THE ELECTROCHEMISTRY OF TANTALUM IN FUSED CHLORIDES

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ABSTRACT

Solutions of tantalum ion in 60:40 mole % CsCl-KCl, prepared by the in-situ anodic oxidation of high purity tantalum metal in the potential range -100 to +200 mV wrt a Ag/AgCl(0.01N)CsCl-KCl/reference electrode, were investigated by a number of electrochemical techniques. The average charge to atom ratio was between 3.36 and 3.77 for the tantalum species thus prepared. The reduction of the tantalum ions in solution occurred in the potential range -200 to -400 mV wrt the reference electrode and resulted in one main reduction process, the product of which was tantalum metal and an unidentified solid product.

The detailed electrochemical results are presented and discussed in conjunction with recent developments in the chemistry of tantalum.
INTRODUCTION.

The growing importance of tantalum as an industrial material has emphasised the need for alternative, more direct routes for its extraction and forming. The metal is obtained commercially either by metallothermic reduction of the penta-fluoride/penta-chloride, or by electrochemical reduction of the potassium hepta-fluoride dissolved in alkali-metal halide baths. The Mellors & Senderoff process which involves pure molten fluorides, enables both electroplating and electroforming of tantalum to be achieved. The need for lower temperature, less corrosive plating baths has been emphasised and the molten alkali-metal chlorides have been suggested as alternative baths. This paper reports some results obtained for the reduction of tantalum halides dissolved molten CsCl-KCl (60:40 mole %) in the temperature range 600-800°C. At the same time some of the complicating factors arising from the complex chemistry of tantalum are reviewed.

Tantalum may exist in a variety of oxidation states ranging from +5 to -1, in which many compounds have still not been well characterised. The covalent nature of the higher oxidation states means that volatility of the compounds is high at relatively low temperatures. A feature of tantalum chemistry is the ability of the element to form metal-atom cluster compounds in the lower oxidation states. The central unit $\text{Ta}_n\text{Cl}_{12}^{n^+}$ where $n = 2, 3, 4$, has been synthesised recently using molten alkali-metal chloride melts in which to carry out the conproportionation reaction:

$$20 \text{MCl} + 16\text{Ta} + 14\text{TaCl}_5 \xrightarrow{T \text{, 24 hrs.}} 5\text{M}_4\text{Ta}_6\text{Cl}_{18}$$

where $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$. The temperature can vary between 500-800°C depending on $\text{M}$. This reaction is carried out in a closed system which suggests that the reaction would be displaced to the left if $\text{TaCl}_5$ was readily removed.

These cluster compounds can be characterised by their X-ray patterns and to some extent their solution (aqueous or non-aqueous) colours and spectra. It is also known that tantalum chlorides in the pure state can undergo disproportionation reactions at relatively low temperatures. The influence of solvation on such processes when the pure halide is dissolved in a molten chloride is not well established, but binary phase data gives some guide to the relative stabilities of tantalum chlorides in molten alkali chlorides (see Table 1).

These data suggest that for example the reaction

$$\text{TaCl}_5^{-}(1) \Leftrightarrow \text{TaCl}_5(g) + \text{Cl}^- (\text{soln})$$
lies well to the right in lithium chloride, resulting in unstable solutions. In CsCl stable solutions of TaV could be expected (see vapour pressure data) but the marked increase of stability of the lower oxidation states in the presence of the softer chloride ions with next nearest neighbour Cs* ions (S.H.A.B. concept), may preclude their formation.

Two types of equilibria are important to the understanding of the molten salt solution chemistry of tantalum.

(a) Homogeneous equilibria, e.g.

\[ 2\text{Ta}^{IV}\text{Cl}_6^{-}\text{(soln.)} \rightleftharpoons \text{Ta}^{V}\text{Cl}_6^{-}\text{(soln.)} + \text{Ta}^{III}\text{Cl}_5^{2-}\text{(soln.)} + \text{Cl}^{-}\text{(soln.)} \]

\[ \text{Ta}^{IV}\text{Cl}_4^{-}\text{(soln.)} + \text{Cl}^{-}\text{(soln.)} \rightleftharpoons \text{Ta}^{IV}\text{Cl}_6^{2-}\text{(soln.)} \]

(b) Heterogeneous equilibria, e.g.

\[ \text{Ta}^{V}\text{Cl}_6^{-}\text{(soln.)} \rightleftharpoons \text{Ta}^{V}\text{Cl}_5^{-}\text{(gas)} + \text{Cl}^{-}\text{(soln.)} \]

\[ 5\text{Ta}_6\text{Cl}_{18}^{4-}\text{(soln.)} \rightleftharpoons 4\text{Ta(solid)} + 14\text{TaCl}_5^{2-}\text{(soln.)} - 16\text{Cl}^{-}\text{(soln.)} \]

The identification of the oxidation state of the tantalum metal ions in solution whether they are added as the pure chloride or anodised into the melt will be dependent (as can be deduced from these equilibria) on solvent cations, anions, and the temperature. Consequently the thermodynamic redox potentials which will be controlled by these equilibria, will lead to a composition dependence of the electrochemical reduction processes. The very nature of many of the solution species will result, a priori, in electrode processes which are severely polarised by coupled chemical processes. Some of these factors will be discussed in more detail in a subsequent publication.

The point we wish to make here is that the choice of alkali-metal halide other than fluoride leads to complications which must involve, intimately, the chemistry of many tantalum species which are currently still being characterised. The choice of the molten CsCl-KCl medium was an attempt to minimise the complications so that a clearer picture of the overall electrochemical process was possible.

EXPERIMENTAL.

The 60:40 mole % CsCl-KCl mixture was prepared by mixing Analar CsCl and KCl in the correct proportions and drying the mixture under
vacuum up to a temperature of 300°C. Dry HCl gas was then passed through the mixture, with continued heating, until fusion took place. Chlorine was then bubbled through the melt for 20 mins, followed by argon sparging to remove the chlorine and HCl. Finally the mixture was pre-electrolysed, under argon, at 2V between two vitreous carbon electrodes until a minimum current density of about 50 micro A cm$^{-2}$ in four hours was achieved. The density of CsCl-KCl was estimated from the density of the pure components assuming ideal behaviour.

The melt was contained in a vitreous carbon pot within a silica envelope which was capped with a water-cooled brass head. Seven holes in the brass head allowed entry of the electrodes and other cell components, vacuum being ensured by means of O-Ring seals.

Platinum or tantalum was fabricated into flag electrodes by cutting from a thin 0.125-0.25 mm sheet, a 2 mm square end with a 0.2 mm projection.

Vitreous carbon electrodes consisted of 3 mm rods which were simply allowed to dip about 2 mm into the melt. The electrode area was estimated by in situ comparison of the results obtained with the v.c. electrode with those obtained with other electrodes during the same experiment. The vitreous carbon pot which contained the melt, was generally used as the counter electrode. The reference electrode (contained within a thin supremax glass (Jena Ltd.) membrane) was based on the Ag/Ag(I) couple (O.01 mole fraction) in CsCl-KCl.

For the chronopotentiometric experiments a constant current generator was used in conjunction with a high input/low output impedance operational amplifier (Type 'O') and a storage oscilloscope (Tektronics 564). Similarly for linear sweep experiments a voltage ramp generator was used in conjunction with a Wenking potentiostat and an X-Y recorder or storage oscilloscope for fast sweeps.

RESULTS.

(a) General observations.

The solutions for electrochemical study were prepared by in-situ anodic oxidation of high purity tantalum metal at potentials between -100 and +200 mV w.r.t. the Ag/AgCl 0.01 mole fraction. The solutions were a red-purple colour and it was observed that, at the end of each experiment, tantalum metal had been deposited over all the surfaces in contact with the melt. On the basis of the number of coulombs passed, the total weight
loss of the anode, the ratio of charge per atom of tantalum was found to range between 3.36 and 3.77. Previous workers have reported values of the ratio of charge per atom between 3.87 and 4.2 for pure CsCl and about 3.2 for KCl. It was therefore inferred that, although the main products of the anodic oxidation were Ta(III) and Ta(IV), lower oxidation states may also have been formed, which subsequently disproportionated to give tantalum metal (see equation 5 perhaps). The resultant solutions were quite stable and produced no TaCl₅ sublimate which had been observed when LiCl-KCl eutectic melts were used. Potentiometry gave a value for n close to four.

The vitreous carbon, platinum, gold microelectrodes, and the vitreous carbon crucible all registered the same potential as the tantalum electrode about 10 mins following an anodic dissolution, confirming the presence of a disproportionation reaction in solution, producing a coating of tantalum metal. A series of electrochemical measurements was carried out mainly at 780°C (except where indicated) on solutions whose concentrations, (based on n = 4) were between 10⁻² to 10⁻¹ molal.

(b) Chronopotentiometry.

In general one well-defined and reproducible transition time was observed over a wide range of current densities on different electrode materials in the temperature interval 630°C - 780°C, Fig. 1 (a), (b), (c), (d). At the lower concentrations and temperature a poorly defined second wave was often observed, Fig. 1 (c), (d). The current reversal chronopotentiogram in Fig. 1(b) shows the limiting anodic oxidation of the platinum electrode, the limiting cathodic deposition of alkali metal and the existence of only one other redox process. When T° was plotted against 1/i the result was a straight line at the higher current densities which passed through the origin. The correspondingly more sensitive plot of i T° versus i, is shown in Fig. 2 (a). The values of i T°/AC at high current densities remained essentially constant on different electrodes, any scatter can be attributed to an imprecise knowledge of the electrode area and the concentration. (Table II)

The electrode potential when plotted against log (T° - t°/t°) gave reasonably straight lines at shorter transition times (i.e. higher current densities) but became S shaped at longer transition times. Alternatively plots of the electrode potential versus log (T° - t°) were reasonably straight for longer transition times (low current densities) but were curved at shorter times.

The values of n calculated from the slopes of the plots varied with current density and were non-integral lying between 1.5 to 3.5 for f(t) =
\[ \left( \frac{t^{\frac{3}{2}} - t^{\frac{1}{2}}}{t^{\frac{3}{2}}} \right) \text{ and } 1 \text{ and } 2 \text{ for } f(t) = \left( t^{\frac{3}{2}} - t^{\frac{1}{2}} \right). \]

The quarter wave potential at 780°C became more anodic as the current density increased eventually passing through a minimum and becoming more cathodic at the highest current densities, Fig. 2(b). The anodic shifts were less pronounced at lower temperatures. In addition the quarter wave potentials became more cathodic as the concentration was increased.

Current reversal at any point along the forward (cathodic) wave (at 780°C) resulted in rather broken and, in some cases depending on applied current and concentration, rather poorly shaped reverse waves. (Fig. 3 (a)(b). The ratio of the forward transition time to that of the total reverse transition time tended to unity as the length of the forward transition time increased. The ratio is expected to be unity for an insoluble product. In addition, a plot of \( \tau_f \text{ versus } \tau_r \) is a straight line passing through the origin which suggests that only reduced material was being oxidised.

Constant anodic current pulses of varying length (applied to produce tantalum ions by the anodic dissolution of a micro tantalum electrode in melts which were previously essentially tantalum-ion free) were followed by cathodic pulses and the resulting chronopotentiograms recorded. Typical transients are shown in Fig. 3 (c) (d). Only one cathodic wave was observed. The ratio of the forward electrolysis time \( \tau_f \) to the reverse transition time \( \tau_r \) is dependent on both the time before reversal and the steady-state potential attained before current reversal.

A plot of \( \frac{\tau_f}{\tau_r} \) at constant \( \tau_f \) versus the steady-state potential is shown in Fig. 2(c). A linear portion between -200 and +200 mV corresponds to \( \frac{\tau_f}{\tau_r} = 4 \). At higher anodic overpotentials the ratio falls to a value of less than two. The theory for this electroanalytical method has been given by Kisza and Twardoch. For \( i_a = i_c \), and \( n_a = n_c \)

\[
\frac{\tau_f}{\tau_r} = 4
\]

where \( i_a \) and \( i_c \) are the anodic and cathodic current densities respectively.

Thus in the middle overpotential region, -200 + 200 mV, the species produced by anodic dissolution is the one reduced by the following cathodic current (a non equilibrium situation).

(c) Cyclic sweep voltammetry.

This technique was applied in a limited way only. At 680°C one cathodic wave
was seen down to the cathodic limit. Three ill-defined anodic peaks were observed during the reverse sweep. A plot of $I_p$ ('or the cathodic peak) versus $\nu^2$ (at high sweep rates) for the case of a vitreous carbon electrode is shown in Fig. 2(d). $I_p/\nu^2$ decreases as the sweep rate increases becoming constant at high sweep rates.

(d) Potential controlled reduction.

At 680°C tantalum ions produced by anodic oxidation of Ta were reduced on to the vitreous carbon crucible at -400 mV (vs. Ag/Ag(I) 0.01 mole fraction), using an isolated counter electrode compartment. Exhaustive reduction at this potential showed that almost as much charge was required to reduce the ions as was used to dissolve the tantalum initially, indicating that the ions were reduced to metal. The well adhering reduced material on the crucible was removed from the surface, washed with distilled water to remove any salts and submitted to X-ray powder analysis. Lines for tantalum as well as for an additional phase were seen. These results are shown in Fig. 4.

Potentiostatic reductions at -300, -400, -500, -600 and -1000 mV w.r.t. the silver reference electrode were performed, using nickel cathodes at 780°C. On completion of the experiment the loosely adherent black powdery material was washed off with distilled water and X-rayed. The results at all the applied potentials were similar. Strong lines for tantalum were seen, but additional lines for some other phase present in small proportions were also registered. but could not be identified. The powder was not affected by dilute mineral acids.

DISCUSSION.

The results obtained for the charge per atom, the potentiometry and the colour of the melt suggest that in the CsCl-KCl solutions containing oxidised tantalum an equilibrium exists between two (or more) oxidation states. From Table I it can be deduced that $K^+$ ions stabilise Ta(IV) whereas $Cs^+$ ions stabilise both Ta(IV) and Ta(III). The stability of lower polynuclear species is unknown but environments of $Cs^+$ ions and $K^+$ ions are certainly favourable. Thus equilibria typified by

$$4TaCl_5^{2-} \leftrightarrow 3TaCl_6^{2-} + Ta + 2Cl^-$$

or

$$18TaCl_5^{2-} \overset{k_a}{\longrightarrow} 6TaCl_6^{2-} + Ta_6Cl_{18}^{4-} + Ta_6Cl_{18}^{2-} + 18Cl^-$$

may be envisaged. Consequently the exact nature of the reduction process
is difficult to identify since the precise nature of these solution entities is unknown. The sequence of reduction potentials will be markedly dependent on the stability and concentration of the ions present in solution, and the overpotential (v.i.).

The experimental observations and results do not allow at this stage a specific choice of model to be made. The decrease in $i^*$ with increasing $i$ at low currents Fig. 2(a), suggests that the surface concentration of the reducible species is augmented by some process other than diffusion. At these high temperatures the influence of convective mass transfer is serious. Measurements for the reduction of silver ions, at similar concentrations to those used for tantalum, at platinum electrodes in the same melt also showed an increase of $i^*$ versus $i$ at low applied current densities (of the order of 15-20 mA cm$^{-2}$). As can be seen from Fig. 2(a) for the tantalum system, the increase occurs in the range 30-70 mA cm$^{-2}$. This suggests that an alternative mode of concentration enhancement must be sought. Two possibilities arise through chemical reactions coupled to the electrode process, which can be illustrated through equations 6 and 7.

1. Slow preceding chemical reaction.

If the reciprocal of $k_b$ is of the same order of time as the observed transition time then an enhancement of the reducing species in this case Ta(III) would occur, whereas at transition times (high currents) less than $1/k_b$ the electrochemical process would be too rapid for the influence of the chemical reaction to be observed.

2. Post chemical reaction.

If the reduction of Ta(III) was to occur only at high overpotentials, then Ta(IV) would be reduced initially and the concentration of Ta(IV) could be augmented by a regeneration process via reaction - following the one electron reduction process thus

$$Ta(IV) + e \longrightarrow Ta(III)$$

The electron transfer process would have to occur four times for every once for the chemical reaction giving an overall process

$$Ta(IV) + 4e \longrightarrow Ta$$

The anodic shift of $E^*/\alpha$ with increasing current density supports these mechanisms, as do the current reversal experiments and the controlled potential reductions which produced metal, albeit a powdery deposit with some non-metallic secondary material.
The uncertainty of the reducible species together with the complexity of the reaction schemes would suggest that the simple interpretation of the potential time analyses could be misleading. Clearly more work, especially using controlled potential techniques, is required.

In general terms, two important conclusions can be drawn from this work. The success of the Mellors and Senderoff process for refractory metal deposition was partly a result of the considerable simplicity of the chemistry of refractory metal ions in the presence of hard fluoride ions. Further, the design of any new process based on chloride melts must take account of the complex solution chemistry which exists (but see also the case of molybdenum $^{13,14}$), and it is unlikely that any major advantage can be achieved through the direct use of these melts. However the application of chloride-fluoride mixed melts suitably designed, might achieve considerable simplification.

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|    | MPt °C | Cong. opd. | MPt °C | Colour | MPt °C | Colour | MPt °C | Colour | MPt °C | Colour |
|----|--------|------------|--------|--------|--------|--------|--------|--------|--------|--------|
| LiCl | 605    | LiTaCl₆    | 350    | yellow | -      | -      | -      | -      | Li₄Ta₆Cl₁₈ | Green |
| NaCl | 800    | NaTaCl₂₆   | 484    | "      | -      | -      | -      | -      | Na₄Ta₆Cl₁₈ | "      |
| KCl  | 772    | KTaCl₆     | 420    | "      | K₂TaCl₆ | 732 | purple | K₂TaCl₅ | 560 | Red | K₄Ta₆Cl₁₈ | "      |
| RbCl | 717    | RbTaCl₆    | 475    | "      | Rb₂TaCl₆ | 756 | "      | Rb₂TaCl₅ | 642 | "      | Rb₄Ta₆Cl₁₈ | "      |
| CsCl | 642    | CsTaCl₆    | 548    | "      | Cs₂TaCl₆ | 796 | "      | Cs₂TaCl₅ | 710 | "      | Cs₄Ta₆Cl₁₈ | "      |

**TABLE I.**
| Temp. (°C) | Density (gm cm\(^{-2}\)) | Electrode | Electrode Area (cm\(^2\)) | Conc. (molal) | \(i_T^{\frac{1}{3}}\) (mA sec\(^{\frac{1}{3}}\)) | \(i_T^{\frac{3}{2}} / AC\) (mA sec\(^{\frac{3}{2}}\) cm\(^{-3}\) Kgm moles\(^{-1}\)) | \(E_{\text{E}}\) (mV) |
|-----------|----------------|-----------|----------------|-------------|----------------|------------------------------------------|----------------|
| 630       | 2.544          | Pt        | 0.13           | 0.022       | 14.0          | 4900                       | ca. -140 |
| 630       | 2.544          | Ta        | 0.13           | 0.022       | 14.0          | 4900                       | ca. -120 |
| 630       | 2.544          | Au        | 0.10           | 0.022       | -             | -                          | ca. -60  |
| 680       | 2.495          | Vit C     | 0.26           | 0.0014      | 1.8           | 4950                       | -190 to -250 |
| 680       | 2.495          | Pt        | 0.115          | 0.0014      | 0.80          | 4970                       | -190 to -250 |
| 780       | 2.400          | Pt        | 0.110          | 0.0013      | 0.70          | 4900                       | -210 to -270 |
| 780       | 2.400          | Pt        | 0.110          | 0.0040      | 2.00          | 4550                       | -245 to -350 |
| 780       | 2.400          | Pt        | 0.110          | 0.012       | 6.40          | 4850                       | -255 to -350 |
| 780       | 2.400          | Pt        | 0.090          | 0.039       | 13.00         | 37.00                      | -315 to -360 |

**TABLE 2**

Chronopotentiometric data for the reduction of Ta from CsCl-KCl (60-40 mole %) melt.

* vs. Ag/Ag(I) 0.1 mole fraction in CsCl-KCl
Fig. 1.
Chronopotentiograms for the reduction of tantalum ions from a CsCl-KCl melt.

a) Pt electrode; area 0.11 cm$^2$; T = 780$^\circ$C; conc. = 0.0012 m;
   x = 0.05 sec/div.; y = 0.1 V/div.; i = (t to b) 14.4, 12.7 & 11.3 mA.

b) Pt electrode; area = 0.13 cm$^2$; T = 630$^\circ$C; conc. = 0.022 m;
   x = 2 sec/div.; y = 0.5 V/div.; i = 21.4 mA.

c) Pt electrode; area = 0.13 cm$^2$; T = 630$^\circ$C; conc. = 0.022 m;
   y = 0.1 V/div.; x = (t to b) 0.2, 0.1 & 0.05 sec/div.;
   i = (t to b) 21.4, 21.4, & 26.0 mA.

d) Ta electrode; area = 0.10 cm$^2$; T = 630$^\circ$C; conc. = 0.022 m;
   x = 0.2 sec/div.; y = 0.1 V/div.; i = (t to b) 21.4, 17.1, 14.4 & 12.7 mA.
Fig. 2.

a) $T_f = 4.3$ sec. for the reduction of tantalum ions in CsCl-KCl at 780°C.

b) Quarter wave potential as a function of applied current, for the reduction of tantalum ions in CsCl-KCl at platinum electrodes.

c) Ratio of forward anodic electrolysis time to reverse transition time versus anodic electrode potential at 630°C tantalum electrode.

d) Peak current versus (sweep rate) for the reduction of tantalum ions in CsCl-KCl at 680°C.
Fig. 3.

Current reversal chronopotentiograms of the reduction of tantalum ions on to platinum electrodes at 780°C in CsCl-KCl melt.

a) Area 0.11 cm\(^2\), conc. 0.0013 m, i = 1.18 mA, x = 0.05 sec/div.
y = 0.1 V/div.

b) Area = 0.1 cm\(^2\), conc. = 0.012 m, i = 4.9 mA, x = 0.5 sec/div.
y = 0.1 V/div.

Anodic-cathodic chronopotentiograms on tantalum electrodes at 630°C in a CsCl-KCl (60:40 mol %) melt. Electrode area ca. 0.12 cm\(^2\).

c) i = 2.1 mA: x = 2 sec/div.; y = 0.2 V/div.

d) i = 21.4 mA: x = 2 sec/div.; y = 0.2 V/div.
X-RAY POWDER DIFFRACTION PATTERN FOR ELECTRODEPOSITS

Fig. 4.

Cobalt radiation: a) Tantalum:
   b) Controlled potential reduction, CsCl-KCl (60 - 40 mol %), 780°C, i) -800 mV vs. Ag/Ag(I)
       0.01 mole fraction; ii) -400 mV vs. Ag/Ag(I) 0.01 mole fraction; iii) -300 mV vs. Ag/Ag(I)
       0.01 mole fraction;
   c) Pure CsCl-KCl (60:40 mole %).