most important parameter; at temperatures above 870° C a smooth plate can be obtained, while at lower temperatures the deposits consist of extensive dendrites embedded in the salt which is the first reduction product of Cr(III).

1. Introduction

Refractory metals of the group IV, V and VI transition elements have many useful properties such as high corrosion and abrasion resistances, in addition to their high melting temperatures [1–3]. Therefore, demands for their practical applications have been increasing. The electrodeposition of these metals from molten salts is of considerable interest for the following reasons. (1) They cannot be electrodeposited from aqueous solution (except chromium). (2) Since they are generally scarce and expensive, it is more desirable to use them as a thin coating on the appropriate substrate or an electroform rather than as a bulk [4, 5]. (3) With molten salt electrolysis a relatively high purity deposit can be obtained free from deleterious impurities such as oxygen, hydrogen, carbon and nitrogen which are apt to form brittle compounds with these metals [1–6]. (4) Deposits of considerable thickness can be prepared. Among these metals chromium is the only one that can be electrodeposited from aqueous solution. However, the chromium plate thus obtained is very brittle due to hydride formation as stated above. On the other hand, chromium electrodeposition from molten salts seems to have promising advantages in that no hydrogen evolution is involved and a thick chromium plate with the possibility of both ductility and high abrasion resistance may be obtained.

In this paper the electroplating of chromium metal from molten FLINAK (46.5 LiF–11.5 NaF–42.0 KF, mol %) has been investigated in detail. The results obtained are discussed on the basis of the electrochemistry of Cr(III) in the same salt [7, 8].

2. Experimental details

The preparations of the FLINAK solvent and K_3CrF_6 soluble chromium source have been described in detail previously [7, 8]. Anhydrous CrF_3 (Cerac, 99.5%) and CrF_2 (Alfa) were also used as the chromium-bearing solute. A high-purity chromium rod (MRC, $>99.9\%$), about 10 mm in diameter, was used as a soluble anode. The same electrolytic cell assembly as described previously [7, 8] was used with minor

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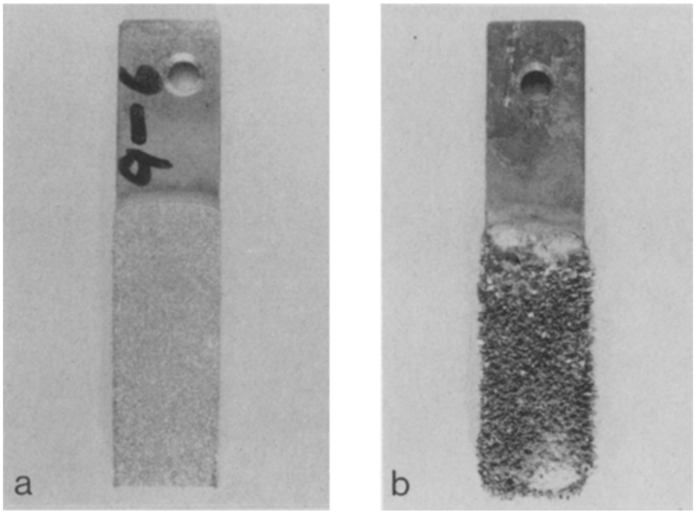

Fig. 1. Chromium deposits electroplated from 12 wt % K_3CrF_6 at (a) 983 and (b) 804° C in molten FLINAK. At 983° C, thickness of deposit = ~120 μm, current density = 24.2 mA cm^{-2}. At 804° C, current density = 33.0 mA cm^{-2}.

modification of the electrode system. Electrolysis was performed at 600–1000° C in an argon atmosphere using a constant current power supply (HP, model 6212A). Prior to electrolysis argon gas was bubbled through the melt, using pure nickel tubing of about 6 mm in outer diameter, in order to mix the melt. Current reversal electrolysis [9, 10] was performed using a relay system with an adjustable time constant.

The substrates used for electrodeposition, chiefly SUH304 stainless steel, were prepared by polishing rectangular (approximately 5 × 1 × 0.4 cm) specimens to a mirror finish with 600 grit grinding paper, followed by acid etching.

3. Results and discussion

3.1. *Mechanism of chromium deposition – effects of bath temperature, concentration and active electrolyte*

The appearances of the chromium deposits electroplated at 983° C and 804° C are shown in Fig. 1. Above 870° C a relatively uniform plate of chromium was deposited. On the other hand, below 850° C needle-like chromium was deposited with stubbornly entrained salts whose amount increased with decreasing temperature. At temperatures at which the electrolysis is carried out, the salt bath undoubtedly should be in the molten state, since the melting temperature of FLINAK is 462° C [11]. When the electrode was left in the bath for a while after electrolysis at such low temperatures, no salt was adherent to the cathode.

According to the electrochemistry of Cr(III) in FLINAK [7, 8], Cr(III) is reduced to Cr(II), followed by a two-electron reduction to Cr(O). Both processes are quasi-reversible and the second step, in particular, is slow. The product of the first step is soluble above 893° C but insoluble below 850° C. Therefore, from the previous electrochemical results and the present observations it may be indicated that the first reduction product of the reaction Cr(III) + $e \rightarrow$ Cr(II) is CrF_2 or a complex compound. The melting point of this compound is more than 850° C and its solubility in FLINAK is relatively low especially at lower temperature, although it dissolves gradually in FLINAK as time elapses. In fact, the melting point of CrF_2 is above 1100° C [12]. The salts adherent to the cathode were analysed by X-ray diffraction and found to contain, in addition to FLINAK and K_3CrF_6, an unknown substance which could not be identified. It is quite possible that CrF_2 forms a compound with alkali fluorides and/or Cr(III) compounds, whose melting point is even higher than that of CrF_2 itself.

Fig. 2 shows the relationship between the current density and the deposition rate estimated from the surface area and the weight gain as well as the relationship between the current density and the current efficiency of the cathode

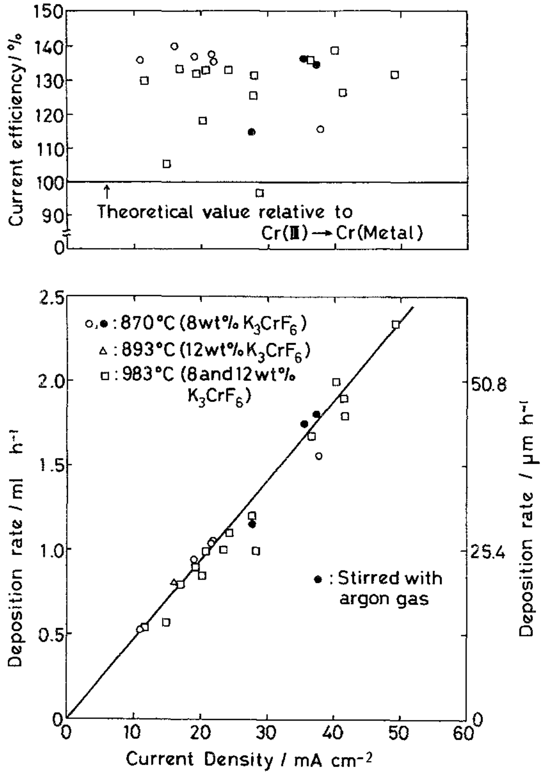

Fig. 2. Plots of the deposition rate and current efficiency of the cathode (Cr(III) → Cr metal) versus current density.

at temperatures above 870° C. It should be noted that below 850° C the deposition rate could not be estimated because of the co-deposition of salt on the cathode with the metal. As clearly seen from Fig. 2, the deposition rate increases linearly with the current density irrespective of temperature ($\geqslant 870°$ C), concentration of the electrolyte and stirring of the melt. The independence of deposition rate on factors which influence mass transfer implies that this rate is controlled by the charge transfer process (or kinetic steps associated with it).

It is of interest to note that the current efficiency at the cathode exceeds 100%, assuming that chromium metal is obtained directly from Cr(III), not from Cr(II). The average valence of chromium ions in the bath is calculated to be 2.7. This clearly means that a significant amount of Cr(II) exists in the melt in addition to Cr(III) and this is necessary for deposition of chromium metal from a Cr(III) source. There are several pieces of evidence for this. First, at the initial stage of a run using K_3CrF_6 as an electroactive electrolyte, no chromium metal was deposited on the cathode, although the chromium anode was dissolved. The constant current cell voltage betwen anode and cathode continued to increase as the electrolysis proceeded in the newly prepared bath until the voltage reached a constant value where the deposition of chromium began. Second, when a vitreous carbon anode (instead of a soluble chromium metal anode) was used in a newly prepared bath containing K_3CrF_6 no chromium metal was deposited on the cathode through several runs. Third, when CrF_2 was added to the bath instead of K_3CrF_6, the cell voltage did not change significantly after electrolysis was begun and chromium metal was deposited on the cathode from the beginning of the electrolysis. Fourth, chemical analysis of melt samples confirmed that the average oxidation state was less than 3 (values between 2.6 and 2.7 were obtained).

These facts indicate that it is not until the concentration of Cr(II) in the bath increases to a certain level that the chromium metal is deposited on the cathode. From the Nernst equation it is clear that the potentials of the Cr(III) → Cr(II) and Cr(II) → Cr(metal) reactions shift toward each other as the Cr(II) concentration in the bath increases, leading to their proximity. The overpotential may also play a role because of the quasi-reversibility of the reactions. Therefore, it is concluded that when Cr(III) is used as an electroactive ion, the presence of a certain amount of Cr(II) is required before chromium metal can be deposited on the cathode. Cr(II) is produced both from the reduction of the Cr(III) and from the anodization reaction at the chromium metal anode. Coulometric dissolution of chromium metal in initially chromium-free FLINAK indicated that the average oxidation state of the dissolved product was about 2.6. It is also known that there is a disproportionation reaction in this system [7, 8]; 3Cr(II) → 2Cr(III) + Cr(O), and that the reverse reaction also generates Cr(II) when chromium metal is present.

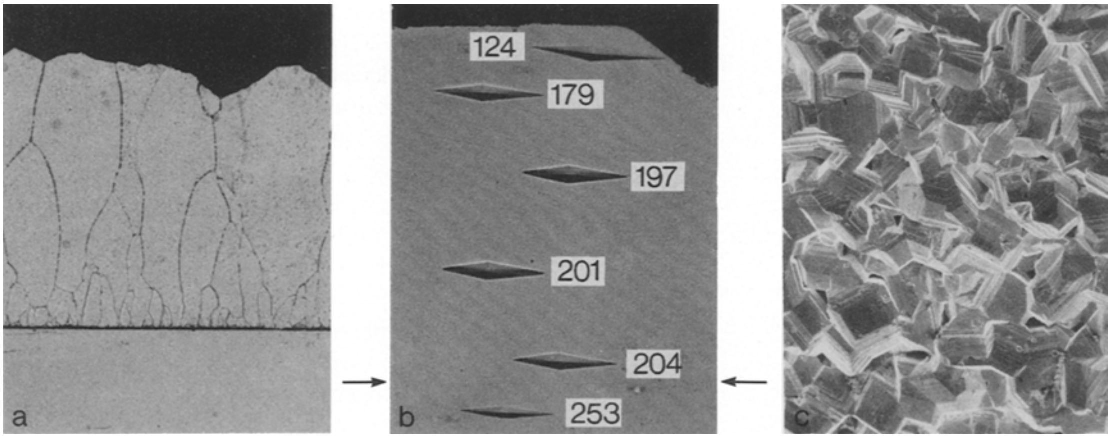

Fig. 3. (a) Etched cross-section, (b) Knoop microhardness and (c) surface structure of chromium electrodeposited from K_3CrF_6 on stainless steel at 870° C in molten FLINAK. (a) Current density, 37.8 mA cm^{-2}; × 145. (b) Current density, 37.8 mA cm^{-2}; × 215. (c) Current density, 10.9 mA cm^{-2}; × 30.

3.2. *Characterization and improvement of chromium plating*

Fig. 3 shows pictures of (a) etched cross-section, (b) Knoop microhardness and (c) surface structure of typical chromium as deposited on the SUH304 stainless steel substrate at 870° C. The arrows denote the interface between the chromium plating and the stainless steel substrate. The etched cross-section ($\sim 170\,\mu$m thick) depicts the columnar structure near the substrate which is characteristic of the plating obtained in molten salts. The grain sizes, however, become large as the coating grows. The surface structure finally shows pyramidal crystal growth when the coating becomes very thick ($\sim 380\,\mu$m). This probably suggests that the deposited chromium is apt to grow with preferential orientation eventually leading to dendrite formation after longer times of electrolysis [10]. Fig. 3b shows the Knoop microhardness of the chromium deposit and stainless steel substrate. The hardness of the chromium deposit is even lower than that of the stainless steel substrate annealed at 870° C. As small amounts of impurities contained in the deposit should increase the hardness [2], it is considered that the purity of the deposited chromium is quite high. In fact, according to energy dispersive X-ray analysis, no significant amounts of impurity elements could be detected in the grains, although very small amounts of alkali metals were found on the grain boundaries. On going from the interface to the surface, the Knoop microhardness becomes lower, corresponding to coarsening of the grains of the deposit.

Many attempts to obtain a thick and smooth chromium plating have been made with conditions as described below.

3.2.1. Bath temperature. As mentioned in the previous section, this is the most important parameter in obtaining good chromium plating. Below 850° C, massive chromium deposits can not be obtained due to co-deposition of needle-like chromium metal and solid salts on the cathode. Above 870° C coherent chromium metal can be electrodeposited on the cathode. However, very much higher bath temperatures seem to result in coarsening of the crystal grains as seen from Fig. 4. Therefore, the lower the bath temperature, the smaller the grain size.

3.2.2. Stirring of the bath during electrolysis. This was performed by bubbling argon gas through the melt. No effect of stirring of the bath on the deposition rate in the current density range used in the present study was found as seen from Fig. 2, which is in accordance with the results of electrochemical studies on Cr(III) [7, 8]. Stirring is rather deleterious in that inclusions seem to increase as seen from Fig. 5, where they exist not

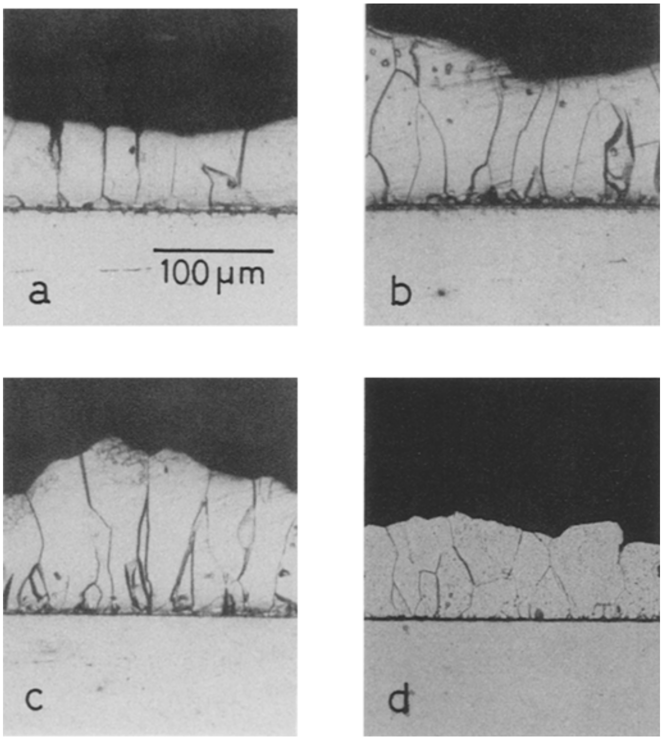

Fig. 4. Etched cross-sections of the chromium electrodeposited from K_3CrF_6 at various temperatures. (a) At 983° C, 23.8 mA cm^{-2}; (b) at 938° C, 23.7 mA cm^{-2}; (c) 893° C, 25.2 mA cm^{-2}; (d) 870° C, 21.2 mA cm^{-2}.

only on the grain boundaries but also within the grains.

3.2.3. Concentration and kind of electroactive electrolyte. The concentration of K_3CrF_6 was varied over the range of 4 to 14 wt %. No significant difference in the deposit was found. Mellors and Senderoff claimed in their US Patent [13] that the optimum concentration of CrF_3 was around 8 wt %. We found no apparent differences in the behaviour of the CrF_3 and K_3CrF_6 (CrF_3 undoubtedly forms CrF_6^{-3} in the melt), and because CrF_3 is not as easily handled, K_3CrF_6 was used in most of the present study.

Also, CrF_2 was used as an electroactive electrolyte. Fig. 6 shows the cross-sections of a chromium deposit obtained at a concentration of 9.3 wt % CrF_2. The microstructure is not essentially different from that when K_3CrF_6 was used, as shown in Figs 3 and 4. As indicated above, the use of CrF_2 as the electroactive material eliminates the initial period in which no deposition is observed, but it is less readily available in high purity than Cr(III) materials.

3.2.4. Current density. The current density does not seem to affect the grain size very much as seen from Fig. 5; rather, grain size is dependent chiefly on the bath temperature as stated above. High current density tends to cause severe dendrite formation especially at the edge of the cathode facing the anode. In order to avoid this it may be necessary to operate electrolysis at lower current density or to rotate the cathode. In the present study the latter method was not attempted due to limitations of the apparatus used. Under static conditions the optimum current density seems to be around 20–30 mA cm^{-2}.

3.2.5. Periodic current reversal. Cohen [9] applied the periodic reversal current technique to electrodeposition of niobium in molten fluorides and found that this method was very effective for obtaining a smooth plate of uni-directional columnar structure at a higher rate. This technique was also applied to the present chromium plating with K_3CrF_6. The same anodic current as cathodic was applied to the substrate but for

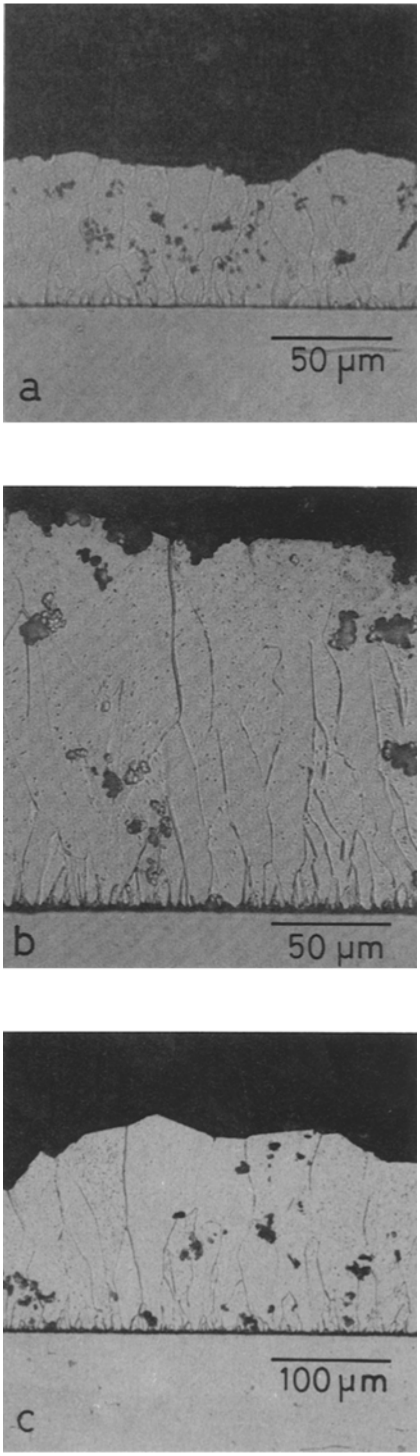

Fig. 5. Etched cross-sections of the chromium electrodeposited from K_3CrF_6 with stirring of the melt at 870° C and at various current densities: (a) 27.7 mA cm^{-2}; (b) 35.3 mA cm^{-2}; (c) 63.5 mA cm^{-2}.

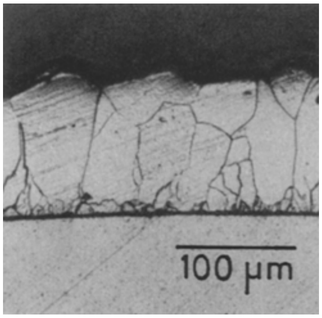

Fig. 6. Etched cross-section of the chromium electrodeposited from CrF_2 active electrolyte at 938° C and 28.8 mA cm^{-2}.

shorter periods. Two Q-ratios as defined by Cohen [9] were employed as follows: $Q = 3.3$ ($t_c = 48.4$ s, $t_a = 14.6$ s) and $Q = 5.3$ ($t_c = 76.8$ s, $t_a = 14.6$ s). Some results are shown in Fig. 7. As seen from these pictures the columnar grain growth becomes more pronounced with this technique than without it. This is probably due to the dissolution of nuclei formed during the cathodic process as pointed out by Cohen [9]. Differences in the value of Q do not seem to affect the columnar structure. However, a lower value of Q leads to the prolongation of electrodeposition which at higher temperatures might cause coarsening of the grains of the deposits as well as the substrate, which will be discussed further below. By comparing Fig. 7a and b it is suggested that, even with this technique, deposits with smaller grains seem to be obtainable at lower temperature.

3.2.6. Period current interruption and superposition of alternating current on direct current. The periodic current interruption technique was attempted for better plating from CrF_2 where, after electrolysis for 76.8 s, the current was interrupted for another 25.2 s. A typical result is shown in Fig. 8. The structure of the deposit is quite similar to that obtained previously by conventional direct current electrolysis and accordingly cannot be improved using this technique in the current density range used.

The superposition of alternating current (60 Hz) on direct current was also attempted. The Q-ratio was varied in the range of 2.2 to 17.

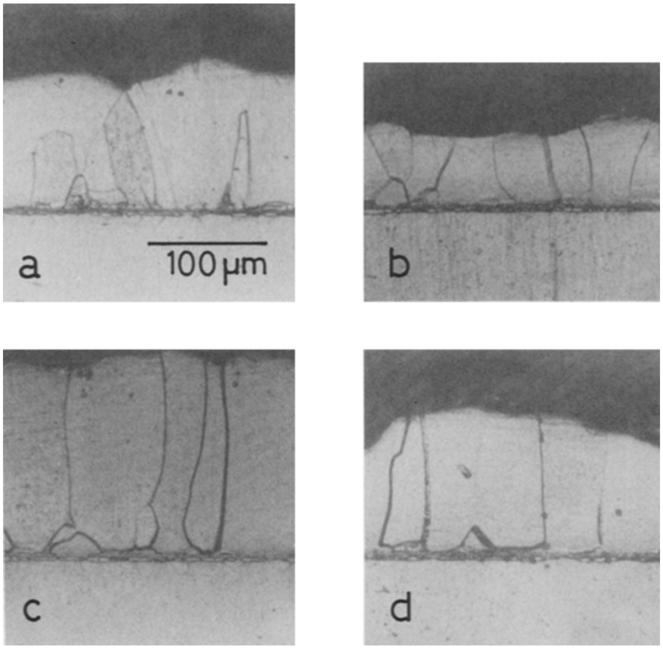

Fig. 7. Etched cross-section of the chromium electrodeposited from K_3CrF_6 using the periodic reversal current technique. (a) At 893° C, 40.4 mA cm^{-2}, $Q = 3.3$. (b) At 938° C, 41.0 mA cm^{-2}, $Q = 3.3$. (c) At 938° C, 47.8 mA cm^{-2}, $Q = 3.3$. (d) At 938° C, 30.3 mA cm^{-2}, $Q = 5.3$.

However, the result was not attractive probably due to too high a frequency imposed.

3.2.7. Substrate materials. The surface structure of the deposit was found to depend markedly on the substrate materials. When copper and mild steel were used as a substrate much rougher deposits were obtained compared to the stainless steel substrate mainly used in the present study. This is probably due to coarsening of the grains of the substrate materials at the temperature where the electrolysis is conducted, because copper and mild steel are considered to recrystallize at high temperature. Cohen [9] reported the heteroepitaxial growth of niobium deposits on a copper substrate, indicating that the deposit with larger grains is likely to grow on the substrate with larger grains. Therefore, a special pre-treatment must be taken when these materials are used as a substrate. For instance, with a nickel-coated copper substrate, a chromium deposit as smooth as with a stainless steel substrate was successfully obtained.

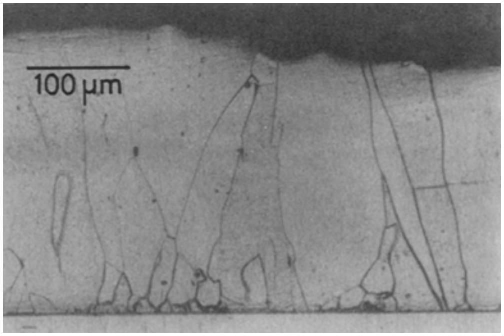

Fig. 8. Etched cross-section of the chromium electrodeposited from CrF_2 using the periodic current interruption technique at 938° C and 30.4 mA cm^{-2} (× 200).

3.2.8. Additives. A smooth chromium deposit as thick as 1 mm cannot be obtained due to coarsening of the deposit followed by the pyramidal growth. To overcome this problem, the addition of a third component as an alloying element or a nucleation modifier to the bath may be effective, as has been reported for tantalum-based chromium and chromium-based tantalum alloys by Ahmad *et al.* [2]. In the present study, silicon added to the bath in the form of Na_2SiF_6 resulted in a thick, very smooth and lustrous deposit which, however, was very brittle and easily cracked through the thermal shock of cooling. This was a deposit of a chromium silicide. A small addition of 0.08 wt % tantalum as K_2TaF_7 to the bath, on the other hand, seemed to have no significant effect on the chromium deposit, differing from the previous study [2]. Addition of several other metal ions as fluorides at about 1 wt % levels had visible effects on the deposits. Nickel fluoride produced a flattening of the pyramidal surface growth but with more voids. Other metals caused increased dendrite formation and variable results; even the NiF_2 additive led to extreme dendrite formation if an impure material was used.

3.2.8. Melt composition. Several experiments were carried out with NaF–KF as the solvent. The electrodeposits were not markedly different from those from FLINAK, but such differences as there were indicated a somewhat smoother surface with less tendency toward dendrite formation for the lithium-free plating performed under otherwise identical conditions. We attribute this to greater stability of the chromium complexes in the absence of the small Li^+ cation, thereby modifying to some degree the electrochemistry. Vapourization of this melt, however, renders it impractical for extended use.

4. Summary

Electroplating of chromium has been investigated in molten FLINAK over a temperature range of 600 to 1000° C. As a result it is found that the presence of a certain amount of Cr(II) in addition to Cr(III) is required to obtain a chromium deposit when Cr(III) is used as an electroactive ion. Among the parameters tested in the present study, the bath temperature is found to be the most important; at temperatures above 870° C a smooth plate is obtained, whereas at temperatures below 850° C the deposits consist of extensive dendrites embedded in the salt which is the first reduction product of Cr(III). At temperatures above 870° C the grains of the deposit are found to grow with increasing thickness, eventually leading to pyramidal surface structure. Columnar grains with larger size grow perpendicular to the surface of the substrate, particularly when the periodic current reversal technique is employed.

In order to obtain a smooth chromium plating with fine columnar grains, rotation of the cathode during electrolysis is suggested. The addition of alloying or nucleating elements has not been found to improve the deposits, but deposition is sensitive to impurity levels and trials with other additives may be effective.

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