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REVIEW

*The production of refractory metals by the electrolysis of molten salts; design factors and limitations**

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The following basic physico-chemical and electrochemical factors, along with the considerations of electrochemical engineering science, are all important in the optimum design of electrolytic cells for the winning, refining, plating and forming of refractory metals: (a) anionic composition of the molten salt solvent; (b) cationic composition of the molten salt solvent; (c) concentration of the solute; (d) temperature of operation of the cell; (e) cathode potential; (f) cathode current density; and (g) acid-base, redox and complexation reactions that can be carried out in the electrolytic bath. In addition, practical limitations arise from such factors as the corrosion of cell and electrode materials, the hydrolysis of many of the hygroscopic salts employed as solutes and solvents and the reactions that occur at the counterelectrodes. More fundamental limitations which have been particularly recognized and characterized recently, arise from highly volatile, high-valency state compounds, insoluble cluster-type compounds and disproportionation reactions that involve intermediate valency state compounds. Examples of the above factors and limitations that have been applied or encountered in recent studies of the electrodeposition of titanium, molybdenum and tantalum are given and discussed. Ways to avoid these limitations are suggested and, in addition, scale-up and cell design are considered within the constraints of total energy and conventional economic process costing.

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1. Introduction

The nine transition elements of Groups IVA, VA and VIA of the periodic table are known as the refractory metals because of their high melting points and the refractory nature of their compounds (Table 1). They have become increasingly important in recent years because of the needs of the nuclear and aerospace industries for materials which will withstand extreme conditions and the demands for titanium, niobium and zirconium particularly have increased. Very high quality metal is required for the particular applications and this leads to difficult problems in their extraction and refining [1]. Thus there has been a need to develop both thermal [2, 3] and electrolytic procedures [3, 4] to recover these metals (Table 1). It is generally necessary to upgrade the ore considerably before the metal can be extracted and refined. This, together with difficulties associated with both the thermal and existing molten salt electrolytic routes, has motivated much research work on more favourable electrolytic routes involving molten salts.

It is obviously completely impossible to review all the earlier research work in this area within the confines of this article. Several reviews, however, are available which cover the large number of processes which have been researched, developed and sometimes (but rarely) put into commercial practice in the long history of the electrolytic metallurgy of the refractory metals [5–13].

For most of these metals, electro-hydrometallurgical routes are not viable for one or more of the following reasons:

(a) Thermodynamic data show that most of these metals can only be electodeposited at electrode potentials more negative than those required for hydrogen evolution, even after allowing for hydrogen overvoltage (the exception being Cr).

(b) The metals rapidly take up oxygen and become protected by oxide films in oxidizing environments (this remains a problem even using fused-salt systems).

(c) The metallic ions are often converted to stable oxy-cations in aqueous solutions, e.g. $VCl_3 \rightarrow VOCl$, or the metallic ions undergo redox reactions with the solvent, the metallic ions of low oxidation states (for example Ti^{2+}) reduce water and the metallic ions of high oxidation states (for example Ta^{5+}) oxidize water.

Thus reports of the electrodeposition of pure refractory metals (excepting, of course, chromium) from aqueous solutions can be discounted. Electrolytes based on organic solvents have much to commend them and the application of electolytes of this type (which have been developed for high power–high energy density batteries [14]) to problems in extractive metallurgy may be a fruitful line of research for the future. Generally speaking however, although organic solvents have the extremely useful attribute of a high decomposition voltage, their electrical conductivities, even with added electrolytes, and their solvent properties are, even in the most promising solvents, only as good as water [15]. The electrodeposition of refractory metals from molten salts at high temperatures is thus the favoured route. Senderoff has described the very successful *electroforming* process for the refractory metals (excepting titanium) developed by his team at Union Carbide [16].

It is noteworthy that, notwithstanding the many successful commercial processes for *electrowinning* liquid non-refractory metals (for example, aluminium, magnesium) from molten salts, it is only in the case of tantalum that there are major electrolytic routes in commercial operation which recover a solid metal product [17, 18]. The reasons for this state of affairs are complex, combining accidents of history, conservatism, capital investment, the high costs of preparing suitable feeds for electrolytic operations, etc. Nevertheless, the most noteworthy feature of commercially successful molten-salt electrolytic operations is that they involve liquid metals which are easily separated from the liquid electrolytes after electrolytic production. From this viewpoint, it is unfortunate that the refractory metals have high melting points and although attempts have been made to electrodeposit some of them in the liquid form [19], solvent limitations and materials problems generally preclude the production of these metals at temperatures above their melting points (Table 1).

Much of the research work in the past has been of two main types, that is electrometallurgical work designed to obtain pure metal in whatever

Table 1

Metal	*Melting point* (° C)	*Boiling point* (° C)	*Annual production* (tonnes)	*US* (cap)	*Electrowinning*	*Electrorefining*	*Electroforming*	*Thermal*
Ti	1668	3287	10^4–10^5	10^5–10^6	IPP*	IPP		MPR†
V	1900	3380				IPP	LPP‡	MPR
Cr	1875	2672			LS[a]	LS§	LPP	MPR
Zr	1855	4377			IPP	LS	LPP	MPR
Nb	2468	4742	150	300	LPP		LPP	MPR
Mo	2610	4612				LS	LPP	MPR
Hf	2130	4602	60		IPP	IPP	LPP	MPR
Ta	2996	5425	150	300	IPP		LPP	
W	3410	5660					LPP	MPR

* Industrial or pilot plant
† Major processing route
‡ Laboratory/pilot plant
§ Laboratory scale
[a] Aqueous route

form possible (i.e. dendrites, powders, etc [20]) and quite separate electrochemical investigations of the kinetics and mechanisms of electrode processes using similar, but often simpler and more amenable, systems [21]. It is our view that the coupling of these two approaches in investigations of the natures, morphologies and structures of deposits as functions of the kinetics and mechanisms of the associated electrode processes offers a more fruitful line of development. But, above all, we wish to emphasize that it is now possible to design and optimize electrolytic processes on a firm electrochemical basis and this constitutes our main purpose.

In this paper we intend to show how the industrial (national) requirements of good space–time yields, Y_t, for an electrometallurgical reactor and the minimization of the specific energy requirements, e_s, of that reactor, i.e. process optimization, can only follow from the concomitant use of electrochemical engineering and scientific principles with the particular process. However, because of the special nature of high temperature molten salt processing, two design objectives assume particular importance. These are the specification of the (molten) electrolyte and the form in which the electrowon metal is obtained. Thus the overall design of electrochemical reactors involves considerable feedback–feed-forward loops which might be best modelled using computer system dynamics. In a static approach we shall now examine some of these factors, utilizing some of the relevant features of our recent experimental studies on the electrochemistry of titanium [22], molybdenum [23, 24], chromium [25] and tantalum [26, 27] from molten chloride (fluoride) solvents, a consideration of the successful Union Carbide *electroforming* process [28] and some associated techno-economic studies.

2. Advantages of molten salts as solvents in electrolytic operations

Molten salts possess a number of unique properties which enable efficient electrolytic processing to be achieved. The most important properties are discussed below.

Of the salts which may be considered as solvent components, those of the alkali and alkaline earth halides, together with mixtures of these with aluminium fluoride, all possess very negative free energies of formation. In electrochemical terms this implies a high decomposition voltage for the solvent [29–31]. This decomposition voltage may be decreased when the activity of the deposited solvent metal is lowered, either through its interactions with the solvent cations [32] or through its interactions with the electrode substrate [33, 34], or both.

The good ionic conductivity [2–9 $(\Omega\ \mathrm{cm})^{-1}$] for the above mentioned solvents [35] ensures that, with good cell design, Joule heating in the cell can be used in a controlled way to provide the necessary heat input to the cell contents. The cell current may thus be limited by the rate of Joule heat dissipation and the maximum operating temperature necessitated by the electrolyte properties.

They are powerful solvents for inorganic materials. However, this can be a disadvantage when it comes to choosing electrical and thermal insulating materials for the cell components [36].

Overvoltages due to cathodic polarization are often small [37]. From the point of view of energy efficiency this is a desirable feature, but as we shall see below, mass transfer-controlled processes generally lead to dendritic deposits [38] rather than the coherent massive and continuous deposits which are necessary. However, the energy expended in any cathodic polarization which leads to a massive coherent deposit may be seen as energy well spent in avoiding the subsequent metal recovery/processing needed with dendritic deposits.

Chemical reactions between metal ions and solvents, of the sort cited above for aqueous solutions, are generally absent. However, because of the multiplicity of oxidation states for the refractory metals, interaction between the deposited metal and the solute ions must be carefully controlled [26].

3. Disadvantages of molten salts as solvents in electrolytic operations

As mentioned above, the main disadvantage is that, unless special precautions (Section 6·4) are taken, the metal deposits arising from the electrolysis of molten salt solutions will be dendritic and/or powdery [39]. This product may therefore offer no special advantages over that obtained by conventional pyrometallurgical routes (for example, the Kroll process [2, 3] for titanium), although the purity levels and ease of separation may be more advantageous. This recovery of the deposit from the solidified solvent is a process analogous to the benefication of a crude ore, involving energy intensive and wasteful leaching, grinding and flotation operations which must be followed by suitable consolidation process [39] (arc melting, electron beam melting, etc.).

The hydrolysis of many of the hygroscopic salts employed as solutes and solvents [26, 40, 41] can cause difficulty when their use is required on a large scale, necessitating considerable peripheral handling facilities.

Other disadvantages arise from the high volatility of many of the high valency refractory metal halides (particularly chlorides) and from the propensity of their lower valency halides (particularly chlorides) to form insoluble cluster-type compounds. The disproportionation of intermediate valency state compounds also poses difficulties (e.g. Ti [26, 42]). These topics will be discussed further (Sections 5·3·2 and 5·3·3).

In the case of the concomitant anodic reaction, energy considerations often conflict with cathode product purity because of the nature of the refractory metals and the small scale of the operations (for example, the substitution of oxygen evolution at an inert anode by CO_2/CO at a carbon anode saves electrical energy but those latter products can back-react with the refractory metal deposited on the cathode to produce carbides).

Practical limitations can arise from such factors as the corrosion of cell and electrode materials. Materials problems can also arise through the oxidation of a lower valency state compound by the anode product (for example, chlorine). This in turn necessitates the use of porous diaphragms which, if inorganic [43, 44], are more easily corroded by the melts than are the bulk materials (large surface areas involved).

4. Cell design/optimization

The design and optimization of an electrochemical reactor requires a consideration of the complex interplay of both scientific and socio-economic factors. In general terms, the minimal expenditure of energy and a high space–time yield, are the major factors in optimizing the reactor design. The choice of engineering materials for high temperature operations will also play an important role, particularly from an economic point of view.

The rate of metal production by weight, based on Faraday's laws can be expressed as

$$\frac{dW}{dt} = k\,I\,A\,C_E \qquad (1)$$

where k is a constant depending on the metal and the overall electrode process (kg A^{-1} h^{-1}), I is the current density, A the cathode area and C_E the fractional cathodic current efficiency.

On the other hand, the specific energy is given by

$$e_s = KE_0 + KE_0\frac{(1-C_E)}{C_E} + \frac{K}{C_E}J_{cell}\sum_i R_i + \frac{K}{C_E}\eta_c + \frac{K}{C_E}\eta_a \qquad (2)$$

where

$$K = \frac{nF}{3600 \times \text{at.wt.(M)}} = \frac{1}{k} = \frac{1}{Q_E\rho_M} \qquad (3)$$

where η_c = cathodic overvoltage, η_a = anodic overvoltage, J_{cell} = cell current.

The overvoltages η_i are related to the cell current density, the exchange current densities (which are concentration-dependent) and the limiting current densities. Thus the electrochemical factors for a particular reactor operation can be related to the specific energy requirements of that reactor.

The yield of metal product as a function of electrolysis time and the reactor volume has been expressed as the space–time yield which can be defined as

$$Y_t = \frac{\text{amount of product M produced (m}^3\text{)}}{\text{Electrolysis time} \times \text{cell volume}}$$

$$Y_t = (A_s \times I \times Q_E) \times C_E \qquad (4)$$

where A_S = the specific area

$= \dfrac{\text{Geometric area}}{\text{reactor volume}}$ (m^{-1})

I = current density (A m^{-2})

C_E = cathodic current efficiency (fractional)

Q_E = amount produced per ampere hour at $C_E = 1$ [m^3 $(A\,h)^{-1}$]

$$= \frac{3600 \times \text{at.wt.(M)}}{nF\rho_{\text{M}}}$$

$$\rho_{\text{M}} = \text{density of metal (kg m}^{-3}\text{)}.$$

The space–time yield has dimensions of h^{-1} as expressed above. Y_{t} depends on the current density and the specific area which, in most currently operating electrolytic reactors, is small and is a major factor in their low space–time yields compared with conventional pyrometallurgical reactors (Table 2).

These equations may be combined to give the space–time yield in terms of the rate of metal product, the density of the metal and the specific area, and the specific energy in terms of $Y_{\text{t}}A_{\text{s}}$ and the cell voltage, and the current density.

$$Y_{\text{t}} = \frac{\mathrm{d}WA_{\text{s}}}{\mathrm{d}tA\,\rho_{\text{M}}} \qquad (5)$$

and

$$e_{\text{s}} = \frac{A_{\text{s}}IE_{\text{cell}}}{\rho_{\text{M}}\,Y_{\text{t}}}\,. \qquad (6)$$

From these two expressions the electrochemical conditions for optimal cell operations may be deduced for a given reactor geometry and a particular metal. The need to maximize Y_{t} as a function of I and at the same time minimize e_{s} as a function of I leads to a paradox best optimized by a dynamic systems analysis. To our knowledge such an overall approach has only been attempted for electrochemical machining [45] but would clearly be advantageous in electrometallurgical reactor design.

A final constraint on the cell design which must be carefully considered is the inter-relationship between the cell constituents, reaction products, and the materials used in reactor construction. The necessity of high temperatures has a limiting effect on the choice of materials for construction, and it is only in more recent years that a wider range of suitable materials has become available. The design of the new Alcoa cell [46] which uses $\text{SiO}_2/\text{Si}_3\text{N}_4$ refractory bricks [47] lining a glass bricked vessel, illustrates the use of new materials and ingenuity in design.

Table 2. Some space–time yields for different industrial practices involving fused-salt electrowinning (based on the reactors' volumes)

Metal	*Process*	$Y_{\text{t}}(\text{h}^{-1})$
Aluminium	Hall Heroult	$0{\cdot}45 \times 10^{-4}$
Magnesium	German/GF	$12{\cdot}7 \times 10^{-4}$
Sodium	German	$40{\cdot}2 \times 10^{-4}$
Titanium	NJ Zinc Co. (pilot plant)	$9{\cdot}1 \times 10^{-4}$
Tantalum	Union Carbide	$0{\cdot}68 \times 10^{-4}$
Iron	Open hearth	$1{\cdot}6 \times 10^{-2}$
	Spray steel making	$7{\cdot}76 \times 10^{-1}$
Copper	Converting	$2{\cdot}7 \times 10^{-2}$

5. Electrolytic baths

5.1. *Solvents*

Any molten solvent to be used in an electrolytic operation should have the following properties and attributes. It should have (i) a low vapour pressure; (ii) as low a melting point as possible; (iii) a high electrical conductivity; (iv) a low viscosity; (v) a large decomposition voltage and be (vi) as non-corrosive as possible; (vii) readily purified; (viii) non-polluting and above all (ix) inexpensive.

In spite of the very wide range of molten inorganic solvents, there are very few which possess all the properties listed above. For large-scale operations the choice of solvents can be confined to the alkali and alkaline earth halides and their mixtures with aluminium halides [35] (Table 3). In the present context some oxyanic melts such as borates, phosphates and silicates [35] are appropriate in certain cases.

5.2. *Solutes (feeds)*

In order to avoid expensive preliminary chemical stages, the form of the solute should be as closely related to the original minerals as possible. Of course, ideally it would be desirable to win the metals directly from their minerals and some only partly successful attempts [48] to achieve this have been made. Generally, however, the minerals are both very refractory and thus poorly soluble and, more important, contain undesirable and difficult-to-separate components. The feeds, of course, should be in a form which facilitates their dissolution in the solvent melt. It is in this respect that the very marked degrees of miscibility for molten inorganic materials having a common anion and for reciprocal mixtures are particularly useful. The remarkable solubility of alumina (which can

Table 3

	E^0 *at 500° C* (V)			KE^0 *at 500° C* ($\mathrm{kW\,h\,kg^{-1}}$)		
Metal	*Oxide*	*Chloride*	*Fluoride*	*Oxide*	*Chloride*	*Fluoride*
Hf(IV)	−2·49	−2·2	−4·13	1·49	1·32	2·48
Zr(IV)	−2·45	−1·9*	−4·24	2·88	2·32	4·98
Ti(IV)	−2·09	−1·4*	−3·5*	4·68	3·13	7·83
Ta(V)	−1·76			1·30		
Nb(V)	−1·62			2·34		
Cr(III)	−1·40	−1·34	−3·27	2·16	2·07	5·05
V(V)	−1·26			2·63		
W(VI)	−1·12	−0·2*		0·98	0·17	
Mo(VI)	−0·91	−0·28		1·52	0·47	

* Estimated

be readily obtained from the mineral bauxite) in molten cryolite is no doubt a major factor which has contributed to the success of the Hall–Héroult aluminium electrowinning process. The use of Al_2O_3 in aluminium winning, together with Ta_2O_5/K_2TaF_7 feed in tantalum electrowinning, represent the only examples of processes employing oxide feeds.

A discussion of the factors determining the solubility of a substance is beyond the scope of this paper. Nevertheless, the strengths of the interactions between the cations of the solute and the anions of the solvent on the one hand and that between the anions of the solute and the cations of the solvent on the other hand, are of major importance [49]. In at least one case (Section 5·3·4) the nature of the deposit is affected in a major manner by a change of solvent cation.

5.3. *The resulting solutions*

5.3.1. Loss of feed by volatilization. Fluoride solutes are, on the whole, much less prone to be lost by volatilization from fluoride solvents than are chloride solutes from chloride solvents. (The mixed case is an interesting one but one which has not been fully explored. Fluoride ions will complex refractory metal ions of the highest oxidation numbers more strongly than chloride ions, so that fluoride ions *in the bulk melts* are likely to displace chloride ions from the co-ordination shells of high-oxidation number refractory metal ions [50].)

This effect can be illustrated in the case of tantalum by the measurement of the potential of a tantalum electrode as a function of the number of moles of F^- ions added (Fig. 1). An interpretation in terms of complex-ion formation is complicated by the effect of the disproportionation reaction of the Ta(IV) chloride into Ta(V) fluoride, thus

$$5\mathrm{Ta(IV)} \rightarrow 4\mathrm{Ta(V)} + \mathrm{Ta}^0 \qquad (7)$$

and Ta(V) may then exhibit dynamic equilibria amongst the following species [51]

$$\mathrm{Ta(V)F_6^-} \overset{F^-}{\rightleftharpoons} \mathrm{TaF_7^{2-}} \overset{Cl^-}{\rightleftharpoons} \mathrm{TaF_7Cl^{3-}} \overset{F^-}{\rightleftharpoons} \mathrm{TaF_8^{3-}}. \qquad (8)$$

Partial pressure data for solutions of refractory metal chlorides show that not only do the solvent anions have a specific effect but that the cationic nature of the solvent can be quite important or even critical. Thus the partial pressures of Ti(IV), Zr(IV), and Hf(IV) above lithium chloride solution approach 10^3 Torr but above CsCl solution, the vapour pressures are only of the order of 1 Torr at 1000 K [52, 53]. In the case of the tantalum chlorides, binary phase data give some guide to the relative stabilities of tantalum chlorides in molten alkali chlorides [54, 55]. These data suggest that, for example, the reaction

$$\mathrm{TaCl_6^-}_{(\mathrm{soln})} \rightarrow \mathrm{TaCl_5}_{(\mathrm{g})} + \mathrm{Cl^-}_{(\mathrm{soln})} \qquad (9)$$

lies well to the right in lithium chloride, resulting in unstable solutions ('covalency predominates')

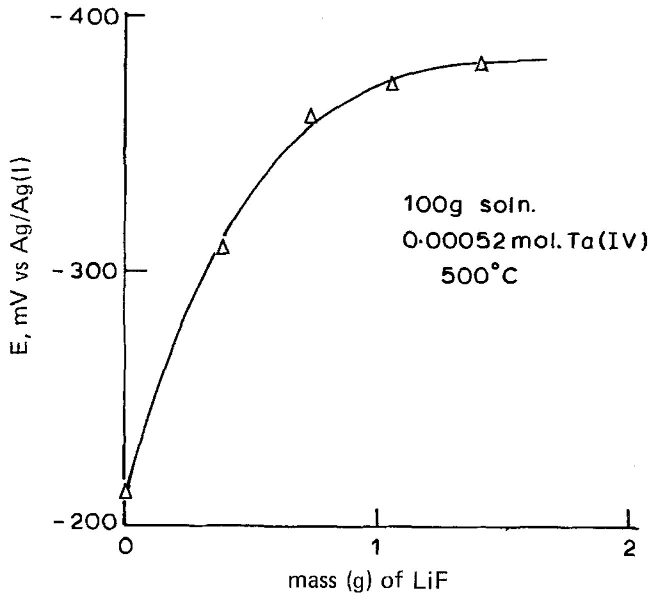

Fig. 1. Electrode potential of a tantalum electrode versus an Ag/Ag(I) reference electrode as a function of weight of LiF added to the Ta(IV) in the LiCl–KCl eutectic.

whereas in CsCl, stable solutions of Ta(V) would be expected (ligand field effect predominates). Unfortunately, the situation is complicated by the increased tendency for lower oxidation states to be formed in the presence of the Cs^+ cation (Equation 13).

Our work with molybdenum further illustrates these points. At any one temperature the thermal stability of the bath (containing $MoCl_3$) increases as the sizes of the alkali metal cations of the solvent increase [56, 57]. Thus, within the confines of relatively cheap solvent chlorides we found the solvent NaCl:KCl of 20 mol%: 80 mol% used at around 750° C, to be particularly advantageous in this respect. But an even more interesting observation [58] in this case, which can be put to good use, is that the thermal stability of the bath increases (i.e. the vapour pressure of the $MoCl_3$ decreases) as the concentration of $MoCl_3$ increases, probably due to the stabilization of $Mo_2Cl_9^{3-}$ species, i.e. $2MoCl_3 + 3Cl^- \rightarrow Mo_2Cl_9^{3-}$, which, as noted above, may be favoured by the presence of cations of low surface charge density (Z/r) [26].

The choice of solvent and solute will place initial constraints on the reactor operating temperature but it may be the optimum cell current and the heat transfer characteristics of the reactor which ultimately determine the operating temperature.

5.3.2. Disproportionation. All the refractory metals may exist in a variety of oxidation states. For example, tantalum exhibits oxidation states ranging from +5 to −1, but many of the compounds have not been well characterized [26]. It is also known that tantalum chlorides in the pure state can undergo disproportionation reactions at relatively low temperatures. The influence of solvation on these processes when the pure halide is dissolved in a molten alkali halide is not well established [55]. Two types of disproportionation equilibria are possible in chlorides, for example, using tantalum as our example, namely

$$2Ta(IV) \rightarrow Ta(V) + Ta(III) \qquad (10)$$

a homogeneous equilibrium; or

$$3Ta_6Cl_{18}^{4-} + 16Cl^- \rightarrow 4Ta + 14TaCl_5^{-2} \qquad (11)$$

a heterogeneous equilibrium.

These equilibria are also evidenced by other refractory metals, for example the addition of fluoride ions to a melt containing Ti(II) (produced by anodic dissolution) led to the enhancement of the disproportionation reaction

$$2Ti(II) \rightarrow Ti + Ti(IV) \quad \text{or } 3Ti(II) \rightarrow Ti + Ti(III) \qquad (12)$$

through the stabilization of the higher oxidation state by fluoride anions. (This behaviour was evidenced by the formation of large quantities of seemingly colloidal titanium throughout the melt).

5.3.3. Polymerization-formation of cluster compounds. Cluster compounds are a particular feature of the lower oxidation states of the heavier refractory metals. Metal atom cluster compounds have been synthesized using molten alkali metal chloride melts [59–61]; for example the tantalum cluster complex $Ta_6Cl_{18}^{4-}$ is produced by the conproportionation reaction

$$20MCl + 16Ta + 14TaCl_5 \underset{24\,h}{\overset{T^0\,C}{\rightarrow}} 5M_4\,Ta_6Cl_{18} \tag{13}$$

where M = Li, Na, K, Rb, Cs. Temperatures vary between 500° C and 800° C depending on M, the reaction being carried out in a closed system to avoid loss of $TaCl_5$. It was argued [59] that the appropriate choice of M^+ will determine (*inter alia*) the success (yield) of the preparation. This choice is made on the relative stabilities of M_2RCl_6, $M_3R_2Cl_9$, MR_4Cl_{11} and $M_4R_5Cl_{18}$. A reasonable choice of M when R is Nb was Na^+ or K^+. The chemical formation of such complex ions is probably kinetically hindered although thermodynamically favoured. Since $TaCl_5$ is readily produced on Ta anodes at high E, it would also appear that electrochemically the anodic formation of clusters is also kinetically hindered [27, 54]. This may have important consequences in electrodeposition. For example, the production of tantalum from $TaCl_{5\,(g)}$ [18] (CIBA process) is feasible and proceeds at a reasonably high C_E (0·85–0·88) because Reaction 13 is hindered. On the other hand, niobium production is achieved only at low current efficiency (0·30) perhaps due to the favoured cluster formation reactions in the presence of NaCl in the melt. Similarly in the case of molybdenum, Senderoff and Mellors reported that the stability and metal plating characteristics decreased with increasing temperature in LiCl–KCl solvent [58]. These observations may be rationalized in terms of the increased reaction rate which produces different polynuclear compounds at the higher temperature, thus changing the bath composition and the electrode process. These examples serve to illustrate how important the complex chemistry of these metals is in determining the nature and quality of the electrodeposition process.

5.3.4. Formation of insoluble oxides and oxyhalides and stable oxy-cations. The oxides are rather refractory materials and it is obviously necessary to ensure their complete solubility prior to electrolysis. The effects of alkali and alkaline earth metal oxides present as impurities may however be more insidious. For example, oxypolynuclear anions or insoluble oxides [27, 54, 56] may be formed (as insoluble films on electrode surfaces) by reaction with lower-valency ions formed as intermediates in the electrodeposition process proper in all-chloride or all-fluoride melts and thus their deleterious effects may be totally unexpected. The deposition of the metal oxides from stable oxy-cations can be a more inherent feature of molten salt electrolysis. For example, when UO_2Cl_2 is dissolved in a halide melt, the stable cation UO_2^{2+} is formed and cathodic reduction gives UO_2 [62]. The differing behaviour of V_2O_5 in LiCl–KCl and $CaCl_2$ has previously been discussed [63].

On the other hand, there is evidence for the formation of stable oxy-*anions* in the aluminium electrowinning bath (for example, $AlOF_5^{4-}$, $AlOF_3^{2-}$) which are discharged at the anode [64]; the formation of $Al_2OF_x^{4-2x}$ ($x = 3$ or 5) at low alumina content has been put forward as a possible precursor in the anode effect. Recently Monnier and co-workers [65, 66] have proposed that the addition of Ta_2O_5 to cryolite results in the formation of oxy-tantalate species and fluorotantalate species whose subsequent reduction is indistiguishable in a chronopotentiometric experiment. This may imply (a) the reduction is preceded by an equilibrium involving these species; (b) that one or other of these is reduced at a potential more cathodic than that of the solvent. The precise nature of such species in cryolite melts is not known but the established technology associated with cryolite suggests that such systems are worthy of consideration as solvents for winning the less noble refractory metals particularly Ti, Ta and Nb, from their oxide/ores. Our current work involves the examination of the behaviour of titanium oxide/fluorides in cryolite melts [67].

In this respect, it is even possible, under certain circumstances, cathodically to deposit the main elements from such stable anions as CO_3^{2-}, SO_4^{2-}, borates, silicates and phosphates [68–73]. It is doubtful whether any general conclusion can be drawn from the fact that it seems to be anions which yield the elements and cations which yield the oxides as deposits.

6. Cell reaction

6.1. *Thermodynamic factors*

Equation 2 shows that the specific energy requirement of an electrochemical reactor depends not only on the cell geometry (IR, C_E) and the electrode kinetics (i.e. overpotentials η_i) but also on the thermodynamics of the overall cell reaction, (the KE_0 term) E_0 is directly related to the free energies of the reactions

$$MO \rightarrow M + \tfrac{1}{2}O_2 \qquad (14)$$

$$MX \rightarrow M + \tfrac{1}{2}X_2 \qquad (15)$$

$$2MX + 2BO \rightarrow 2M + O_2 + BX_2. \qquad (16)$$

The problem arises of minimizing the quantity E_0 for the particular process concerned. A consideration of the thermodynamics of the relevant refractory metal compounds suggests that Reaction 16 may be the most favourable but it will be Cation B-dependent and hence solvent-dependent and must be calculated for each individual case. Within these confines it would be beneficial to work with solutes in their lowest oxidation states (lowest electrochemical equivalent) (Table 3) but as discussed there are complications with the refractory metals because of solvent effects, i.e. complex-ion formation and polynuclear complex formation. Since these effects are not well understood in the case of refractory metals, the data in Table 3 can only act as a guide. It is clear that the recovery of metal from chlorides or oxides consumes a lower specific energy than that from fluoride-based electrolytes. Unfortunately the use of oxide-based systems may be excluded in the cases of the less noble metals because the reduction of the solvent anion, i.e. borate, phosphate, silicate, precedes or parallels that of the desired metal resulting in low current efficiency and/or metal borides, phosphides, silicides, etc. [71, 72]. On the other hand, tungsten [74] and molybdenum [75] have been successfully recovered from mixed borate–phosphate halide melts in massive but non-coherent form. However, the use of fluorides is indicated because of the solubility of oxides in such melts [76, 77], the apparent absence of polynuclear complex-ion formation and the ability, albeit in pure fluorides, to produce coherent plates (Section 6·4).

6.2. *Kinetic factors*

At first sight it might be expected that kinetic limitations would be minimal at the high temperatures at which these processes are operated. However, in the case of the anode reaction which involves oxide species and graphite anodes there is the complication of coupled heterogeneous chemical reactions (dependent on the surface properties of the electrode) the result of which is a lowering of the rate of the anodic reaction [78, 79]. In the case of the cathodic processes three major factors must be considered (i) solute mass transport, (ii) electron transfer and (iii) crystal nucleation and growth. Because of the good solvent properties shown by molten salts the actual concentration of electroactive solute can, in principle, be very high but specific solvent effects may preclude or predetermine the use of certain conditions (Section 5·3). In spite of these restrictions the reactor could be operated at high current densities without interference from mass transport control and the concomitant dendritic growth [if (ii) or (iii) above can be optimized].

Electron transfer involving metal ions at interfaces is generally rapid in molten salt systems at high temperatures (standard exchange current density $> 1\ \mathrm{A\,cm^{-2}}$) although from a superficial examination of results in the literature [57, 58] this may not appear to be the case for refractory metals. For example, the reduction of Mo(III) in NaCl–KCl has the apparent characteristics of a slow charge-transfer process.

$$\mathrm{Mo(III)} + 3e \rightarrow \mathrm{Mo}.$$

Closer experimental examination discloses that the process is controlled by a preceding chemical reaction (involving Mo polynuclear complex ions) and not by a slow electron transfer [23, 24]. Other examples have been quoted in the literature [80] which suggest that when $M^{n+} + ne \rightarrow M$ is irreversible there will be some coupled chemical reaction. At the same time it should be recalled that the reduction of a complexed, high oxidation state metal ion to metal will involve, amongst other things, during the reduction process a shedding of the anionic partners, together with the passage of the atoms from the diffuse multilayer on to the metal electrode in such a way that the new metal atoms can be incorporated into a growing crystal lattice. It was the view that nucleation overvoltages were absent in molten salt processes [81], but recent observations [54, 80] and results [82–84] have indicated otherwise. The importance of the structure of the electrical double-layer and specific anionic effects [85–87] cannot be emphasized enough in relation to an understanding of this aspect of metal deposition and, to date, little or no information is available on refractory metal winning systems [87–89]. All that can be said here is that the remarkable influence that both oxide ions and chloride ions have on coherent metal deposition from fluoride melts may be, at least partially, attributed to double-layer effects. Thus the contribution to the specific energy of the reactor by the cathodic process will be small.

6.3. *Electrolyte conductivity requirements*

The maximum conductivity is exhibited by the fluorides of the lighter alkali and alkaline earth metals and their mixtures so that from the point of view of minimizing the ohmic overvoltage, these solvents are desirable. Of course it must be remembered that the source of thermal power for fused salt electrolytic reactors is this internal Joule heating and therefore this factor must be optimized for the particular reactor design. The high thermal conductivities and the moderately high heat capacities make the heat transfer in a reactor readily controllable by suitable choice of electrolyte mass, surface area to reactor volume ratio, the reactor insulation and the cell current.

The electrolyte resistance will also depend on the electrode geometry and the interelectrode spacing. For solid metal production either rectangular or cylindrical cathodes are used in either parallel or concentric anode geometries. The limitations are the poor specific areas involved (in conventional reactors) and the influence on the cathodic current efficiency of the proximity of anode reaction products (low Y_t). For example in the Union Carbide tantalum electrowinning cell it can be estimated that *IR* losses are of the order of 2·0 V for the separations necessary (0·15 m) for high current efficiency, good recovery and to accommodate the voluminous dendritic cathodic product (see Section 6·4, need for coherent deposit). The high interelectrode resistance will, of course, restrict the maximum cell current (hence Y_t) through the heat transfer/dissipation characteristics of the electrolyte and reactor vessel (in this case some 1·5 kJ s^{-1}).

6.4. *The form of the deposit*

The form of the deposit is much more critical in molten-salt electrolysis than in its aqueous counterpart for a variety of reasons, not least because the solvents do not remain in the liquid state when cathodes are withdrawn from the melts after electrolysis. Thus if the deposits are dendritic, they occlude solidified melt and a major leaching-type operation is needed to separate the metal from the melt [39]. In addition, dendritic deposits mean that the cathodes are dimensionally unstable which may lead to lower current efficiencies and even, in extreme cases, to shorting of the cell [5, 17]. Powdery deposits, arising from secondary electrode processes either involving disproportionation reactions near the surface or chemical reactions between deposited alkali metals and metal ions away from the electrode surfaces, require separation operations which, because of the high metal surface to volume ratios, lead to the gross pick-up of impurities [4]. Secondary deposition of this sort is frequently encountered in poorly designed molten-salt processes.

Liquid metal deposits are ideal (cf. Al and Mg) although in this case the relative densities of the metal and the melt should be such ($>$ unity) that there is sufficient separation between the metal and the anode gases. However, a clean separation of metal and melt can be achieved even if the metal is less dense than the melt (cf. magnesium, sodium, etc.)

The production of alloys of refractory metals in liquid cathodes of metals which are readily separated from the desired refractory metal may be considered as an alternative to coherent, or dendritic deposition. The metals available as liquid cathodes for this process are strictly limited [Zn (boiling point 906° C) Bi (boiling point 1560° C) and Sb (boiling point 1380° C)]. Liquid Sb and Ga have been used to recover actinides such as Th, U [90] and the lanthanons [91]. Recently Ivanovskii reported the use of zinc cathodes to recover zirconium and niobium from a mixed fluoride–chloride bath [92, 93]. Not only does this technique enable ready separation and recovery of the cathode product but it has the advantage of depolarizing the cathode process through alloy formation. This technique warrants a closer examination for the least noble metals where secondary deposition seems to be a major problem (cf. Zr, Hf, Ti). Of course other noble metals might be considered as solvents if one thinks of a two-stage electrowinning/electrorefining programme. The mineral or the concentrate is electrolysed to recover the refractory metal in solution in a liquid metal cathode using a halide/oxide melt. Subsequently the liquid cathode is fed to an all-fluoride bath from which the refractory metal is deposited in a coherent form.

The recovery of primary metal is ensured by using, as solvent, a melt having a much larger decomposition voltage than that of the solute and an inert cathode. If the decomposition voltage of the solute is close to that of the solvent, the use of controlled cathode potentials [versus a third (reference) electrode, not part of the main electrolysis circuit] may avoid the formation of secondary deposits. The application of controlled cathode potentials is obligatory for selectively depositing the more noble metallic components from, say, minerals directly dissolved in molten salts. A manual or feedback control (using a microprocessor and a servomotor controlling the cell current) of cell voltage to maintain the cathode potential sensibly constant versus a reference electrode, will suffice in technological practice. However, current density should not be regarded as the primary variable. The vital point is to control the cathode potential to ensure the primary deposition of the metal required and to ensure that the overall cathodic process is not controlled by the rate of mass transfer of the electroactive species. The latter is difficult to achieve, *a priori*, in molten salts at high temperatures (at one time it was thought to be impossible) but the successes in the all-fluoride and in some chloride systems have indicated the way in which this may be achieved on the premise that control of the electrodeposition of metal by rate processes other than mass transfer, will lead to coherent deposits close to theoretical bulk density, which are readily separated from the solidified melt. Some ways of achieving this state of affairs will now be considered.

Mellors and Senderoff first focused attention on the need to employ fluoride electrolytic baths to obtain refractory metal electroforms in a general way. The process they developed worked well for Zr [94], Hf [95], V [95], Cr [95], Ta [96], Nb [97], Mo [98], and W [98], but not for Ti. The baths were susceptible to anionic impurities, the tolerance for Cl^- and O^{2-} being very low in the case of zirconium [94], and to oxidizing atmospheres. This necessitated inert gas–closed cell operations. Perhaps what is surprising is that, with such markedly different chemical behaviour amongst the refractory metals, a generalized process for forming electroplates is possible.

In their analysis of the process Mellors and Senderoff centred their attention on the effect of solvent cations on the complex anions (for example, TaF_7^{2-} in K_2TaF_7) added to their electroforming baths [96, 99]. In addition, laboratory experiments using chronopotentiometry led to the suggestion that it was necessary for the overall reduction process to involve at least one slow step [96] (electron transfer or reaction control [23]) in order that smooth plates of metal could be produced. Their detailed results do not stand up to more critical analysis. For example, the failure to produce Ti plates and the problems with zirconium deposition may have resulted from secondary deposition because of the small differences between the deposition potentials for these metals and for alkali metal of the chosen solvents. Although the fluoro-complexes in the bulk melts may have only a secondary influence on the deposition potentials, the kinetics of complex formation and/or dissociation are slowly emerging as a key factor. The fact that these solutions were in contact with the respective metals could have led to the production of a lower halide in equilibrium with the high oxidation state which then controlled the deposition process (for example, the situation with Mo and W). On the other hand, the reduction of the tantalum and niobium fluorides may have produced species, based on the cluster [100, 101] M_6F_{15}, which were reduced subsequently in a rate-controlling step. (The nature of the intermediates proposed by the original authors is inconsistent with the known chemistry.) Zirconium was produced only in baths which contained K^+ ions. It is known that ZrF_6^{2-} exists in a polymeric eight-coordinated state in K_2ZrF_6. Coordination geometries of the ZrF_6^{2-} anions are specifically determined by the counter ion [100]. It is thus possible to conclude that the coordination of the metal ion being reduced is the important factor in determining the conditions for a slow reduction step in the overall process. This is supported by subsequent studies by Mellors and Senderoff [58] and ourselves for the cases of Mo reduction [23, 24] and Cr reduction [80].

The influence of small quantities of foreign ions such as chloride, oxide, etc. would seem unlikely to be effective in changing the bulk complex species but if they were surface active then chloride, for example, might well replace fluoride at the metal surface (the order of surface activity [87] is $I^- > Br^- > Cl^- > F^-$) thus interfering with the formation of the necessary intermediate. Oxide might behave in a similar way by producing an oxyfluorocomplex [102, 103] in the interface. The metal deposition process is probably specific to each metal but nevertheless there is growing evidence that complex structural species may be rate-controlling in specific ways. What these are exactly and how they operate is an exciting and technologically rewarding area for future research. The influence of oxide ion in two not too disssimilar systems is exemplified by the recent work of Monnier [66] on the reduction of $NaTaO_3/Ta_2O_5$ in cryolite and the previous studies of Mellors and Senderoff [96]. Monnier reported that there was a single five-electron reduction step which contrasts with that proposed for TaF_x^{5-x} in FLiNaK for example, namely $Ta(V) \rightarrow Ta(II) \rightarrow Ta(0)$. It would appear that Ta(V) coordinated by oxide reduces without the formation of a stable rate-controlling intermediate and that TaF_x^{5-x} is only reduced at potentials negative to those of the solvent species in cryolite.

6.5. *The anode process*

In the past, considerations of electrowinning processes have concentrated, quite rightly, on the cathodic process. It must be remembered that any electrolytic process involves pairs of electrodes for which the proper choice of the anodic process can mean the difference between success and failure of the electrolytic route. When one considers, for example, that the anode overvoltage in the aluminium-winning industry can be valued at hundreds of thousands of dollars per millivolt per annum, both the economic and energetic importance of this aspect of cell design cannot be overstated. Nevertheless, research into the basic science of such processes is minimal.

The recovery of metals in an electrolytic reactor can proceed in two directions: either the concentrated ore (carnalite, wolframite, molybdenite) is used as feed for the electrolysis or this concentrate is treated through a series of unit operations to a refined product (for example, Al_2O_3, K_2TaF_7, $TaCl_5$) for subsequent use. The anodic processes will be determined by each of these potential feedstocks and can be divided into four main types: the discharge of (i) fluorine/carbon fluorides, (ii) chlorine, (iii) oxygen/carbon oxides and (iv) sulphur/metal ions. Of these, the discharge of fluorine and chlorine are undesirable because of their high anodic potentials, and their subsequently oxidative nature *vis-à-vis* the solute/cathode product, their corrosive nature and high toxicity. The depolarization of these anodic processes by the discharge of oxygen, carbon monoxide or carbon dioxide is well established in aluminium extraction, tantalum winning, etc. and results in a considerable energy saving by reducing the anodic contribution to the overall cell voltage. Unfortunately the kinetics of the CO/CO_2 discharge reaction are slow on commercial carbon anodes [78, 79, 104], with the result that considerable savings in energy/cost might be achieved through an improvement in anode characteristics. Further, the much less oxidizing conditions (for CO/CO_2 evolution) result in a more stable solute/cathode environment with consequent improvements in electrode geometry. (To this end good dimensional stability of the anode is a prerequisite of a well-designed anodic process.)

The alkali industry has developed anode materials [105] which combine dimensional stability and good electrocatalytic properties for the chlorine discharge reaction at low temperatures in aqueous solution. Other inorganic materials for consideration with the oxygen evolution reaction have recently been reviewed [106]. It seems likely that such electrodes might be extended and developed for fused-salt systems which will enable the overvoltage for say the oxygen evolution reaction to be lowered. For example the use of a SrO–La_2O_3–CoO electrode developed in fuel cell research [107] was reported to be particularly useful in electrocatalysing the oxygen evolution reaction at temperatures around 450 K; clearly the application to higher temperature molten-salt electrolytic processing should be exploited. The need for oxide-containing electrolytes prevents the direct use in electrowinning operations of the principles of the Union Carbide electroforming process. A knowledge of the way in which the presence of oxide influences the cathodic deposition characteristics of, for example, tantalum in the same system would be desirable.

Recently the suggestion that the anode reaction might be depolarized by the use of a natural gas feed has been made, thus making an overall saving in the energy efficiency with respect to the primary fuel source [108]. That is to say the energy content of the natural gas is best used depolarizing the anode of the electrolytic cell which is perhaps run off hydroelectric power.

The direct use of sulphide-rich ores, processed to form anodes, is not new (cf. INCO) [109] but may offer advantages for processing certain minerals. The anode process then consists of the oxidation of metal sulphide to sulphur and metal ions [110] which can subsequently be recovered at the cathode, i.e. the mineral is subjected to an electrowinning/electrorefining process. An example of this idea has been the production of molybdenum from refined molybdenum sulphide anodes [111, 112]. Of course, the control of a process involving molybdenite directly would be much more involved because of the need to separate other more noble constituents of the basic ore concentrate. Overvoltages for such electrolytic processes are small and the overall energy requirements will be much less than conventional electrowinning operations. (Perhaps all metal resources should be converted into their sulphides when the latter are good electronic conductors at high temperatures!)

7. Conclusions

(a) In order to achieve efficient electrowinning of the refractory metals it is necessary to give careful consideration to both chemical and electrochemical factors. It is now possible to place reactor design on a scientific basis.

(b) A dynamic systems approach to electrometallurgical reactor design would be timely.

(c) Electrowon refractory metal is generally of a better quality than the thermal reduction product, especially if the electrodeposit is obtained in coherent form.

(d) It may be misleading to regard these elements as a coherent group (as was done for electroforming) as each will exhibit its own characteristic electrodeposition mechanism. It has become clear that the more noble of these metals are more versatile in respect to the solvents from which good electroplates can be obtained, for example, Mo, Cr, W.

(e) A better understanding of the way in which the chemical nature of the intermediates, in the reduction process, control the rate of deposition, and hence the morphology of the deposit, is necessary to optimize metal recovery. An understanding of the influence of oxide, chloride and oxyanions such as phosphate, borate, silicate on the metal deposition reactions would facilitate the development of processes for winning these metals directly from their ore concentrates.

(f) The design of the concomitant anode process is important to the overall success of a winning process and research to develop new anode materials needs extending. Such an effort would have far reaching consequences in fused-salt electrowinning operations in general.

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