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Studies of Chromium Carbide Electrodeposition in Molten Fluorides

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ABSTRACT

The chemistry and electrochemistry related to the electrodeposition of chromium carbide from fluoride melts has been explored. Plating of chromium metal and chromium carbide was attempted where the source of chromium was varied from chromate (CrO_4^{2-}) to anodized chromium to chromium(II) fluoride. Chromate cannot be reduced up to the cathodic limit of the melt; however, an oxidation was observed via cyclic voltammetry. The oxidation must be coupled with chemical steps since multiple re-reduction processes occur. Neither chromium metal nor chromium carbides could be obtained when anodized chromium was the source of ionic chromium. The simultaneous reduction of Cr(II), from CrF_2, and CO_3^{2-} at 850°-900°C leads to chromium carbide formation, although an acid-base reaction between these two substances somewhat interferes with the process. X-ray photoelectron spectroscopy (XPS) was used to probe the chemical nature and environment of quenched melt samples and of the chromium carbide coatings.

The chromium carbides are materials potentially useful as high-temperature wear coatings: hardness has been reported to be in the 1000-1400 kg/mm^2 range, and massive samples are reported to oxidize only slowly, even at 1000°C (1).

As part of a continuing program to produce refractory carbides by electrodeposition from molten fluorides, primarily the ternary (Li, Na, K)F fluoride eutectic, FLINAK (2, 3), we report here studies of chromium carbide deposition. The electrodeposition of the refractory metals was reported by Senderoff and Mellors (4) to be best carried out from solutions of the complex fluorides of these metals, generally in high valence states, in FLINAK. For electroplating their carbides, which requires the simultaneous reduction of carbonate to carbon, this is not necessarily the best way, because acid-base reactions between the complex metal ion and CO_3^{2-} may result in CO_2 evolution. However, there may exist a narrow concentration "window" in which carbide formation is possible. This phenomenon has been studied in detail for tantalum carbide (5). A similar situation may exist for titanium (6).

An alternate method for carbide plating starts with an oxyanion of the metal. This avoids CO_2 evolution, but requires that (*i*) the oxyanion is soluble and (*ii*) that it can be reduced below the cathodic limit of the melt. Both conditions are obtained for WO_4^{2-} and MoO_4^{2-} and have resulted in excellent W_2C (3) and Mo_2C (7) coatings.

In the present work, we report on an exploration of both of these reported paths to refractory carbides. For chromium carbides: the reduction of chromium fluoride (CrF_2) and the reduction of chromate ion (CrO_4^{2-}) in the presence of carbonate.

The plating of chromium metal from molten salts has been studied by several workers since the original patent by Senderoff and Mellors (4), which mentions only plating from a 8 weight percent (w/o) K_3CrF_6 solution in FLINAK at 750°-800°C. Inman and co-workers (8, 9) have reported detailed kinetics to proceed as Cr(III) → Cr(II) → Cr(0), but this work is not directly applicable since it was carried out in LiCl-KCl at 500°C, a temperature too low for CO_3^{2-} reduction (10). Smith (11) obtained good Cr deposits from a solution of Cr(III) at 800°C, produced by anodic dissolution of Cr metal. Periodic reversal plating reduced dendrite formation and seemed to lead to some Cr(II) formation. Yoko and Bailey (12) carried out plating and mechanistic studies at 612°-983°C. They obtained evidence that some Cr(II) must be present in the melt before plating starts, and that this species partly disproportionates to Cr(III) and Cr(0). They also observed that the deposit structure of the chromium metal is better when formed above 870°C, rather than at the lower end of the temperature range, concluding that this was probably because CrF_2 is insoluble at the lower temperatures.

The work reported here attempts to apply previous results on chromium deposition (8, 9, 11, 12) and carbide formation (2, 3) to investigate possible electrochemical paths

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to chromium carbide electrodeposition. Three such paths, all in FLINAK and all in the presence of CO_3^{2-}, were investigated: (*i*) reduction of Cr(III), produced by anodic dissolution of Cr metal; (*ii*) reduction of Cr(II), added as CrF_2; and (*iii*) reduction of CrO_4^{2-}, added as K_2CrO_4.

Experimental

Pretreatment of the FLINAK constituents and melt, as well as the general arrangement of the experiments have been reported previously (2, 3). Anhydrous CrF_2 (90%, Alfa) was used as received. Reagent grade K_2CrO_4 was dried at 120°C. High purity metallic chromium, used as anodes, was obtained as 1.3 cm diam rods from Materials Research Corporation.

For thermodynamic studies at 750°C, reversible reference electrodes based on Ni/NiF_2, as designed by Mamantov and co-workers (13) were used. At higher temperatures these electrodes fail too rapidly to be practical, so Pt reference electrodes were used, although their potential shifts with changes in the oxide activity of the melt (14). The Pt quasi-reference electrode (QRE) was used for the cyclic voltammetric studies with a Pt coil auxiliary electrode and a 1/8 in. Ni rod as the working electrode.

Coatings electrodeposited on Ni coupons and frozen plugs of melt were analyzed using a Surface Science/UHV Instruments x-ray photoelectron spectrometer to obtain elemental compositions and to assess the Cr and C speciation of the samples. Melt samples were analyzed with and without an inert atmospheric transfer into the spectrometer. Binding energies were referenced to adventitious C (assigned at 284.6 eV); melt samples were cross-referenced to K2$p_{3/2}$ at 292.3 eV, as previously described (5). Sputtering experiments were performed with a 5 kV Xe ion gun operated at 10 mA. Deconvolution of spectral envelopes was performed with a chi-squared minimization program after assigning peak positions and widths with a graphic editing routine.

Frozen plugs of the melt constituents were obtained by withdrawing a nickel rod from the melt into the ambient environment of the glove box. The frozen melt was chipped off the rod and finely ground in a helium or nitrogen atmosphere; a fine film of the powdered sample was pressed into indium foil to minimize charging of these insulating solids. Due to the greater than anticipated width of the Cr2$p_{3/2}$ and Fls lines for CrF_2, one sample of this solid was ground in a mortar with a graphite coating to lightly coat the CrF_2 with the conducting graphite prior to XPS analysis.

Results and Discussion

Chromate studies.—As mentioned above, the reduction of CrO_4^{2-}, if possible, would provide a convenient path to chromium carbide formation. K_2CrO_4 is quite soluble in FLINAK, producing intensely yellow solutions. Two studies were carried out on chromate in FLINAK. The first investigated the stability of CrO_4^{2-} with respect to dissociation and association with O^{2-}, similar to studies of other oxyanions in FLINAK (14). The second consisted of current-voltage and voltammetric studies to test the reducibility of CrO_4^{2-}.

The stability of an oxyanion with respect to O^{2-} can be determined by potentiometric studies of a cell reversible to O^{2-}. In this case

Ni|NiO|YSZ|FLINAK

$$+ K_2CrO_4, Na_2O|BN|NiF_2(sat) \text{ in FLINAK}|Ni \qquad [A]$$

where YSZ is Y_2O_3-stabilized ZrO_2, a ceramic reversible to O^{2-} in the melt. A change in the EMF of cell A indicates a change in the O^{2-} activity in the melt, the direction of change being indicative of increase or decrease (14).

Figure 1 shows that CrO_4^{2-} is quite stable to dissociation, although a slight increase of O^{2-} can be noted near a mole fraction of 10^{-3}. Two possible reactions can be postulated

$$CrO_4^{2-} = CrO_3 + O^{2-} \qquad [1]$$

and

$$2CrO_4^{2-} = Cr_2O_7^{2-} + O^{2-} \qquad [2]$$

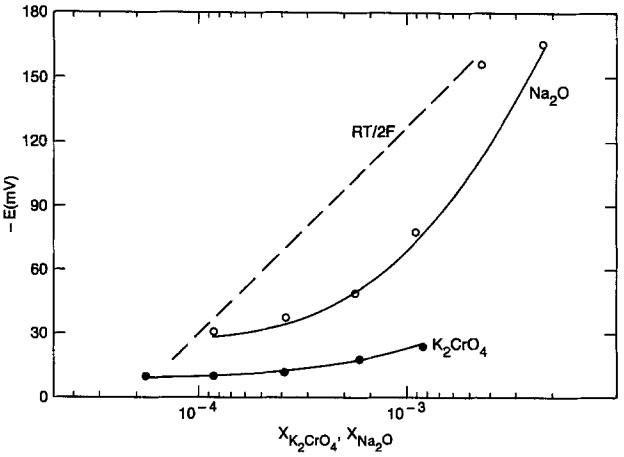

Fig. 1. EMF at 750°C, as a function of the mole fractions of K_2CrO_4 and Na_2O, of the cell: Ni|NiO|YSZ|FLINAK + K_2CrO_4, Na_2O|BN|NiF_2(sat) in FLINAK|Ni. (●) Addition of K_2CrO_4 to FLINAK; (○) addition of Na_2O to FLINAK melt containing 0.2 m/o K_2CrO_4.

The measurements do not distinguish between these two equilibria which, in either case, must lie far to the left. Spectrophotometric measurements would be useful to study these and similar (14) oxyanion-oxide equilibria, however, such measurements were beyond the scope of this study.

More surprising is the effect of adding Na_2O to a melt containing K_2CrO_4. If no reaction occurred, a slope of *RT*/2**F** should be obtained, but when concentrations of the two solutes are comparable, the slope is much less than *RT*/2**F**, indicating a removal of O^{2-} from the melt. If this occurs by reaction with CrO_4^{2-}, *e.g.*

$$CrO_4^{2-} + O^{2-} = CrO_5^{4-} \qquad [3]$$

an ion would be produced which has not previously been reported either in solution or in the solid state. A more likely explanation, suggested by a reviewer, is that O^{2-} is oxidized to O_2 by Cr(VI) in the melt. When the added O^{2-} concentration exceeds that of CrO_4^{2-}, the slope increases to ~*RT*/2**F**, consistent with this interpretation.

The next property of CrO_4^{2-} to be investigated was its stability with respect to reduction. This was done in two ways: (*i*) steady-state current-voltage curves; and (*ii*) cyclic voltammetric studies. Both of these were done at 750°C.

Current-voltage curves were obtained potentiostatically using a nickel working electrode, glassy carbon auxiliary electrode, and Ni/NiF_2 reference electrode (13), at various K_2CrO_4 concentrations. Curves were obtained up to ~1.6V, which is the cathodic limit of the melt. Surprisingly, currents at first decrease (at fixed voltages) with increasing concentration, but begin to increase again at higher concentrations [*e.g.*, 0.34 mole percent (m/o)]. Perhaps adsorption is involved. At any rate, for any concentration of K_2CrO_4, even prolonged electrolysis at the cathodic limit does not result in Cr plating, indicating that CrO_4^{2-} is resistant to reduction by alkali metal. This differs from the reduction of CO_3^{2-}, which occurs at the cathodic limit (10). The addition of K_2CO_3 to a K_2CrO_4 melt produces only carbon on reduction.

Adding chromate to FLINAK results in increased anodic voltammetric currents; this is shown in Fig. 2 by contrasting the background for pre-electrolyzed FLINAK (curve A) with the voltammograms obtained after small additions of K_2CrO_4 (0.3 mmol, curve B and 1.7 mmol, curve C). Slight potential shifts are expected when exposing the Pt quasi-reference electrode to melts containing soluble oxides (14). For a current density of 50 mA/cm^2, the negative potential limit only shifts negative by 50 mV (from −0.95 to −1.00 V/Pt) for the FLINAK solution with no chromate to the one with 1.7 mmol K_2CrO_4 added. Meanwhile the positive potential limit at a current density of 25 mA/cm^2 moves 260 mV more negative (from +0.16 to −0.10 V/Pt) with increasing concentration of chromate,

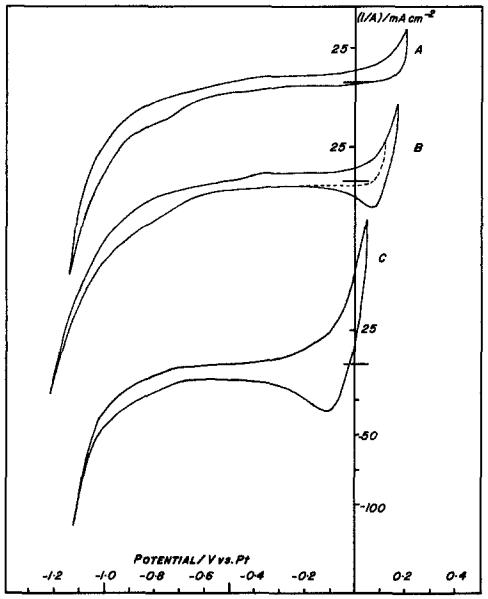

Fig. 2. Cyclic voltammetry of K_2CrO_4 in FLINAK: Ni working electrode, scan rate = 20 mV/s, scans were initiated positive of the open-circuit potential (~ −0.1 V/Pt). (A) 200g of pre-electrolyzed FLINAK: (B) 0.3 mmol K_2CrO_4; (C) 1.7 mmol K_2CrO_4.

Fig. 2, curves A and C, respectively. This significant shift to less positive potentials is due to an oxidation reaction, not a QRE-induced shift.

The voltammograms in Fig. 2 were obtained by scanning positive of the open-circuit potential (~ −0.1 V/Pt). A reduction process can be observed, but only if a clean Ni rod is used as the working electrode and the first potential scan is initiated negative of −0.5 V/Pt. As seen in Fig. 3, curve A, no reoxidation process is observed upon scan reversal. When the second cycle is restricted to potentials negative of the oxidation process beginning at approximately −0.2 V/Pt (see Fig. 2, curve C), the cathodic peak at −1.2 V/Pt is also absent; the voltammogram indicates that the electrode surface is passivated in this potential region. By then scanning positive of −0.5 V/Pt, an oxidation is observed, Fig. 3, curve B. Note: this oxidation occurs at the electrode already passivated to chromate reduction, see Fig. 3, curve A. Reversing the scan in the vicinity of −0.5V

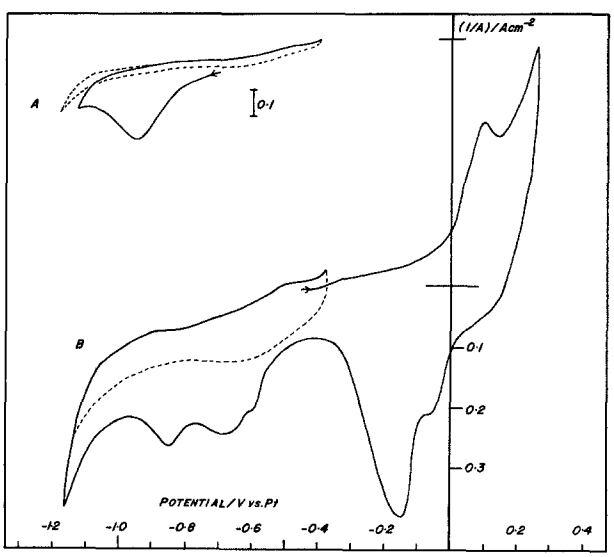

Fig. 3. Cyclic voltammetry of K_2CrO_4 in FLINAK: 8.8 mmol K_2CrO_4/200g FLINAK, Ni working electrode, scan rate = 20 mV/s. (A): Scan initiated negative of −0.5 V/Pt, (-) first scan, (--) second scan; (B): scan continued to positive voltages after obtaining the voltammogram in A, (-) first cycle, (--) second cycle.

reproduces the featureless response out to the cathodic limit of the melt.

The voltammetry of CrO_4^{2-} in FLINAK confirms the steady-state current-voltage results, *i.e.*, negligible chromate reduction occurs at nickel cathodes. The passivating nature of the first-shot reduction at clean nickel to continued direct reduction of chromate does not, however, affect the ability to oxidize something in the CrO_4^{2-}-FLINAK solution at the nickel working electrode. Since Cr in CrO_4^{2-} is already in the +6 oxidation state, a direct oxidation of CrO_4^{2-} is not indicated. The wealth of re-reduction processes resulting after the oxidation at ~0.1 V/Pt implies that multiple species, probably produced by an oxidatively induced dissociation of chromate, are generated by chemical reactions and available for re-reduction.

Consumption of chromate, by processes other than direct reduction, is also implied by the following: extensive voltammetry in the oxidation regime followed by a plating experiment in which a lot of current was passed, but no Cr metal plated at the cathode yielded a colorless, not bright yellow, melt in which the one-shot reduction at −1.21 V/Pt was no longer observed at a fresh nickel working electrode. X-ray photoelectron spectroscopic (XPS) analysis of a frozen plug of this colorless melt showed no Cr, even after averaging 64 scans of the $Cr2p_{3/2}$ region.

Cr(II) studies.—Potentiometry.—Since we planned to use CrF_2 as a source of chromium in plating studies and since Yoko and Bailey (12) had reported that CrF_2 was insoluble below 893°C and that above this temperature Cr(II) may disproportionate to Cr(III) and Cr(0), we carried out a potentiometric study of CrF_2 in FLINAK to ascertain the valence of chromium. The EMF of the cell

$$Cr|CrF_2 \text{ in FLINAK}|BN|NiF_2(sat)|Ni \qquad [B]$$

is shown in Fig. 4 as a function of CrF_2 concentrations at 750°C. Between 0.03 and 0.8 m/o, the Nernst plot is linear, showing that CrF_2 is soluble, contrary to the previous report (12). The obtained slope of (2.303)0.79[$RT/2\mathbf{F}$] for the Nernst plot shows that Cr(II) disproportionates only slightly, if at all. Accordingly, we conclude that CeF_2 is usable as a source of chromium above 750°C.

Current-voltage curves.—To assess the reducibility of Cr(II) in FLINAK, current-voltage curves for CrF_2 were obtained at 750°C by the same technique as used for K_2CrO_4. In contrast to the results obtained for that compounds, the curves obtained for CrF_2 (Fig. 5) show current increasing with voltage and concentration from very low voltages up, clearly indicating that Cr(II) is electroactive and can be reduced.

Chemical studies.—Plating chromium carbide from FLINAK solutions containing carbonate and Cr(II) or Cr(III) requires that carbonate is not removed by chemical reaction with a chromium species. Reactions of this type were observed to occur between Ta(V) and CO_3^{2-} to produce CO_2 (5). In the tantalum-carbonate system, carbide

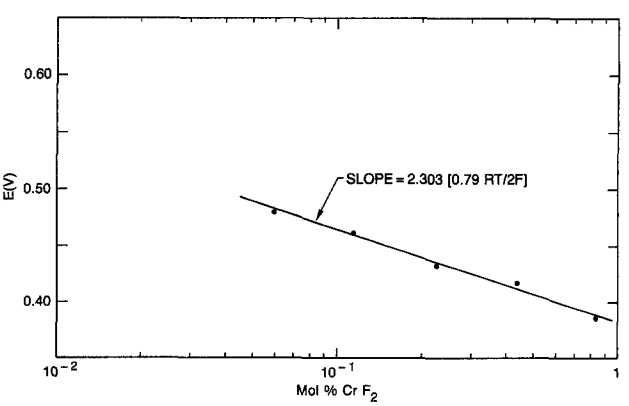

Fig. 4. EMF at 750° of the cell: Cr|FLINAK + CrF_2|BN|NiF_2(sat)|Ni

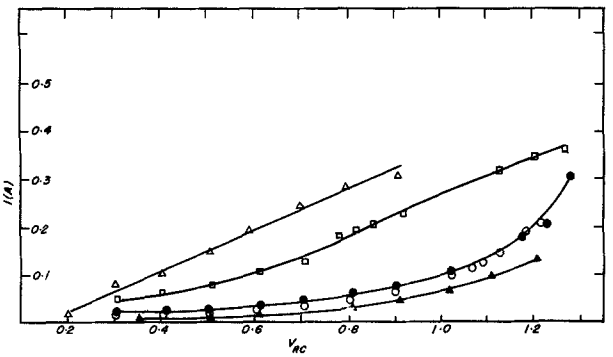

Fig. 5. Current-voltage curves of the cell at 750°C: C|FLINAK + CrF_2|Ni with Ni/NiF_2 reference. m/o CrF_2: (▲) 0.019; (○) 0.0407; (●) 0.0931; (□) 0.193; (△) 0.382.

plating is possible because the acid-base reaction, which produced TaO_3^-, does not go to completion.

The case of chromium is somewhat different because Cr(II) is the lowest stable valence state of Cr and any redox reaction must lead to Cr oxidation and CO_3^{2-} reduction, *viz.*

$$4CrF_2 + K_2CO_3 + 3K_2O = 2Cr_2O_3 + C + 8KF \quad [4]$$

Another possibility is an acid-base reaction without valence change, *viz.*

$$CrF_2 + K_2CO_3 = CrO + CO_2 + 2KF \quad [5]$$

Not enough is known of the properties of CrO to predict its behavior in FLINAK at 750°C.

To study any possible reaction, K_2CO_3 was added incrementally to a solution of 2g CrF_2 in 75g FLINAK at 750°C. Gas evolution was observed until the molar ratio Cr/CO_3^{2-} was 1. Further addition of K_2CO_3 produced no further gas evolution. The very dark CrF_2 melt gradually lightened to light green as carbonate was added. These observations are consistent with the type of acid-base chemistry previously observed between TaF_7^{2-} and CO_3^{2-} in FLINAK (5). Quenched samples of the melt at various stages of the reaction were obtained for XPS analysis.

The XPS results for this reaction series are summarized in Table I, which also includes the obtained and literature binding energies for reference compounds. An example of a Cr(II) species included in a list of literature binding energies for $Cr2p_{3/2}$ (15), that of chromocene dichloride at 577.2 eV, is in good agreement with our obtained binding energy for CrF_2 of 577.3 eV. The obtained F1s binding energy of 684.6 eV is consistent with that for other transition metal difluorides (15). Less clear is why the F1s line is so broad (3.2 eV for the sample of graphite-ground powder which exhibited minimal charging of C1s and O1s lines).

Dissolving 2g of CrF_2 in 75g of FLINAK (not previously pre-electrolyzed) yields a quenched sample with two clearly resolved Cr bands—the positions of which do not significantly shift with addition of K_2CO_3—at 577.9 and 574.7 eV. In the absence of carbonate the relative intensities are ~3:1, respectively, and increase to ~6:1 with the addition of carbonate. Assigning the predominant line at 577.9 eV to Cr(II) is in keeping with its value in the undiluted state. While shifts of 1 eV to lower binding energy were observed for $Ta4f_{7/2}$ and F1s lines in a quenched sample of dissolved K_2TaF_7 in FLINAK (5), the $Cr2p_{3/2}$ line at 574.7 eV is unlikely to be due to a comparable phenomenon. This binding energy for $Cr2p_{3/2}$ is indicative of Cr in aryl complexes such as chromocene (15). The generation of two chromium species just by dissolving CrF_2 in FLINAK is not understood at this time.

The F1s binding energy of 683.1 eV is identical to that previously observed for pure FLINAK (5), dominated as it is by the KF-influenced environment of FLINAK. The K2p-C1s region was used in the previous Ta-CO_3^{2-} study (5) to follow the presence of carbonate. An additional carbon species is present in this Cr-CO_3^{2-} reaction series, but present for all samples in this series, with or without intentional carbonate addition to the melt, see Table I. This is true for the powders introduced into the spectrometer by inert transfer or subsequently reanalyzed after air exposure. The binding energy is consistent with an oxygenated carbon, but its presence in the CrF_2/FLINAK sample in the absence of carbonate requires that this line cannot be assigned as unreacted CO_3^{2-} for the samples quenched after additions of K_2CO_3. While this oxygenated carbon species might have been a contaminant of the FLINAK, it is more probable that it is an external contaminant due to alcoholic traces on metal stages, spatulas, etc. This line is occasionally observed on samples never exposed to FLINAK, see Table I.

In keeping with the assignment of the C1s line at 288 eV as a contaminant, the ratio of the relative area of the C1s line at 288 eV to that of adventitious carbon at 284.6 eV or to that of the $K2p_{3/2}$ line does not significantly vary for all samples of this series. This at least indicates that extensive amounts of carbonate are not contributing to the line at 288 eV and, therefore, that carbonate does not remain in

Table I. X-ray photoelectron spectroscopic peak positions and widths for reference compounds and melt samples

Sample	$Cr2p_{3/2}$ BE(FWHM)/eV	F1s BE(FWHM)/eV	Cr/F[a]	C1s[b] BE(FWHM)/eV
$Cr(CO)_6$	576.8[c]			
$Cr(C_5H_5)_2Cl_2$	577.2[c]			
$CrCl_3$	577.4[c]			
CrF_3	580.1[c]			
Cr_2O_3	576.1[d]			
	576.2 (3.1)	—	—	288.5 (2.2)
CrF_2, inert transfer[e]	577.5 (4.8)	685.1 (4.0)	0.22	287.3 (3.1)
CrF_2, air exposed[f]	576.8 ± 0.2	684.4 ± 0.3	0.25 ± 0.02	
CrF_2, graphite ground	577.3 (4.2)	684.6 (3.2)	0.27	—
2g CrF_2/FLINAK[g]	574.7 ± 0.2	683.3 (2.0)	0.0052[h]	288.2 (2.9)
	578.2 ± 0.1			
2g CrF_2 + 0.36g K_2CO_3 in FLINAK	574.6 (2.5)	683.1 (1.9)	0.0048[h]	287.9 (1.8)
	577.9 (2.6)			
2g CrF_2 + 1.53g K_2CO_3 in FLINAK	574.7 (1.8)	682.9 (1.8)	0.0090[h]	288.2 (2.6)
	577.7 (2.4)			
(CrF_2-K_2CO_3)/FLINAK[i]	574.7 ± 0.1	683.1 ± 0.2		288.1 ± 0.1
	577.9 ± 0.2			
Anodized Cr/FLINAK	577.5 (3.2)	683.9 (2.1)	0.0013	—

[a] Ratio of the relative areas of the $Cr2p_{3/2}$ and F1s lines.
[b] A C1s line, other than that at 284.6 eV, is present.
[c] Taken from Ref. (15).
[d] Taken from Ref. (16).
[e] Charging problems for this sample were evidenced by C1s FWHM > 2.0 eV and by tailing on the low binding energy side of the F1s line.
[f] Three samples were run of the air-exposed CrF_2 powder.
[g] This series reports the results for air-exposed samples; the same qualitative features were observed (including the additional C1s line) for the samples analyzed after inert transfer, but charging problems (as in [e]) compromised the analytical results.
[h] This ratio of the relative areas was calculated using the sum of the two $Cr2p_{3/2}$ lines.
[i] These numbers represent the averaged values for this series.

the melt at the C/Cr molar ratios of these samples (0.12 and 0.50).

Chromium was also dissolved in FLINAK anodically, since this was the procedure used by Smith (11) for plating chromium metal. Presumably this procedure leads to Cr(III). After the concentration, calculated from the charge passed, had reached 0.62 m/o a quenched melt sample was taken for XPS analysis. The XPS results for this sample are also listed in Table I. Only one $Cr2p_{3/2}$ line was observed with a binding energy of 577.5 eV. This is a binding energy more characteristic of $CrCl_3$, not that expected for a Cr(III) ion in a fluoride environment: CrF_3 has a literature binding energy of 580.1 eV, see Table I. The binding energy is also quite consistent with that for CrF_2 in FLINAK, so that assignment of an oxidation state of +3 on the basis of XPS cannot be definitively made. Rather, in the absence of XPS experiments on CrF_3 dissolved in FLINAK, the XPS results imply that, in FLINAK, the anodized Cr is more divalent in nature.

Plating studies.—Chromium metal.—Based on previous work (11, 12), we first tried plating from a FLINAK solution into which Cr had been anodized. Even when the Cr concentration was ~2 m/o, only a very slight coating of Cr metal was obtained between 750° and 900°C. This is consistent with the observation of both Smith (11) and Yoko and Bailey (12) that, in addition to Cr(III), some Cr(II) must be in the melt for practical plating. These workers obtained Cr metal after some Cr(II) had been generated by electrolysis. Whether the difference between their result and ours is the consequence of their adding Cr(III) as CrF_3, rather than by electrolysis, remains to be investigated.

Plating experiments were, therefore, carried out using melts containing only CrF_2 as added solute. [Some Cr(III) was probably introduced into the melt by dissolution of the Cr anode.] The following observations were made, all consistent with previous work: (*i*) chromium can be plated from a melt containing only Cr(II); (*ii*) although some dendrite formation usually occurs after a smooth chromium plate has formed, this is much reduced above 850°C; (*iii*) current efficiency is strongly dependent on concentration, *e.g.*, at 0.4 m/o, C.E. was ~10%; at 2.4 m/o, it was >50%. With further work the C. E. could probably be increased.

Chromium carbide.—The chromium-carbon phase diagram exhibits three carbides: $Cr_{23}C_6$, Cr_7C_3, and Cr_3C_2, corresponding to molar C/Cr ratios of 0.26, 0.43, and 0.67, respectively. X-ray patterns for these compounds are known (1). However, identification of potential chromium carbide coatings is complicated by the fact that although Cr metal exhibits only a few, widely spaced lines, all three carbides have many, closely spaced lines over the same d-spacing range. Similarly, although carbidic carbon can be identified by XPS (see below), the C/Cr ratio could not be used to distinguish between individual carbides in this study. Thus, we can only determine whether carbide is present.

Approximately fifty plating experiments were carried out in the temperature range 850°-900°C, in which melt species and their concentration and voltage were varied. All of these studies were done potentiostatically with Pt quasi-reference, Cr auxiliary, and polished nickel coupon cathodes. Current was thus a dependent variable.

The results obtained can be summarized as follows:

1. No carbide coating is obtained from K_2CrO_4-K_2CO_3 melts (see above).

2. No carbide coating is obtained from Cr(III)-CO_3^{2-} melt, which is not surprising since no Cr metal was obtained from Cr(III) melts either.

3. Chromium-carbide coatings were obtained from CrF_2-K_2CO_3 melts, but in all cases the current efficiency did not exceed 10%, not counting dendrites. Best results were obtained at higher CrF_2 concentrations (as for Cr metal) near 900°C rather than at lower temperatures; for C/Cr ratios near 1.0, rather than at lower ratios, not surprising in view of the acid-base reaction, and shortly after a K_2CO_3 addition had been made. This last result may be due to the evaporation of K_2CO_3 from the melt (10), which also tends to limit the temperature to values ≤ 900°C. Voltages near 1.0V (*vs.* Pt QRE) were required for carbide formation. At lower voltages, only Cr metal was obtained. Although dendrites always occurred in the later stages of plating, a thin, smooth adherent coating of chromium carbide always remained after removal of the dendrites by ultrasonic washing.

X-ray Photoelectron Spectroscopic Analyses of Chromium Carbide Coatings

Figure 6 displays the Cr2p region, after 90s Xe^+ sputtering to remove surface contaminants, for three coatings obtained from plating out of CrF_2-K_2CO_3 melts. At least three Cr species must be fit in the resulting envelope, and four are possible; Fig. 6 shows the conservative three-peak fit. The XPS data and plating parameters are collected in Table II. One narrow (FWHM ~ 1.5 eV) C1s line at 282.3 eV is observed for all samples and is characteristic of carbide as seen in WC (15). The sputtering is sufficiently mild, so that some traces of melt (evidenced by K2p, Na1s, and F1s lines and a C1s line at 284.6 eV) remain.

The line at 575.2 eV is assigned to chromium carbide. CrN has a reported $Cr2p_{3/2}$ binding energy of 575.4 eV (15), while CrSi is reported at 573.6 eV (16), indistinguishable from Cr(0) metal. We also observe a line at 573.6 eV, and due to the narrowness of the line [$Cr2p_{3/2}$ for Cr(0) has a FWHM about half of that for Cr_2O_3 (15)], and the absence of a second carbidic carbon line in the C1s region, it is assigned to Cr(0) metal. Due to the nature of the electrodeposition, the presence of Cr(0) metal is expected and actually is the predominant species for one of the samples (Fig. 6, curve C). The highest binding energy $Cr2p_{3/2}$ line at 577 eV is consistent with the CrF_2 and the CrF_2/FLINAK results previously obtained, see Table I.

Unfortunately, the C/Cr ratios obtained from the XPS analyses (see Table II), do not permit an unambiguous assignment of specific chromium carbides.

Conclusions

Chromium carbide can be electroplated from CrF_2-K_2CO_3-FLINAK melts at ~900°C, but not from FLINAK

Table II. Plating parameters and x-ray photoelectron spectroscopic and x-ray diffraction results for chromium carbide coatings as a function of Xe^+ sputtering time

Sample	*t*/s	CO_3^{2-}/Cr	$V_{A\text{-}C}/V$(i/A)	BE $Cr2p_{3/2}$/eV			BE C1s/eV	C/Cr[a]	XRD lines
				Cr(0)	Cr carbide	Cr(II)			
A	0	0.26	0.50 (0.30)	573.7	576.0	577.4	—	—	Cr_7C_3,
	90			573.4	575.4	577.1	282.2	0.23	Cr_3C_2,
	690			573.5	575.4	577.0	282.3	0.52	Cr
	1200			573.6	575.4	576.9	282.3	0.56	
B	0	0.42	0.51 (0.35)	573.3	575.7	577.3	282.3	0.87	$Cr_{23}C_6$,
	90			573.1	575.0	576.6	281.9	0.57	Cr_3C_2, Cr
C	0	0.81	0.53 (0.22)	573.6	575.1	576.7	—	—	$Cr_{23}C_6$
	90			573.6	575.2	576.7	282.4	2.33	
	900			573.6	575.1	577.0	282.4	1.85	
Cr_3C_2								0.67	
Cr_7C_3								0.43	
$Cr_{23}C_6$								0.26	

[a] The C/Cr ratio is calculated using the relative area of the carbide-C1s line only and the relative area of the line assigned to carbidic $Cr2p_{3/2}$ only.

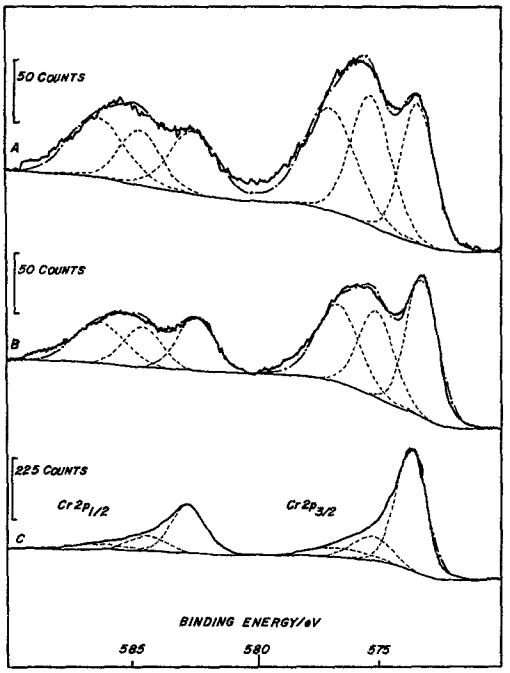

Fig. 6. X-ray photoelectron spectroscopic analysis of chromium carbide coatings electroplated at various anode-cathode voltages and carbonate/chromium ratios: Cr2p region. (A): $CO_3^{2-}/Cr = 0.26$, $V_{A\text{-}C} = 0.50V$: (B): $CO_3^{2-}/Cr = 0.42$, $V_{A\text{-}C} = 0.51V$; (C) $CO_3^{2-}/Cr = 0.81$, $V_{A\text{-}C} = 0.53V$.

solutions where K_2CrO_4 or Cr(III) is the source of chromium. Higher current efficiencies could probably be obtained if dendrite formation could be suppressed. Variables which could be manipulated are concentrations, voltage, and temperature.

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Technical Notes

The Absolute Value of the Standard Partial Molar Entropy of the Hydrogen Ion in Aqueous Solution at 25°C

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The absolute value of the standard partial molar entropy of the hydrogen ion in aqueous solution has been determined to be -19.03 ± 0.15 J $K^{-1}mol^{-1}$ at 25°C. First, the standard transported entropy of the hydrogen ion has been calculated from literature values and from the infinite dilution value of thermoelectric powers (corrected by the mass-action term), which were obtained from experimental data for hydrogen electrode thermocells. Then, the heat of transport of the hydrogen ion has been obtained from an extra thermodynamic argument for the single-ion heat of transport. Finally, these results have been combined in order to determine the absolute value of the standard partial molar entropy of the hydrogen ion.

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The standard partial molar entropy of the hydrogen ion $S^{o}_{H^+}$ may be determined from Eq. [1]

$$\bar{\bar{S}}^{o}_{H^+} = S^{o}_{H^+} + (Q^{*o}_{H^+}/T) \quad [1]$$

The standard partial molar entropy of the hydrogen ion can be used in calculations of electrophoretic contributions to the limiting slopes of heats of transport, transported entropies, and thermoelectric powers in aqueous electrolytes. In the next section, the standard transported entropy of the hydrogen ion $\bar{\bar{S}}^{o}_{H^+}$ is determined. It is a single ion property not based on an arbitrary convention (1). Then we use an extra thermodynamic argument to calculate the infinite dilution limiting value of the heat (enthalpy) of transport of the hydrogen ion $Q^{*o}_{H^+}$. This quan-