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Electrodeposition of refractory metals (Ti, Zr, Nb, Ta) from molten salt electrolytes

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A selective review of the anodic and cathodic processes associated with electroextraction, electrorefining and plating of refractory metals (Ti, Zr, Nb and Ta) from molten salt-based electrolytes is presented with regard to the results obtained during the last two decades. Special attention is paid to the mechanism of cathodic reduction and its rate-limiting steps, as well as to the parallel chemical reactions of disproportionation and complexing. The anodic processes in corrosion and electrodissolution of Ti, Zr, Nb and Ta in molten electrolytes are also discussed. As a conclusion, a few contradictory subject-related questions are outlined and some new trends of investigation are suggested.

1. Introduction

Early literature on the electrochemistry of refractory metals (IV, V and VIb groups) in molten salt electrolytes was summarized by Inman and White [1] in a review which served as a major reference point in many authors' attempts to describe the associated processes over the years.

During the last decade and a half, however, the processes of electroextraction and refining, as well as the electroplating of high melting metals focused scientific interest due to their use in advanced technological systems. The ultimate aim of the investigations was the optimization of cathodic deposition of these metals and coatings. This fact prompted a selective review by White and Twardoch [2], dealing with the electroplating of Cr, Mo and W from fused salt electrolytes. The considerable amount of data collected on the electrochemical behaviour of the IVb and Vb group metals (namely, Ti, Zr, Nb and Ta) necessitated a review of these results.

From the point of view of fundamental electrochemistry, the study of electroreduction of polyvalent complex metal ions, as in the case of refractory metals in molten electrolytes, offers wide possibilities for modelling multistep electrode processes in the absence of side reactions (oxidation/reduction of water in conventional electrochemistry).

The purpose of the present electrochemical review of Ti, Zr, Nb, Ta, during their deposition from molten salt based electrolytes, is as follows:

(i) A brief overview of the basic experimental techniques, the most widely used electrolytes, working, counter and reference electrodes.
(ii) An overview of the standard potentials of reduction processes of polyvalent electroactive species of refractory metals.
(iii) An attempt to classify the data available on the electrodeposition kinetics of Ti, Zr, Nb and Ta from different electrolytes, diffusion and charge transfer steps, as well as the associated complementary chemical reactions of disproportionation and complex formation.
(iv) A concise overview of the anodic processes during corrosion and electrodissolution of Ti, Zr, Nb and Ta in different molten salt electrolytes.

2. Experimental techniques

2.1. *Electrolytes*

Two main types of electrolyte employed in the electrodeposition of refractory metals were chloride- and fluoride-based. Combinations with or without the addition of oxyanion-containing compounds (oxides etc.) were also investigated. Some basic characteristics of these and other common molten electrolytes are collected in Table 1 [3].

Binary chlorides, fluorides and oxides of refractory metals, as well as chloro-, fluoro- and oxycomplexes were used as electroactive ionic components (e.g., K_2TiF_6, K_2NbF_7 etc.)

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Table 1. A collection of basic data on the most commonly used molten salt electrolytes

System	*Composition* /mol %	*Standard temperature* /°C	*Melting point* /°C	*Conductivity* $/\Omega^{-1}\,\mathrm{cm}^{-1}$
LiCl–KCl	59–41	450	350	1.57
NaCl–KCl	50–50	727	658	2.42
$AlCl_3$–NaCl	63–37	175	117	0.239
NaOH–KOH	51–49	500	185	1.81
FLINAK–LiF	46.5	500	459	–
FLINAK–NaF	11.5			
FLINAK–KF	42.0			
$NaPO_3$–KPO_3	50–50	700	567	–

2.2. *Electrodes*

The working electrodes (cathodes) most commonly used in molten salt electrodeposition were chosen from Pt, graphite, glassy carbon, Mo, W, Cu, Ni etc. including electrodes of the refractory metal itself (e.g., in electrorefining). The counter electrodes (anodes) were normally Pt, Mo, W and carbon-based materials. Anodes were also produced from the refractory metal to be refined.

The choice of a reference electrode is a major problem in molten salt electrochemistry; it is well-known that no standard reference scale of potentials in melts exists [3]. The most widely used reference electrodes were Ag(I)/Ag (fluoride and chloride electrolytes, electroactive salt with AgCl at different concentration scales, namely, molar, molal, mole fraction etc.), the quasireversible Pt(II)/Pt electrode (the potential of which is not stable) and the Ni(II)/Ni electrode (used mostly in fluoride melts with NiF_2 electroactive salt). Among the most recent reference electrode systems, the newly proposed internal reference electrodes [4] deserve special attention. A detailed overview of reference electrodes in fused salt systems is, however, beyond the scope of the present paper.

2.3. *Standard equilibrium potentials*

Data for the standard electrode potentials of metal ion/metal systems for Ti, Zr, Nb and Ta in a range of molten electrolytes are shown in Table 2.

It is evident that the standard potentials of metal ion/metal couples are strongly dependent on the nature of the solvent. Moreover, the reaction path of electrodeposition is also a function of the molten electrolyte composition.

2.4. *Experimental techniques*

Quasisteady state d.c. electrochemical methods (namely, chronopotentiometry, chronoamperometry) as well as linear and cyclic voltammetry are most widely used in studying molten salt electrode processes. Recently, transient techniques, such as a.c. impedance spectroscopy over a wide range of frequencies, have found increasing application. Because the reaction rates were considerably higher than in conventional water electrochemistry, due to the high electrolyte temperature and conductivity, fast rise-time potentiostats/galvanostats coupled with function generators capable of ensuring scan rates ranging from 1 to $100\,\mathrm{V\,s^{-1}}$ were needed. To record $i-t$, $E-t$ transients and voltammograms at very high scan rates digital oscilloscopes and personal computer-based data acquisition systems found application. Both scanning and transmission electron microscopy, X-ray diffraction, energy dispersive X-ray absorption (EDXA), X-ray photoelectron spectroscopy etc. were used to assess the composition and properties of coatings obtained.

3. Electrodeposition kinetics of refractory metals

3.1. *Titanium* [5–64]

A simplified diagram of the main chemical and electrochemical reactions during the interaction of Ti metal and Ti-ion containing melts is presented in Fig. 1(a) and (b). The basic kinetic parameters of electrodeposition of Ti from a range of molten electrolytes (reaction paths, number of electrons involved in rate determining steps, exchange current density, rate constant, transfer coefficient and diffusion coefficient) are listed in Table 3.

From the collected data the following conclusions may be drawn:

(i) Kinetic parameters for the charge transfer steps were determined mainly in the LiCl–KCl eutectic, whereas in the remaining electrolytes mostly reaction sequences were postulated.

(ii) Little was known of the rate constants and orders of the chemical reactions coupled to the electrochemical stages.

(iii) No quantitative evaluation of the kinetic parameters of anodic processes of dissolution of Ti metal in various melts was available. Tafel kinetics of the latter was postulated in NaCl–KCl–KF melts only [35].

3.1.1. *Chloride electrolytes*

(a) *Chemical equilibria*

Chassaing *et al.* [15] demonstrated the interaction between Ti metal and Ti-ion containing melts in melts with a small alkali cation (LiCl) as defined by Equations 1 and 4 (Fig. 1(a)). The increase of the alkali cation radius (CsCl) favoured the interaction via Equation 5 (Fig. 2).

The existence of three anionic forms of Ti(III) was corroborated in chloride melts [16]:

$$\mathrm{TiCl_6^{3-} = TiCl_4^- + 2Cl^-}$$

$$\mathrm{TiCl_6^{3-} = 0.5Ti_2Cl_9^{3-} + 1.5Cl^-}$$

The above equilibria shifted to the right with increased LiCl content in the melt, whereas CsCl in the electrolyte was supposed to stabilize Ti(III) [15].

Table 2. Apparent standard potentials of the redox couples metal ion/metal for Ti, Zr, Nb and Ta and complementary chemical reactions of metal/molten electrolyte interaction. Legend: RE = reference electrode; subscripts on the individual reference electrodes: m = molal scale; x = mole fraction scale; mol: molar scale; mol. %: molar percent scale

Metal	*Electrolyte*	*Reactions*	E^0_{ref} /V	*RE*	*References*
Ti	LiCl–KCl	Ti(IV)/(III)	−0.41	Ag(I)$_m$	[8–10]
		Ti(IV)/(II)	−0.50		
		Ti(IV)/(0)	−0.767		
		Ti(III)/(II)	−0.61		
		Ti(III)/(0)	−0.88		
		Ti(II)/(0)	−1.01		
		Ti/Ti(II)	−2.01		[42]
		TiC/Ti(III)	−1.24		
		Ti → Ti(II)	−2.14		
		Ti(II)/(III)	−1.82		
Zr	LiCl–KCl	Zr(IV)/(II)	−1.153		[64, 67]
		Zr(IV)/(0)	−1.088		
		Zr(II)/(0)	−1.020		
Nb	LiCl–KCl	Nb(III)/(0)	−0.43		[93]
		Nb(V)/(IV)	−0.32	Cl_2/Cl^-	[107]
		Nb(IV)/(III)	−1.09		
		Nb(III)/(II)	−1.32		
		Nb(III)/(0)	−1.48		
Ta	LiCl–KCl	Ta(V)/(IV)	−0.59	Ag(I)$_x$	[98, 121]
		Ta(IV)/(II)	−1.37		
		Ta(IV)/(0)	−1.03		
		Ta(II)/(0)	−1.57		
Ti	NaCl–KCl	Ti(IV)/(III)	+0.35	Ag(I)$_x$	[8]
		Ti(IV)/(II)	−0.274		
		Ti(IV)/(0)	−0.686		
		Ti(III)/(II)	−0.899		
		Ti(III)/(0)	−1.032		
		Ti(II)/(0)	−1.098		
		Ti(IV)/(III)	−0.6	AgCl/Ag	[33]
		Ti(III)/(II)	−1.0		
		Ti(II)/Ti(Pt)	−1.55		
		Ti(II)/Ti$_{pure}$	−1.85		
Zr	NaCl–KCl	Zr(IV)/(II)	−0.665		[10, 63]
		Zr(IV)/(0)	−1.02		
		Zr(III)/(II)	−0.0954		
		Zr(III)/(0)	−1.21		
		Zr(II)/(0)	−1.338		
Zr	NaCl	Zr(IV)/(II)	−1.74	AgCl/Ag	[68]
		$ZrCl_4$/Zr(II)	−1.88		
		Zr(II)/(0)	−1.93		
		Zr(IV)/(0)	−2.03		
Nb	NaCl–KCl	Nb(IV)/(0)	−0.33		[100]
		Nb(IV)/(0)	−0.64	AgCl/Ag	[102]
		Nb(V)/(IV)	+0.74		
Ta	NaCl–KCl + TaF_7^{2-}	Ta(V)/(0)	−0.34	Ni/NiF_2 (1 mol %)	[130]
Ti	$AlCl_3$–NaCl	Ti(III)/(II)	+0.436	Al(III)$_x$	[44, 45]
		Ti(IV)/(III)	+1.017		
Nb	$AlCl_3$–NaCl–KCl	Nb(V)/(IV)	+0.95		[89]
		Nb(V)/(III)	+0.90		
		Nb(IV)/(III)	+0.85		
Ta	$AlCl_3$–NaCl–KCl	Ta(V)/(III)	+0.35		[120]
Ti	FLINAK	Ti(IV)/(III)	−0.058	Ni(II)$_x$	[50]
		Ti(III)/(0)	−1.798		
		Ti(IV)/(0)	−1.363		
		Ti(IV)/(III)	−1.70	Pt(II)/Pt	[55]
		Ti(III)/(0)	−2.4		
Zr	FLINAK	Zr(IV)/(0)	−1.25		[88]
Nb	FLINAK	Nb(V)/(IV)	−0.11	Ni^{2+}/Ni	[96]
		Nb(IV)/(I)	−0.76		
		Nb(I)/(0)	−1.02		
Nb	LiF–NaF	Nb(V)/(IV)	−0.06	Ni/NiF_2 (1 mol %)	[115]
		Nb(IV)/(0)	−0.17		
Ta	FLINAK	Ta(V)/(0)	−0.05	Mo, Ta(V)/Ta	[118]

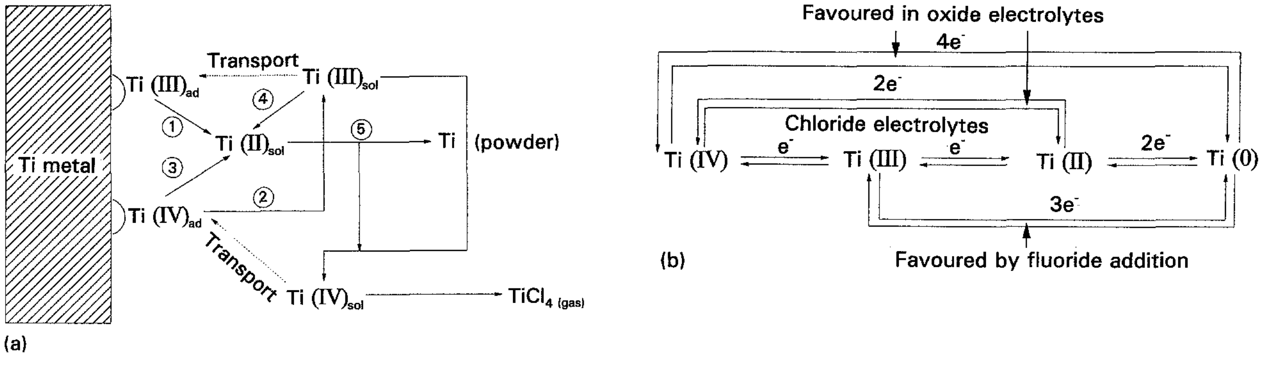

Fig. 1. Summary of the interactions between Ti metal and Ti ions for a range of molten salt electrolytes: (a) chemical reactions; (b) electrochemical processes. For (a): Reactions 1 and 4 favoured in chloride melts with small cations; Reaction 2 favoured in mixed melts >2.8% TiF_6^{2-}; Reaction 3 favoured in mixed melts >0.8% TiF_6^{2-}; and Reaction 5 favoured in chloride melts with large cations.

(b) *Cathodic processes*

Ferry and Picard [37, 38] explained the two waves in the cathodic branch of the quasistationary voltammogram of the Ti^{3+}/LiCl–KCl system by a two-step mechanism (Fig. 1(b)). Numerical simulation of the voltammograms was carried out on the basis of classical diffusional and charge-transfer equations:

$$k_i = k_i^0 \exp\left(-\alpha_i F/RT(E - E_i^0)\right) \qquad \text{for } i = \pm 1, \pm 2$$

$$i_F = -k_1 c_{30} + k_{-1} c_{20} - k_2 c_{20} + k_{-2}$$

$$D(c_{3s} - c_{30})/\delta = FS(k_1 c_{30} - k_{-1} c_{20})$$

$$D(c_{2s} - c_{20})/\delta = FS(-k_1 c_{30} + k_{-1} c_{20} + k_2 c_{20} - k_{-2})$$

where c_{is} and c_{io} are the surface and bulk concentrations of Ti^{3+} and Ti^{2+}, respectively. The values obtained for the rate constants, transfer coefficients and standard potentials are shown in Tables 2 and 3.

(c) *Anodic processes*

Kinetic information on the Ti^{4+}/Ti^{3+} reaction was obtained by the same authors [39] using a.c.

Table 3. Summary of kinetic data concerning the chemical, anodic and cathodic reactions of Ti for a range of molten salt electrolytes

Electrolyte	*Reaction(s)*	*n*	*Kinetic parameters*	*D* /$cm^2\,s^{-1}$	*References*
LiClCsCl	Ti(III)/(II)	1			[15, 16]
	Ti(II)/(0)	2			
LiCl–KCl	Ti(III)/(IV)	1	$k_0 = 0.25\,cm/s$		[40]
	Ti(IV)/K_2TiF_6		$\alpha = 0.3$		
LiCl–KCl	Ti/Ti(II)	2	reaction order 1 (against Ti(III))		[42]
	TiC/Ti(III)	3			
	Ti → Ti(II)	2	$\beta_{app} = 1.5$		
	Ti(II)/(III)				
LiCl–KCl	Ti(III)/(IV)	1	$k_0 = 0.2\,cm\,s^{-1}$	$1 \cdot 10^{-5}$	[39]
				(Ti(III))	
			$\alpha = 0.7$ (an)		
	Ti(II)/(III)	1	$0.002\,cm\,s^{-1}$		
			$\alpha = 0.5$		
	Ti(0)/Ti(II)	2	$3 \times 10^{-6}\,cm\,s^{-1}$		
			$\alpha = 0.6$ (cat)		
NaCl–KCl$TiCl_3$	Ti(IV)/(III)	1		$1.5 \cdot 10^{-5}$	[25]
				(Ti(IV))	
	Ti(III)/(0)	3			
TiF_6^{2-}	Ti(IV) + Ti(0) → 2Ti(III)		$\lg K = -10.17 + 27.2 \times 10^3/T$		
	Ti(IV)/(III)	1		1.6×10^{-5}	[32]
	Ti(III)/(0)	3		(Ti(IV))	
	Ti(III) + Ti → $Ti(II)_{compl}$				[34]
	Ti(IV) + Ti → Ti(III)				
NaCl–KCl	Ti(IV)/(III)	1			[33]
	Ti(III)/(II)	1			
	Ti(II)/Ti(Pt)	2			
	Ti(II)/Ti	2			
NaCl–KCl + KF	Ti/Ti(II)/Ti(III)/Ti(IV)		an. Tafel		[35]
	Ti(IV)/Ti(III)	1			
	Ti(III)/Ti(II)	1			
	Ti(II)/Ti(Pt)	2			
	Ti(II)/Ti	2			
LiF–KF	TiF_6^{2-} + Ti → TiF_6^{3-}				[53]
FLINAK	TiF_6^{3-}/Ti	3			
FLINAK	Ti(III)/Ti	3	$i_0 = 2.2\,A\,cm^{-2}$		[57]

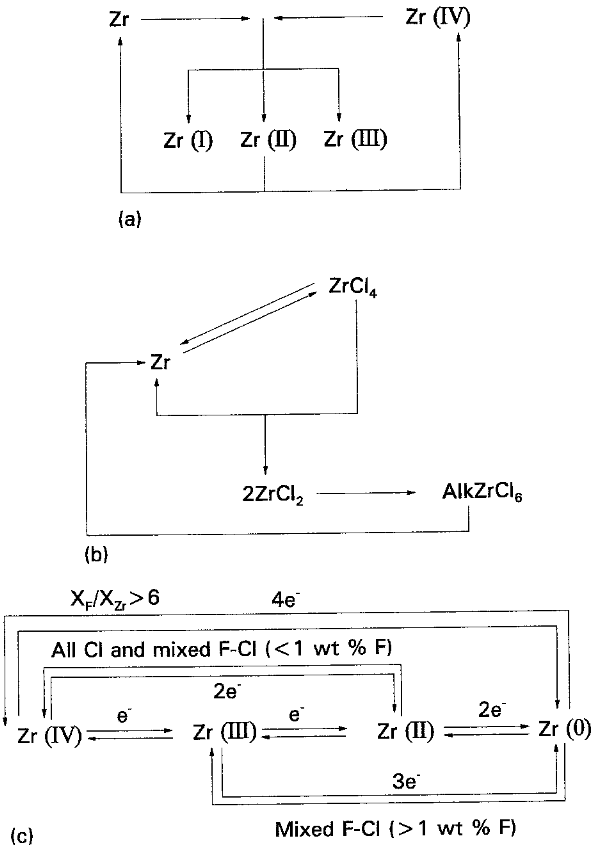

Fig. 2. Summary of the interactions between Zr metal and Zr ions for a range of molten salt electrolytes: (a) chemical reactions; (b) corrosion; (c) electrochemical processes.

impedance spectroscopy. The results were interpreted by means of a diffusional-charge transfer kinetic model of the reaction. For potentials more cathodic than -0.48 V vs Cl^-/Cl_2 dissolved Ti^{4+} was obtained upon anodic oxidation of Ti^{3+} [40]. The higher potentials fostered a K_2TiCl_6 layer deposited on the electrode leading to partial passivation. A model of this layer structure comprising a thin barrier film (0.1 μm) at the metal side and a thick porous layer thereupon (70 μm) was advanced [40].

It was demonstrated in [41] that the open-circuit potentials of Ti and TiC electrodes in the LiCl–KCl eutectic behaved as a redox potential of the reaction $Ti + 2TiCl_3 = 3TiCl_2$. A two-step path of anodic dissolution of Ti was suggested:

$$Ti + TiCl_6^{3-} \longrightarrow Ti_2Cl_6^{2-}(s) + e^-$$

$$Ti_2Cl_6^{2-}(s) \longrightarrow Ti(II)sol + TiCl_6^{3-} + e^-$$

The reaction order against Ti(III) and the apparent transfer coefficient are given in Table 3.

3.1.2. *Mixed electrolytes*

(a) *Chemical equilibria*

The interaction of Ti(metal) and Ti(III)-containing NaCl–KCl melts at TiF_6^{2-} concentrations higher than 2.8 mol % obeyed Equation 2 (Fig. 1(a)) [34] whereas in melts with the composition NaCl–KCl–$TiCl_3$ the reaction equation was Equation 1 (Fig. 1(a)). For TiF_6^{2-} concentrations of about 0.8 mol % the interaction was described by Equation 3 (Fig. 1(a)). With decrease in the TiF_6^{2-} concentration the composition of the Ti(IV) complexes changed from $TiF_x^{(x-4)-}$ through $TiF_xCl_y^{(x+y-4)-}$ to $TiCl_y^{(y-4)-}$.

(b) *Cathodic processes*

On the basis of voltammetric and a.c. impedance measurements a three step mechanism of reduction of Ti(IV) (as TiF_6^{2-}) in NaCl–KCl melts was proposed in [33] (Fig. 1(b)). The impedance spectra were interpreted by the authors [33] using a Randles model; that is, mixed kinetics seemed to govern all the four stages of the electroreduction process. If KF was added to the electrolyte in concentrations >10%, only two reduction steps were observed [35] (Fig. 1(b)).

(c) *Anodic processes*

Guang-sen *et al.* [35] obtained three Tafel-like zones of the anodic polarization curve of Ti in pure NaCl–KCl melts and interpreted their results by a reaction mechanism including three irreversible steps analogous to those of Ti reduction in pure chlorides (Fig. 1(b)).

The mechanism of the anodic process was not altered when 10% KF was added to the electrolyte, but the potential range of the first oxidation step was narrowed by the increased KF concentration. This could be due to the different composition of Ti-complexes in both melts [33–35].

3.1.3. Fluoride electrolytes. The two-step mechanism of TiF_6^{2-} reduction [35] remained valid in all-fluoride electrolytes (LiF–KF and FLINAK) as demonstrated in [52, 53]. De Lepinay *et al.* [52] suggested the formation of an interdiffusion sublayer of Ti–Cu phases such as Ti_2Cu, TiCu, Ti_2Cu_3 and $TiCu_4$ deposited in a narrow potential range preceding pure Ti deposition [53]. The results of Guang-sen *et al.* [33–35], however, were in contradiction with the chronopotentiometric ones of Sequeira [32] who found that at TiF_6^{2-} concentrations ranging from 0.01 to 0.5 mol dm^{-3} in a NaCl–KCl melt the process of Ti reduction was a two-step one (in analogy with the results of Guang-sen *et al.* [33–35] for high KF and/or TiF_6^{2-} content, Table 3).

3.1.4. *Oxide electrolytes*

(a) *Cathodic processes*

Ti reduction from synthetic slag melts (SiO_2–Na_2O–CaO–MgO, Ti as TiO_2) was studied by Tzvetkoff and Lingorsky [59]. The following mechanism of Ti(IV) reduction was suggested [59]:

$$Ti(IV) + 2e^- \longrightarrow Ti(II)$$

$$Ti(IV) + 4e^- \longrightarrow Ti(0)$$

The process was found to be complicated by the formation of a low-dissociated compound of the $4CaO \cdot TiO_2$ type [59].

(b) *Anodic processes*

In connection with the use of Ti in technological systems for electrochemical finishing of ceramic cast equipment the same authors [60] studied the corrosion kinetics of Ti in NaOH–NaCl–Na_2CO_3 melts. A topochemical reaction appeared to be the limiting stage of the overall process, since its kinetics obeyed the following equation:

$$P_0^{0.33} - P^{0.33} = Zt$$

where Z is the formal rate constant of the dissolution process. Its temperature dependence was investigated and the influence of preliminary plastic deformation on the rate of Ti corrosion in such melts was estimated [60].

3.2. *Zirconium* [63–91]

A simplified diagram of the main chemical and electrochemical processes during the interaction of Zr and Zr ions in molten salt electrolytes is presented in Fig. 2(a)–(c).

The main parameters of Zr electrodeposition from a range of molten salts are given in Table 4. The following main points may be emphasized: (i) that almost no data on the kinetic parameters of the charge transfer steps during the electroreduction of Zr-containing species are available in literature; (ii) that the diffusion coefficients of Zr-containing ions in solution have not been determined; and (iii) that little attention was paid to the anodic processes of Zr dissolution which are important for electrorefining.

3.2.1. Chloride electrolytes. Flengas *et al.* [77–84] studied in detail the chemical equilibria between Zr compounds both in the melt and in the gas phase. It was established that the stability of Zr(IV) in solution increased in the range $Li < Na < K < Cs$ both for the chloride and fluoride complexes.

Basile *et al.* [68] showed that the reduction process in fused NaCl comprised four stages (Fig. 2(c)) [68]. The process was a two-stage one in LiCl–KCl mixtures [68, 85, 86] (consisting of the first and the fourth steps in Fig. 2(c)). The third stage was predominant in fused CsCl due to the stabilization of the Zr(IV) complex with the increase of the alkali cation radius. The authors [68] demonstrated that $ZrCl_2$ was formed on the metal surface in non-negligible amounts only during Zr corrosion in fused CsCl.

3.2.2. Mixed electrolytes. Smirnov *et al.* [63] demonstrated the validity of the two step reduction mechanism in chloride-fluoride melts (Fig. 2(c)) whereas Winand [65] found a one-step reaction of Zr^{4+} reduction in fused NaCl or $CaCl_2$–$BaCl_2$ with ZrF_4 (Fig. 2(c)).

Guang-sen *et al.* [87] reported that the following mechanism held in melts of a NaCl–KCl–K_2ZrF_6 (1 wt %) composition:

$$ZrCl_{6-x}F_x^{2-} + 2e^- \longrightarrow ZrCl_{6-x}F_x^{4-}$$

$$ZrCl_{6-x}F_x^{4-} + 2e^- \longrightarrow Zr + (6-x)Cl^- + xF^-$$

Upon increase of the K_2ZrF_6 concentration, another mixed fluoro-chlorocomplex was found to be reduced:

$$ZrCl_{6-x}F_x^{2-} + e^- \longrightarrow ZrCl_{6-x}F_x^{3-}$$

$$ZrCl_{6-x}F_x^{3-} + 3e^- \longrightarrow Zr + (6-x)Cl^- + xF^-$$

whereas at high concentrations of the fluoride ion the one-step reaction Zr(IV)/Zr(O) prevailed [87]. Flengas *et al.* suggested possible anodic and cathodic reactions during Zr electrorefining [84]. In chloride electrolytes the main cathodic process was thought to be

$$ZrCl_6^{2-} + 4e^- \longrightarrow Zr^0 + 6Cl^-$$

but reactions of the type in Fig. 2(a), as well as one-electron transfer steps (e.g., (Zr(IV)/Zr(III)) reducing the current efficiency, had to be taken into account. Disproportionation reactions (Fig. 2(a)) lending to

Table 4. Summary of kinetic data concerning the chemical, anodic and cathodic reactions of Zr for a range of molten salt electrolytes

Electrolyte	*Reactions*	*n*	*Kinetic parameters*	*D* /$cm^2\,s^{-1}$	*References*
NaCl	Zr(IV)/Zr(II)	2			[68]
	$ZrCl_4$/Zr(II)	2			
	Zr(II)/Zr(0)	2			
	Zr(IV)/Zr(0)	4			
LiCl/KCl	2 steps				
CsCl	4 steps				
AlkCl	$ZrCl_6^{2-}/Zr$	4			[80–84]
	Zr + Zr(IV) = Zr(III)				
	Zr + Zr(IV) = Zr(II)				
	Zr + Zr(IV) = Zr(I)				
AlkF	ZrF_6^{2-}/Zr	4			
AlkCl	Zr(IV)/Zr(II)	2			
	Zr(II)/Zr	2			
+ Low AF	F–Cl complexes				
+ High AF	Zr(IV)/Zr(III)	1			
	Zr(III)/Zr(0)	3			
AlkCl	Zr(IV)/Zr(II)	2			[85]
	Zr(II)/Zr(0)	2			[86]
AF	Zr(IV)/Zr(0)	4			[76]
FLINAK	Zr(IV)/Zr(0)	4	$i_0 = 1.3\,A\,cm^{-2}$		[57]

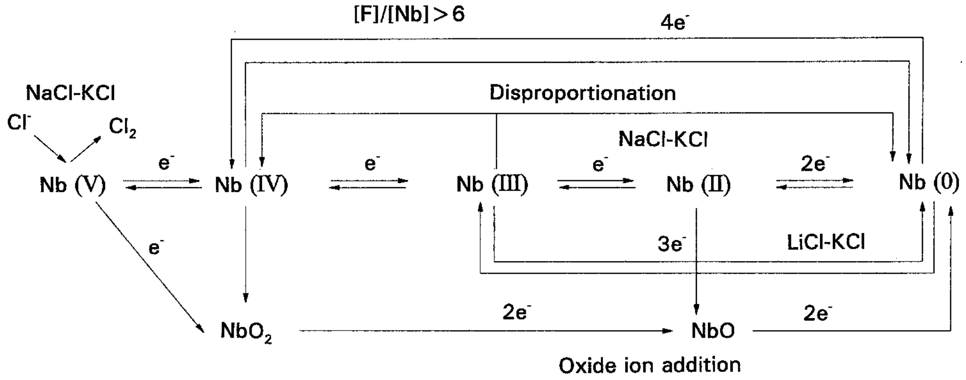

Fig. 3. Summary of the electrochemical reactions of Nb metal and Nb ions for a range of molten salt electrolytes.

the formation of metal powders were also considered [84].

3.2.3. *Fluoride electrolytes.* In fluoride electrolytes the main cathodic process was assumed to be $ZrF_6^{2-} + 4e^- \rightarrow Zr^0 + 6F^-$ [84], accounting for a significant side reaction with potassium evolution: $Zr + nKF \rightarrow ZrF_n + nK$.

3.3. *Niobium* [89–115]

A summary of the reaction paths for Nb reduction in different electrolytes is presented in Fig. 3. The parameters characteristic of Nb electrodeposition from a range of fused electrolytes are collected in Table 5. The following are noteworthy when studying the collected data:

(i) As in the case of titanium, quantitative kinetic data are available for the electroreduction of Nb-containing species in LiCl–KCl eutectic only; and the results in other electrolytes comprise mainly qualitative estimates of the influence of different factors (oxide ion addition, fluoride addition and temperature) on the reduction processes.

(ii) New data on the processes of Nb reduction in FLINAK melts are missing in the literature of the last 15 years, which is surprising considering the use of the melt in industrial production of Nb coatings.

3.3.1. *Chloride electrolytes.* Picard and Bocage [103] demonstrated that in LiCl–KCl melts the oxidation state of Nb(V), Nb(IV) and Nb(III) was stable. It was established [106, 107] that the reduction of $NbCl_5$ in that melt follows a multistep path (Fig. 3). The last step was presumably complicated by the formation of the insoluble nonstoichiometric compounds [104, 105]. Lantelme *et al.* [107] demonstrated that the reactions Nb(V)/Nb(IV) and Nb(IV)/Nb(III) were significantly reversible and the diffusion coefficients of Nb(IV) and Nb(III) practically coincided. The process of Nb(III) reduction was found to occur via the formation of nonstoichiometric chlorides [107]:

$$(y+1)\mathrm{Nb(III)} + (3y+2)\mathrm{Cl}^- + e^- \longrightarrow \mathrm{Nb}_{y+1}\mathrm{Cl}_{3y+2} \quad \text{for } y = 0.5, 2 \div 7$$

Table 5. Summary of kinetic data concerning the chemical, anodic and cathodic reactions of Nb for a range of molten salt electrolytes

Electrolyte	*Reactions*	*n*	*Kinetic parameters*	*D* /$cm^2\ s^{-1}$	*References*
LiCl-KCl	Nb(V)/Nb(IV)	1		$0.0192\exp(-5910/T)$ (Nb(III)) = (Nb(IV))	[107]
	Nb(IV)/Nb(III)	1			
	Nb(III)/Nb(II)	1	$i_0 = 20\,\mathrm{mA\,cm^{-2}}$		
	Nb(III)/Nb(0)	3	$i_0 = 5\,\mathrm{mA\,cm^{-2}}$		
$+Na_2O$	NbO_2, NbO				
NaCl–KCl	Nb(IV)/Nb(0)	4.5			[102]
	Nb(V)/Nb(IV)	1			
KCL–KF	Nb(V)/Nb(IV)	1			[114]
	Nb(IV)/Nb(0)	4			
$+Nb_2O_5$	Nb(V)/NbO_2	1			
	NbO_2/NbO	2			
	NbO/Nb	2			
LiF–NaF	Nb(V)/Nb(IV)	1			[115]
	Nb(IV)/Nb(0)	4			
	Nb + Nb(IV) → Nb(IV)				
LiF–NaF	Nb(V)/Nb(IV)	1			[118]
	Nb(IV)/Nb(0)	4		4×10^{-6} (Nb(IV))	

and to obey the kinetic equation

$$i = i^0_{\mathrm{III/II}}(\theta \exp[(1-\alpha)(F/RT)(E-E^*)] - (c_{\mathrm{Nb(III)}}/c^*_{\mathrm{Nb(III)}})\exp[-\alpha(F/RT)(E-E^*)]$$

where θ is the surface coverage with a reaction product, and E^* is the apparent equilibrium potential corresponding to the concentration $c^*_{\mathrm{Nb(III)}}$. Thus, exchange current densities of the processes Nb(III)/Nb(II) and Nb(III)/Nb were determined (Table 5).

3.3.2. Mixed electrolytes. The addition of oxide anion to the melt resulted in the formation of NbO_2 and NbO phases on the electrode [107]. The potential of the Nb(V)/Nb(IV) couple moved in the negative direction with increase in the $[F^-]/[Nb]$ ratio. At potentials, more negative than −1.5 V, the electrode is passivated probably via the formation of insoluble fluorides of the K_2NbF_4 type [107]. The temperature rise offset the standard potential of both the Nb(V)/(IV) and Nb(III)/Nb couples in the positive direction [107] and favoured disproportionation (Fig. 3). Khalidi and Bouteillon [102] demonstrated that in excess chloride ions, Nb(V) was unstable and evolved chlorine (Fig. 3). The addition of fluoride ions produced a shift in the equilibrium $NbCl_n^{y-} + nF^- = NbF_n^{y-} + nCl^-$ completely to the right and the reduction maximum was displaced in the negative direction. When the ratio $[F^-]/[Nb] \geqslant 6$, the reduction of niobium (IV) ions proceeded as a one-step reaction (Fig. 3) [102, 114]. The mechanism of the cathodic process was found to be strongly influenced by the addition of Nb_2O_5 to the melt. The equivalent point of fluoride and oxyfluoride stability corresponded to a ratio $[Nb_2O_5]/[NbF_7^{2-}]$ close to 1 : 3 [114]. Upon further increase in the concentration of the oxide anion, the extra peaks detected in voltammograms were interpreted by the equilibria [114]:

$$NbF_7^{2-} + 2Nb_2O_5 + 13F^- = 5NbO_2F_4^{3-}$$

$$NbOF_6^{3-} + Nb_2O_5 + 6F^- = 3NbO_2F_4^{3-}$$

In the presence of high Nb_2O_5 concentrations the authors [114] derived a three-step reduction mechanism (Fig. 3) taking into account the possible formation of mixed oxides and oxyfluorides.

3.3.3. Fluoride electrolytes. The process of Nb reduction is a two-step reaction in fused LiF–NaF mixtures [115] (Fig. 3) the last step being quasireversible and diffusion controlled. A further paper also supported this mechanism [118] in FLINAK melts and the diffusion coefficient of Nb(IV) was determined (Table 5).

3.4. *Tantalum* [115–134]

The main electrochemical reactions of Ta metal and Ta ions in molten salt solutions are summarized in Fig. 4. The parameters typical of Ta electrodeposition from a range of fused electrolytes are listed in Table 6.

Table 6 suggests that the mechanism of Ta electrodeposition is not yet fully clarified. Diffusion coefficients in chloride and fluoride melts differ by approximately an order of magnitude, rather unexpected as compared to the data for other refractory metals. No qualitative evaluation of the kinetic parameters of charge transfer and chemical steps has been found in the literature.

3.4.1. Chloride electrolytes. Picard *et al.* [129] demonstrated reduction in the LiCl–KCl–$TaCl_5$ system via two stages (Fig. 4). Lantelme *et al.* [130] confirmed a single step mechanism in NaCl–KCl–K_2TaF_7 melts (Fig. 4). That fact was tentatively explained [130] by the occurrence of a multistep reaction of five one-electron steps being undistinguishable by rate on a normal time scale. The appearance of extra peaks at potentials more anodic than that of the main oxidation peak was perhaps due to the formation of insoluble compounds on the electrode surface [130]. The extra anodic peaks before the metal oxidation wave were tentatively explained by the formation of Ta-rich oxides, or compounds containing metal clusters of Ta_4O and $Ta_6X_{12}^{n+}$ (X = F ÷ Cl) type, respectively. The main conclusion of the authors [130] was that electrodeposition of

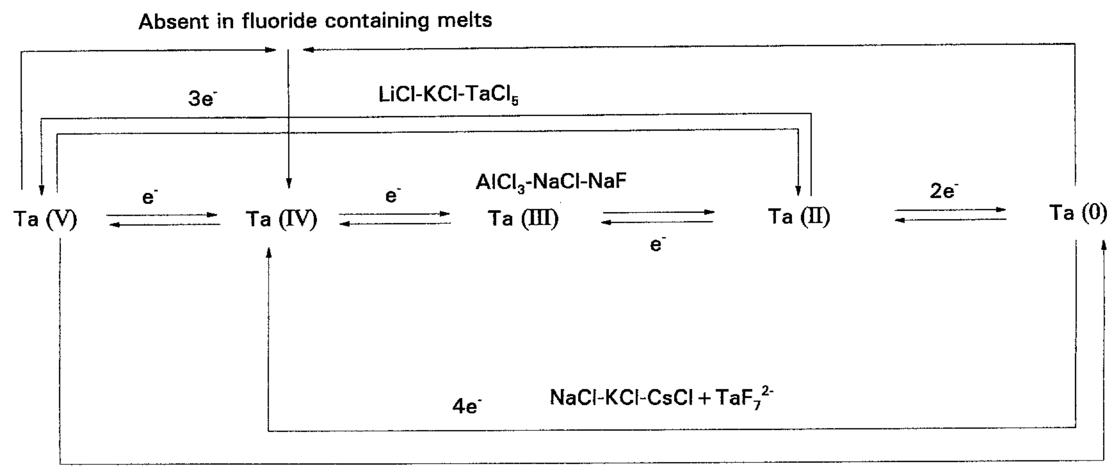

Fig. 4. Summary of the electrochemical reactions of Ta metal and Ta ions for a range of molten salt electrolytes.

Table 6. Summary of kinetic data concerning the chemical, anodic and cathodic reactions of Ta for a range of molten salt electrolytes

Electrolyte	*Reactions*	*n*	*Kinetic parameters*	*D* /cm^2 s^{-1}	*References*
LiCl–KCl	Ta(V)/Ta(II)	3			[121]
	Ta(II)/Ta(0)	2			
NaCl–KCl + TaF_7^{2-}	Ta(V)/Ta(III)	2			[126]
	Ta(III)/Ta(0)	3			
NaCl–KCl	Ta(V)/Ta(0)	5		1.3×10^{-5} (CV)	[130]
				1.6×10^{-5} (CP)	
+ NaF				1.4×10^{-5}	
+ O^{2-}	Ta_2O, TaO				
$AlCl_3$–NaCl	Ta(V)/Ta(IV)	1			[133]
	Ta(IV)/Ta(III)	2			
	Ta(III)/Ta(II)	2			
	Ta(II)/Ta, Ta_6^{14+}	2			
LiF–NaF	Ta(V)/Ta(II)	3			[112, 117]
	Ta(II)/Ta(0)	2			
LiF–NaF + Ta_2O_5	Ta(V)/Ta(0)	5			[127]
FLINAK	Ta(V)/Ta(0)	5		2.8×10^{-6}	[118]

microcrystalline Ta took place in a narrow potential range in chloride melts.

The addition of metallic Ta to the ternary NaCl–KCl–CsCl melt resulted in a shift of the conproportionation reaction completely to the right (Fig. 4) [128]. The formation of the Ta(IV) complex was verified by using X-ray diffraction analysis. The anodic dissolution of Ta in NaCl–KCl–CsCl melts proceeded via three stages [128]: Ta → Ta(IV) ions, Ta(IV) → Ta(V) and chlorine evolution.

3.4.2. Mixed electrolytes. The standard potential of the Ta(V)/Ta couple was shifted by about 0.33 V in the negative direction in ternary NaCl–KCl–NaF melt. Fluoride addition hampered the formation of insoluble oxide compounds observed in the NaCl–KCl electrolyte [130–132]. The increase in TaF_7^{2-} concentration in NaCl–KCl–CsCl electrolytes was related to an extra wave at negative potentials due to Ta dissolution to fluorocomplexes. The small amounts of free F^- which determined the limiting current [128] were assumed to be formed via dissociation of TaF_7^{2-} or partial substitution of fluoride ions by chloride ones.

Ta(V) reduction in chloroaluminate melts of the $AlCl_3$–NaCl(sat.) and $NaAlCl_4$–NaF(10 mol %) type developed in three cathodic waves [133]. The first wave at most positive potentials with a one-electron transfer was identified with the following reactions:

$$Ta^{5+} + e^- \longrightarrow Ta^{4+}$$

$$2Ta^{4+} \longrightarrow Ta_2^{8+}$$

The process underlying the second wave was assumed to be [133] as follows:

$$Ta_2^{8+} + 2e^- \longrightarrow Ta_2^{6+}$$

$$9Ta_2^{6+} \longrightarrow 6Ta^{4+}(\text{or } 3Ta_2^{8+}) + 2Ta_6^{15+}$$

The temperature increase destabilized the trivalent Ta species [133]. A similar reduction mechanism explained Ta(IV) behaviour in acidic $AlCl_3$–NaCl melts at temperatures lower than 200 °C [134].

The third reduction wave was interpreted by the authors [133] in terms of the following process:

$$Ta_2^{6+} + 2e^- \longrightarrow Ta_2^{4+}$$

$$7Ta_2^{4+} \longrightarrow 2Ta_6^{14+} + 2Ta(0)$$

Oxide anion addition at a ratio of $n_{O(II)}/n_{Ta(V)} < 1$ [130] resulted in a second cathodic wave at a current proportional to the oxide amount. Such an increase correlated with the decrease in intensity of the first wave, which disappeared at $n_{O(II)}/n_{Ta(V)} = 1$. The latter was assumed to be caused by the formation of oxyhalide complexes of Ta as $TaOCl_xF_y^{0^-}$, $z = x + y - 3$ [130]. X-ray diffraction analysis of coatings obtained by reduction of such melts revealed the formation of compounds of the Ta_2O and TaO type [130]; that is, thorough electrolyte purification was needed to obtain a suitable metallic coating.

4. Conclusions

A selective review of the electrodeposition processes of the IVB and VB group refractory metals (Ti, Zr, Nb and Ta) has been presented, dwelling on the kinetic data of reduction mechanisms and secondary chemical reactions. The following major conclusions can be drawn:

(i) There exists a considerable amount of data on Ti electroreduction from a range of molten salt electrolytes and several models have been proposed to explain the experimental facts observed. However, several questions remain unresolved: namely, (a) no exhaustive mechanism of anodic processes with the titanium electrode in Ti-ion containing LiCl–KCl melts has been proposed and no quantitative determination of kinetic parameters given; (ii) (b) no data for kinetic parameters for both the anodic dissolution and cathodic deposition of Ti from NaCl–KCl melts are available; (c) the reduction of Ti(IV) to Ti(III) in FLINAK and other fluoride electrolytes has not been quantitatively studied; and (d) there have been few attempts to describe the interaction processes between Ti metal and Ti-ions in oxide containing melts.

(ii) There is a limited amount of kinetic data on Zr electrodeposition and almost no quantitative determination of parameters characteristic of the charge transfer step. The effect of oxide ion addition on the reduction mechanism seems not to have been studied at all. Further work using transient electrochemical methods is needed to elucidate the reduction mechanisms and anodic reactions of electrorefining. Possible future trends in investigations will involve the search for new electrolyte combinations.

(iii) Reduction kinetics of Nb in basic electrolytes is qualitatively well defined, but the quantitative evaluation of kinetic parameters is still lacking (some parameters are available in LiCl–KCl eutectic only). Nb electrodeposition from FLINAK melts seems not to have been studied for 15 years. Data on anodic dissolution of Nb metal in molten salts are scarce.

(iv) Practically no kinetic parameters have been evaluated in Ta electrodeposition from molten electrolytes. Even some qualitative aspects of the interaction processes of Ta metal and fused salts remain mute questions, especially in all-chloride systems. The effect of oxide ion addition is poorly defined and only scarce qualitative data on the anodic processes of Ta dissolution are available. The very high affinity of Ta to form clusters with metal–metal bonds is a likely subject for further investigations.

(v) Very little attention has been paid to electrocrystallization kinetics of refractory metals and factors influencing that process stage. This area also requires study in the future.

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