THE ELECTROCHEMICAL DEPOSITION OF REFRACTORY METALS FROM CHLORIDE MELTS

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ABSTRACT

The deposition of refractory metals such as chromium and molybdenum is discussed from the standpoint of the solution chemistry and the electrocrystallization phenomena involved in forming coherent metal.

INTRODUCTION

The precious metals, the refractory metals, and other transition elements which are required for use in the advanced technologies of aerospace and the nuclear industry have been plated from molten salt solutions. Molten alkali metal fluorides were proposed as general media from which the majority of the refractory metals might be obtained in coherent form (1). However, there are limitations to these electrolytes, not the least of which concerns the high temperatures required (1,2). On the other hand, control of the morphology of the depositing metal is achieved albeit without a detailed understanding of the associated chemistry and electrochemistry involved. The interrelationship between the electrolyte solution chemistry and the electrode processes is an important feature of these systems, and in the studies reported here, these two aspects are being examined to enable the development of low temperature baths from which the more noble refractory metals can be plated.

EXPERIMENTAL

The LiCl-KCl and the ZnCl₂ based melts were prepared by vacuum drying, hydrogen chloride gas treatment, preelectrolysis with a tungsten cathode and graphite anode, followed by filtration (3). The products were stored and handled in a dry box. The cell design, experimental details, and electrochemical instrumentation were similar to those described earlier (4). The data were recorded on a BT microprocessor/recorder and data analysis was carried out on this instrument and with an Apple computer.

RESULTS AND DISCUSSION

The importance of the acid-base chemistry in relation to refractory metal plating can be deduced from the recent results relating to molybdenum (5,6) in alkali metal chloride-aluminum chloride mixtures in which the pCl is in the range 3 to 5, and measurements (7) in the LiCl-KCl where the pCl is less than 1. The formation of metal in melts of high

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pCl is inhibited by the more favorable reactions to form metal bonded compounds of oxidation state greater than zero. Even at higher temperatures, the low pCl melts may induce this reduction pathway (8). Thus, one of the major problems associated with the development of low temperature, nonfluoride electrolytes, is to understand and then control the solution chemistry in such a way that the reduction pathway to metal avoids the intervention of these intermediates.

Zinc chloride is a weaker acid than aluminum chloride and when mixed with alkali metal chlorides reduces the melting points to less than 300°C. Highly pure, water free melts have an electrochemical window of 1.5V at around 300°C, on appropriate substrates and thus can be employed with the more noble metals. Figure 1 shows that in the acidic composition region of such mixtures the pCl is still too high for successful metal deposition. Compositions excluding zinc chloride at 550°C show good indications that metal is produced, still in coherent form, in contrast to the suggestions of earlier workers (9).

Chromium metal can be plated from the basic LiCl-KCl melt (7,10) in the temperature range 400-500°C in contrast to the 800-1000°C required in the fluoride melts (11). Figure 2 shows the redox behavior of chromium (II) ions, soluble in the LiCl-KCl melt. The oxidation reaction:

$$\text{Cr}^{2+} \not\rightarrow \text{Cr}^{3+} + e$$  (1)

provides a convenient means of determining the diffusion coefficient for the Cr$^{2+}$ species, which in turn enables the chromium content of the bath to be monitored. Cyclic voltammetry, chronoamperometry, chronopotentiometry and normal pulse voltammetry have been employed to determine the diffusion coefficient, but the measurements indicate that the chromium (II) concentration in the solution is a little unstable, especially at the lower concentrations. This is in agreement with the variation in the open circuit potentials of a chromium electrode with time. The cells were leak tight as demonstrated by the absence of oxidation of a piece of chromium suspended just above the melt. The stability of Cr$\text{O}_3$ and the presence of oxidic materials in the cell components may contribute to this behavior. Table 1 compares the results from this work with those of earlier studies (12,13). The diffusion coefficient is typical for that of a transition metal in this medium (13). The availability of this value is helpful in developing an understanding of the phenomena associated with the metal deposition process (14,15).

The evolution of a diffusion coefficient from the reduction of chromium (II) species studied by current pulse, linear sweep, and normal pulse voltammetry gives diffusion coefficients in poor agreement with those from the anodic measurements, under the same conditions (which excludes the concentration variation as a factor). Closer examination of the resultant transients at higher resolution show features at shorter times which can be attributed to the influence of the electrocrystallization process. Examples of these features on different
substrates can be seen in Figures 3-5. Furthermore, the \( E_p/2 \) and the \( E_r/4 \) for the cathodic voltammograms and chronopotentiograms were shifted in the cathodic sense some 50 to 100 mV from the Cr/Cr\(^{2+}\) potential measured simultaneously. Crossover of the return cathodic current after the switching potential was observed at any scan rate, especially if the switching occurred prior to the peak potential.

The previous analytical procedure for voltammograms and chronopotentiograms has involved the assumption that the metal is depositing at an activity of unity and it might be expected, at the early stages of metal formation on foreign substrates, that this condition is not satisfied (16). Conversely, this means that the early stages of the galvanostatic transients or the prepeak region of the voltammograms contain information about the deposition process. The deposition of metal (excluding alloy formation) is a heterogeneous process which disturbs the surface state so that techniques, in which the experimental variables such as voltage and current density can become time dependent simultaneously (7), are not so simple to resolve as the case of potential step measurements where only the time dependent current density reflects the details of the crystallization and growth processes.

Figures 6 and 7 show the potentiostatic transients obtained at gold and nickel electrodes resulting from the application of a single cathodic potential step of decreasing magnitude. The usual monotonous decay of current with time is only observed at the longer times. The initial charging current density decay is followed by an increase in current density reflecting the nucleation and subsequent growth of nuclei, ultimately passing through a maximum and decaying monotonously under diffusion control. The data from the region where the current density is increasing enables some insight to be gained into the way in which nuclei are formed and grow. Qualitatively, the rate of change of this growth current density is rather small, particularly on the nickel electrode. By selecting the digital data recorded in the region, analyses were made by plotting \( \log(i) \) versus \( \log(t) \) to obtain the time dependence of the current density. The results for different overpotentials (vs. Cr/Cr\(^{2+}\)) show that the current depends on the half power of time which suggests that for Cr deposition on gold the nucleation process is instantaneous and the rate controlling step is probably the diffusion controlled growth at the hemispherical nuclei formed. Such a current is given (8) by:

\[
I(t) = 3.14zF\pi N_0 M^{1/2} (2Dc_0)^{3/2} \rho^{-1/2} (1- \exp zFn/RT)^{1/2}
\]

and the potential dependence of the intercept is seen in Figure 8. The number of nuclei were calculated and the relevant results are shown in Table 2. The post-maxima currents were analyzed in the same manner using the digital data and showed a \( t^{-1/2} \) dependence, with an intercept of the log-log plot independent of the potential step. The diffusion coefficient calculated from the values of the intercept shows agreement with the diffusion coefficient obtained from the anodic oxidation of...
Cr$^{2+}$. The spherical diffusion to the nuclei, initially formed, translates into a linear regime at the longer times, consistent with the presence of the current maximum.

The correspondence between the properties of the potential maxima and current maxima from the galvanostatic and potentiostatic pulse measurements on gold is seen by comparison of data in Tables 2 and 3. Using a simple model to relate the charge under the galvanostatic maxima with the charge required to create the nuclei, the radius of the individual nuclei can be calculated (Table 3) for the extremes of nuclei density, measured in the potentiostatic experiment. The results suggest nuclei with radii in the region of 0.2 to 0.3 micrometer. These values are consistent with those reported for aqueous solution (19) and for first row transition metals (14) in the LiCl-KCl at 450°C. Control of the nuclear density and size is clearly possible and may lead to the preparation of coherent deposits of refractory metals with selected grain sizes.

The interpretation of the data obtained so far has ignored the influence of specific substrate metal-deposit metal interactions, as certainly can occur in the case of chromium deposition on gold, platinum, and tungsten. Figure 9 shows cyclic voltammograms that contain oxidation peaks which suggest alloy formation in the case of gold and nickel. Such interactions must be accounted for in any detailed consideration of the deposition process. Finally, the coverage (after the passage of a small amount of charge at low current density) of the less noble electrodes seems such that the conditions referred to earlier concerning the simple theoretical treatments are met, since potential-time analyses of the galvanostatic transients, Figure 10, show excellent fits to the equation:

$$E(t) = E^o + \frac{RT}{ZF} \ln C + \frac{RT}{ZF} \ln \left(1 - \left(\frac{t}{\tau}\right)^{1/2}\right)$$

showing that on copper and nickel at least the base metal is uniformly covered.

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REFERENCES

1. G. W. Mellors and S. Senderoff, Plating (1964).
2. D. Inman and S. H. White, J. Appl. Electrochem., 8, 357 (1978).
3. S. H. White, in Ionic Liquids, D. Inman and G. Lovering, eds (London: Plenum, 1981).
4. S. H. White and U. M. Twardoch, in *Proceedings 3rd Intern. Symposium on Molten Salts* (New Jersey: The Electrochemical Society, Inc., 1981), p. 284.

5. S. H. White, D. Inman, R. Huq, T. Mukherjee and G. F. Warren, I.S.E. Zurich, Extended Abstract No. 254 (1976).

6. J. Phillips and R. A. Osteryoung, J. Electrochem. Soc., 124, 1465 (1977).

7. S. H. White and U. M. Twardoch, unpublished work, 1982.

8. G. F. Warren, S. H. White and D. Inman, in *Proceedings 1st Intern. Symposium on Molten Salts* (New Jersey: The Electrochemical Society, Inc., 1976), p. 218.

9. S. Senderoff and A. Brenner, J. Electrochem. Soc., 101, 16 (1954).

10. T. Vargas and D. Inman, Euchem Conf., Abstract B2 (1982).

11. I. Ahmed, W. A. Spiak and G. J. Janz, J. Appl. Electrochem., 11, 291 (1981).

12. D. Inman, J. C. L. Legey and R. Spencer, Electroanal. Chem., 61, 289 (1975).

13. D. Inman, Dj. Jovanovic and S. H. White, Electroanal. Chem., 43, 37 (1973).

14. F. Lantelme, J-P. Hanselin and M. Chemla, Electroanal. Chem., 97, 49 (1979).

15. S. H. White, C. Bernard and D. Inman, unpublished work, 1978.

16. T. Berzins and P. Delahay, J. Amer. Chem. Soc., 75, 555 (1953).

17. F. Lantelme, J-P. Hanselin and M. Chemla, Electrochim. Acta, 22, 1113 (1977).

18. G. J. Hills, D. J. Schiffrin and J. Thompson, Electrochim. Acta, 19, 657 (1974).

19. G. A. Gunawardena, G. J. Hills and I. Montenegro, Discussions of the Faraday Soc., 12 (1977).
TABLE 1
DATA FOR DIFFUSION OF Cr(II) IONS IN LiCl-KCl EUTECTIC MIXTURE

| Method     | Electrode Materials | Temperature °C | $10^5 D_{Cr(II)}$ cm$^2$sec$^{-1}$ | References |
|------------|---------------------|----------------|-----------------------------------|------------|
| Calculated | -                   | 450            | 1.78                              | 13         |
| Reduction  | CP                  | 500            | 1.53                              | 12         |
| Oxidation  | CP                  | 500            | 2.53                              | 12         |
| Oxidation  | CA                  | 425            | 1.00                              | This Work  |
| Oxidation  | CV                  | 425            | 1.50                              | This Work  |
| Oxidation  | NPV                 | 425            | 1.25                              | This Work  |

CP = Chronopotentiometry; CA = Single Potential Step; CV = Cyclic Voltammetry; NPV = Normal Pulse Voltammetry
TABLE 2
POTENTIOSTATIC TRANSIENT ANALYSIS VIA LOG LOG PLOTS OF THE
PRE-MAXIMA AND POST-MAXIMUM REGIONS AT 425°C
Gold Electrode = 0.4 cm²
Concentration of Cr²⁺ = 8.75 x 10⁻⁶
Potential of Cr/Cr⁺ Electrode = -0.751 vs. Ag/Ag⁺

| Pot. Step | J(max) | t(max) | Slope/ | No. of | Time | Slope/ | 10⁶D |
|-----------|--------|--------|--------|--------|------|--------|------|
| mV        | mA/cm² | msec   | Intercept | Nuclei | Range | Intercept | cm² sec |
| -0.139    | 16.875 | 98     | 0.329    | 1.52   | 0.25-0.50 | -0.518 | 8.25 |
|           |        |        | -2.114   |        |       | -2.961   |      |
| -0.129    | 13.5   | 140    | 0.424    | 1.30   | 0.30-0.50 | -0.525 | 7.96 |
|           |        |        | -2.18    |        |       | -2.969   |      |
| -0.124    | 11.5   | 175    | 0.528    | 1.20   | 0.35-0.50 | -0.513 | 7.88 |
|           |        |        | -2.211   |        |       | -2.971   |      |
| -0.119    | 9.5    | 250    | 0.603    | 0.95   | 0.30-0.50 | -0.427 | 8.52 |
|           |        |        | -2.311   |        |       | -2.954   |      |
| -0.109    | 5.625  | 500    | 0.538    | 0.31   | -      | -        | -    |
|           |        |        | -2.793   |        |       |          |      |

TABLE 3
CALCULATION OF THE NUCLEAR RADIUS FROM GALVANOSTATIC CHARGING CURVES
Gold Substrate Electrode Area = 0.4 cm²
Double Layer Capacitance = 30 μF/cm²
Atomic Wt Metal = 51.996 Density of Metal = 7.1 gm/cm³ at 20°C
No. of Nuclei = 310000 1510000
(see Table 2)

| Eff. Over- | i | t(max) | it(max) | Nuclear Charge Corr. | Nr³ cm⁻³ | Radius | Radius |
|------------|---|--------|---------|----------------------|-----------|--------|--------|
| Potential  | mA| msec   | μCb    | 10⁶ μCb  | 10⁸ μCb | 10⁵ cm | 10⁵ cm |
| -0.154     | 10| 59     | 588     | 577.1     | 1.046     | 3.23   | 1.91   |
| -0.146     | 8 | 69     | 552     | 541.2     | 0.981     | 3.16   | 1.87   |
| -0.139     | 6 | 102    | 612     | 601.3     | 1.090     | 3.28   | 1.94   |
| -0.126     | 4 | 170    | 680     | 669.5     | 1.214     | 3.40   | 2.00   |
| -0.109     | 2 | 420    | 840     | 829.7     | 1.504     | 3.65   | 2.15   |

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Fig. 1. Cyclic voltammograms for the reduction of $K_3MoCl_6$ on gold electrodes, scan rate 50 mV/sec in molten: a) ZnCl_2-KCl (67-33 mol%), temp. 350°C, $C = 2.61 \times 10^{-2}$ mol/kg, $A = 0.57$ cm$^2$; b) LiCl-KCl (59-41 mol%), temp. 550°C, $C = 5.06 \times 10^{-4}$ mol/kg, $A = 0.4$ cm$^2$. Potential vs. the Ag/Ag$^+$ (0.16 mol/kg) reference electrode.

Fig. 2. Cyclic voltammogram (scan rate 100 mV/sec) for reduction-oxidation of Cr(II) ($C = 4.99 \times 10^{-3}$ mol/kg) in molten LiCl-KCl (51.49 mol%) at a gold electrode (0.4 cm$^2$ at 425°C. Potential vs. the Ag/Ag$^+$ (0.16 mol/kg) reference electrode.
Fig. 3. A series of cyclic voltammograms acquired on three different substrates for the reduction of Cr(II) ions at three different concentrations at 500 mV/sec: a) gold flag, CP -751 vs. Ag/Ag(I) ref. at 425°C, C2; b) copper flag(1), CP -738 vs. Ag/Ag(I) ref. at 425°C, C3; c) copper flag(2), CP -723 vs. Ag/Ag(I) ref. at 450°C, C4; d) nickel flag, CP -723 vs. Ag/Ag(I) ref. at 450°C, C4.

Fig. 4. Current reverval chronopotentiograms acquired for the reduction of Cr²⁺ at two different concentrations on a gold electrode: a) conc Cr²⁺≈ 9 x 10⁻³M; b) conc Cr²⁺≈ 6 x 10⁻³M. Applied current density 5 mA cm⁻²; t = 425°C.
Fig. 5. The influence of applied current density on the initial stages of the potential-time transients observed at a gold electrode during the reduction of Cr$^{2+}$ ions. 

a) $i_c = 25$ mA cm$^{-2}$; b) $i_c = 15$ mA cm$^{-2}$; c) $i_c = 5$ mA cm$^{-2}$.

Fig. 6. Cathodic chronoamperograms for gold electrode deposition of Cr at increasingly negative potential steps: 1 = -139, 2 = -129, 3 = -124, 4 = -119, 5 = -109 mV vs. Cr/Cr(II). RP is 0 mV vs. Ag/AgCl (0.163m) in LiCl-KCl at 450°C.
Fig. 7. Potentiostatic transients for the reduction of Cr(II) ions on a Ni electrode at 450°C. Potential steps: 1 = -67 mV; 2 = -77 mV; 3 = -87 mV; 4 = -107 mV; 5 = -127 mV vs. Cr/Cr(II) potential.

Fig. 8. Analysis of potentiostatic growth transients for Cr deposition on gold substrates.
Fig. 9. Cyclic voltammograms acquired on different electrode substrates showing the interaction of deposited Cr with the base metal. (a) Gold substrate at 425°C; (b)-(c) Nickel substrate at 450°C. Scan rate = 0.5 V sec⁻¹.

Fig. 10. Potential time analysis of galvanostatic transient for Cr deposited on chromium coated copper. The slope gives n = 1.999 and from the intercept $E_{\tau/4}$ is calculated to be -0.811 mV vs. reference. $E_{\tau/4} = -0.763V$ based upon $E^0$ and concentration.