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The role of fluoride ions in reduction–oxidation equilibria in CsCl–KCl–NaCl–K_2NbF_7 melts

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Abstract

The spontaneous reduction of Nb^V hepta-coordinated fluoro complexes in a mixed ligand electrolyte at 973–1073 K has been studied by linear voltammetry (which is highly sensitive to the variation of various oxidation states of Nb in the melt) and also by chemical analysis and IR spectroscopy. As the reaction $Nb^V \rightarrow Nb^{IV}$ proceeds, a decrease in the F/Nb mole ratio from the starting value of 7:1 to a final value of 6:1 is observed, the latter corresponding to the presence of only Nb^{IV} in the melt. The rate of the $Nb^V \rightarrow Nb^{IV}$ reduction process at constant temperature was independent of the initial K_2NbF_7 concentration and was independent of time. The concentration of fluoride ions present in the system has a considerable influence on this rate.

Introduction

The study of the interaction between niobium and molten alkaline metal halides containing niobium halides is important both for the development of electrochemical methods for obtaining coatings and for electro-refining. During melting of the electrolyte and its contact with a niobium anode, an active interaction between the metal and the highest oxidation state ions derived from the metal occurs with the formation of intermediate oxidation states. The composition of interaction products, the extent to which the reaction proceeds, the corresponding kinetics and the mechanism of the process appear to be very important. There is some account in the literature [1–3] of the study of the interactions occurring in niobium and chloride–fluoride melts. Thus, Ivanovskiy and Krasilnikov [1] who studied the anodic dissolution of niobium in chloride and in chloride–fluoride melts, reported that in potassium and sodium chloride melts in the presence of fluoride ions (in the form of NaF) the rate of self-dissolution of niobium was 6×10^{-4} g cm^{-2} h^{-1}. According to Ioffe and Novitchkov [2], who studied the interaction between niobium and potassium and sodium chloride melts containing 2.5–20 wt.% NaF or K_2NbF_7, the specific loss of niobium (4.4×10^{-4} g cm^{-2} h^{-1}) in NaCl–KCl melts increased sharply when sodium fluoride was introduced. When the NaF concentration was changed from 2.5 to 20 wt.%, the niobium

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losses varied abruptly over the range $5.5\text{–}13.5 \times 10^{-3}$ g cm^{-2} h^{-1} after potassium heptafluoroniobate was introduced into the melt.

However, these data were obtained some 20 years ago when experiments were not conducted as carefully as they are nowadays. These experiments were undertaken in air in a graphite beaker covered with a graphite lid. The sample was held in the melt for 1 h; however we have shown [3] that since the specific loss of niobium during interaction with melts containing Nb^{V} depend on the rate of the metal–salt reaction, it follows that for a 20 wt.% concentration of K_2NbF_7 the reaction time reported was not sufficient to allow the reaction to go to completion. A subsequent investigation of the mechanism and rate of niobium interaction with $KCl\text{–}KF\text{–}K_2NbF_7$ melts [3] showed that interaction between niobium and such melts occured via Nb^{IV} formation according to the stoichiometry:

$$4Nb^{V} + Nb \rightleftharpoons 5Nb^{IV} \qquad (1)$$

The relationship between the dissolution rate of the metal and the initial K_2NbF_7 concentration was established in this work.

Experimental

The present work focuses on the interaction between niobium and caesium, potassium and sodium chlorides eutectic melts (68.15/16.25/15.6 wt.%) containing potassium heptafluoroniobate. The electrochemical cell was virtually the same as that described previously [4]. It was hermetically sealed and filled with argon purified via a PG apparatus, the melt container being an ampoule made of SU-2000 type glassy carbon. As an alternative, a platinum crucible was used as the container in a number of cases. The background electrolyte was prepared from recrystallized and carefully dehydrated reagent grade salts via step-by-step heating under vacuum and subsequent melting under argon. The potassium heptafluoroniobate employed was obtained from commercial K_2NbF_7 recrystallized from liquid hydrogen fluoride followed by washing with ethanol and drying in a vacuum box at 110–120 °C.

Metal samples of 99.9% purity with a surface area of 3.0–4.0 cm^2 were made in the form of 1.0-mm thick plates. To remove the oxide film, the samples were polished in a $H_2SO_4/HNO_3/HF$ (10:4:3) mixture for 3–4 s and then washed consecutively with water and ethanol, and dried.

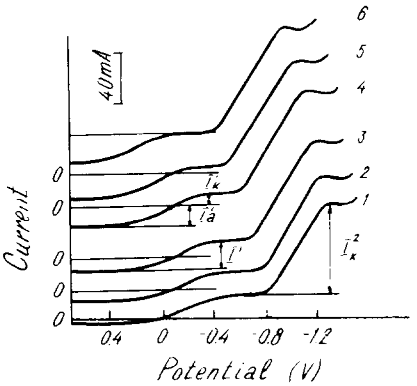
Experiments were conducted over the temperature range 872–1073 K, the specified electrolyte temperature being maintained by a VRT-3 temperature controller. Voltammetric curves were recorded by P-5848 and PI-50-1 potentiostats, the output data being fed into a PR-8 programmer and recorded on a LKD-4 recorder. Glassy carbon and platinum electrodes were used for the voltammograms. Potentials were measured versus an Ag/AgCl reference electrode maintained in a 2 wt.% CsCl–KCl–NaCl eutectic.

No additional waves in either the cathodic and anodic parts of the voltammogram were observed in each experiment.

Results and discussion

Preliminary experiments have established that niobium reduction in CsCl–KCl–NaCl–K_2NbF_7 melts occurs in two sequential stages [5]. With the aid of classical polarography and potentiostatic electrolysis data, the first stage of the process $Nb^V \rightarrow Nb^{IV}$ has been identified as a reduction, while the second stage corresponds to reduction of Nb^{IV} to the metal.

In the present case, the melt was doped with 5 or 10 wt.% potassium heptafluoroniobate and the cathodic voltammogram of the melt recorded after 30–40 min. Two reduction waves were observed: $Nb^V + e^- \rightarrow Nb^{IV}$ with a current I^1 and a four-electron process, i.e. $Nb^{IV} + 4e^- \rightarrow Nb^0$, with a current I_k^2 (Fig. 1, curve 1). A niobium sample attached to an inert molybdenum lead by a platinum wire was then immersed in the melt (the molybdenum was not allowed to come into contact with the melt) in an inert gas flow and was maintained in the electrolyte until equilibrium was established. Interaction between Nb and its pentavalent ions in the melt proceeds according to the equation $4Nb^V + Nb \rightarrow 5Nb^{IV}$, with the reaction equilibrium being shifted almost completely to the right in the melt. As a result, the first stage in the cathodic wave on the voltammetric curve is shifted to the anodic region corresponding to oxidation of Nb^{IV} to Nb^V with a current I_a^1 (Fig. 1). Equilibrium was considered to have been achieved when the first wave had shifted completely to the anodic region and the current values I_a^1 and I_k^2 had stabilized. The sample was then raised from the melt, the retort cooled, the sample removed from the system, washed and weighed. The weight loss of the sample was then compared both with X-ray fluorescence data and the results of chemical analyses of the niobium content in the electrolyte.



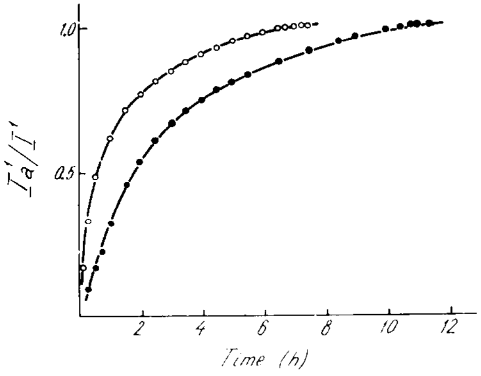


Fig. 1. Voltammetric curves for CsCl–KCl–NaCl–K_2NbF_7 (5 wt.%) melts illustrating the changes occurring with time during the interaction with metallic niobium. Temperature, 1023 K; $S_{el} = 0.1$ cm^2; $V = 0.1$ V s^{-1} Time (h): curve 1, 0; curve 2, 0.2; curve 3, 0.35; curve 4, 0.6; curve 5, 1.1; and curve 6, 4.5.

Fig. 2. Plots of I_a^1/I^1 versus time for niobium interaction with CsCl–KCl–NaCl–10 wt.% K_2NbF_7 melts at 953 K (●) and 1053 K (○).

The variation in the Nb^{IV} concentration whilst the equilibrium depicted in eqn. (1) was established was studied at a constant initial K_2NbF_7 concentration of 5 or 10 wt.% and at different temperatures. The attainment of equilibrium was determined from the ratio I_a^1/I^1 (Fig. 2), where I_a^1 is the current corresponding to the anodic component of the first wave, and I^1 is the sum $I_a^1+I_k^1$. The curves depicted in Fig. 2 exhibit an asymptotic character and approach values corresponding to the attainment of equilibrium (1). The experimental and calculated data are listed in Table 1 (and Fig. 2), and indicate that the rate of the metal–salt reaction increases with an increase in temperature and in potassium heptafluoroniobate concentration. The mass losses from the samples, however, were less than those calculated from equation (1), with the difference between the calculated and experimental values increasing as the temperature increased. Furthermore, it was noticed that, prior to the immersion of the niobium sample in the melt containing potassium heptafluoroniobate, the first wave shifted with time to the anodic region of the curve indicating that tetravalent niobium ions were present in the melt before the metal was introduced (Fig. 1). Characteristically, the rate of the $Nb^V \rightarrow Nb^{IV}$ reduction increased considerably on increasing the temperature.

In order to exclude the possibility of the container material influencing the process, both platinum and glassy carbon crucibles were used. Voltammetric curves were recorded using platinum and glassy carbon electrodes both relative to the crucible and to the silver reference electrode. When the temperature had settled at its working value, potassium heptafluoroniobate was added and voltammetric curves were recorded allowing measurement of changes in the anodic current corresponding to $Nb^{IV} \rightarrow Nb^V$ oxidation. The first wave shifted to the anodic region irrespective of the material of both the container and the indicator electrode, i.e. complete reduction occurred from pentavalent to quadrivalent niobium Simultaneously, the fluoride ion

TABLE 1

Experimental and calculated data for the interaction of niobium with CsCl–NaCl–KCl–K_2NbF_7 melts

Concentration of K_2NbF_7 (wt.%)	Temperature (K)	Mass loss of sample (g)	Sample mass loss calculated for reaction (1) (g)	Time required to achieve equilibrium (h)
5.0	973	0.2042	0.2435	6.1
	1023	0.1945	0.2435	4.5
	1053	0.1828	0.2435	4.0
	1073	0.1796	0.2435	3.5
10.0	953	0.4507	0.5095	11.4
	1023	0.4185	0.5095	8.3
	1053	0.4036	0.5095	7.0
	1073	0.5682	0.7686	6.5

concentration in the melt decreased as a result of sublimation of fluoride from the electrolyte to colder parts of the cell. Thus, the initial concentration of fluoride ions in the melt fell from 4.37 wt.% to 3.7 wt.% while the sublimate contained 36.5 wt.% fluoride ion. At the same time the chloride content in the electrolyte increased (from an initial value of 27.5 wt.%) although the sublimate contained only 2 wt.% chloride. The F/Nb molar ratio changed from an initial value of 7 to 5.96–6.08 at the same time as the $Nb^{V} \rightarrow Nb^{IV}$ reduction occurred. In addition Fe, Cr, Ni and Ti fluorides appeared in the sublimate indicating fluorination of the stainless steel retort.

If a silver reference electrode was used in these experiments in conjunction with an alumina tube inside the glassy carbon shell, more than 3 wt.% Al and up to 0.3 wt.% Si were detected in the sublimate in the hot zone above the melt as a result of the fluorination of alumina. In the case of niobium electrolysis giving rise to powders and coatings, these processes lead inevitably to the contamination of cathodic deposits.

The IR spectra of powdered samples of the initial $CsCl–KCl–NaCl–K_2NbF_7$ system exhibited an absorption band at 550 cm^{-1} with a shoulder at 600 cm^{-1} characteristic of $NbF_7{}^{2-}$ and $NbF_6{}^{-}$ complexes, respectively [6]. When the molten mixture was maintained in contact with niobium, and the electrochemical data indicated a reduction of Nb^{V} to Nb^{IV}, the IR spectra of the resulting solid samples exhibited a 525 cm^{-1} band corresponding to the stretching vibrations of the $Nb^{IV}–F$ bond in $NbF_7{}^{3-}$ or NbF_6Cl^{3-} complexes [5]. Heating the $CsCl–KCl–NaCl–K_2NbF_7$ melt for 5 h at 1073 K, without contact with metallic Nb, led to complete reduction of Nb^{V} to Nb^{IV} and the absence of IR bands characteristic of $Nb^{V}–F$ bonds in hexa- or hepta-coordinated complexes. Hence, there is complete agreement between the spectroscopic and electrochemical data and chemical analysis of the condensed salts in the colder parts of the cell, leading to the conclusion that $Nb^{V} \rightarrow Nb^{IV}$ reduction occurs according to:

$$NbF_xCl_{7-x}^{2-} \rightleftharpoons NbF_{x-1}Cl_{8-x}^{3-} + \tfrac{1}{2}F_2 \qquad (2)$$

Admittedly, this is a simplified scheme for the reaction and must omit some of the intermediate stages.

An active oxidant such as fluorine is unlikely to exist for any length of time under the experimental conditions employed. Thus it may interact *in statu nascendi* with the material of the cell elements or, in passing in the gas phase over the melt, it may fluorinate metallic or ceramic structures with subsequent fluoride transfer and condensation in the cold zone. If such processes are considered, it is not possible to effect an exact evaluation of the system due to the absence of important thermodynamic values. Furthermore, although the reaction proceeded extremely slowly in a molten mixture of sodium and potassium chlorides; the introduction of caesium chloride shifted the equilibrium dramatically to the right showing the effect of the second coordination sphere of caesium.

The rate of the $Nb^{V} \rightarrow Nb^{IV}$ reduction process (K_{red}) has also been determined in a $CsCl–K_2NbF_7$ melt by voltammetric methods. At 700 °C, this rate was 0.014 g h^{-1} K_2NbF_7, i.e. six-times less than in CsCl–KCl–NaCl–K_2NbF_7 melts (0.084 g h^{-1}). When sodium chloride (at 10 wt.%) was added to the CsCl–K_2NbF_7 melt, the reduction rate increased to 0.033 g h^{-1}.

Similar processes of partial reduction, i.e. $Re^{VII} \rightarrow Re^{VI}$ [7] and $Nb^{V} \rightarrow Nb^{IV}$ [8], have been observed during previous studies of oxyfluoride compounds.

Experiments to estimate the reaction rates [2] have been performed using initial potassium heptafluoroniobate concentration of 1.41, 5.0 and 10.0 wt.%. The rate of the reduction process $Nb^{V} \rightarrow Nb^{IV}$ (K_{red}) was evaluated by determination of the voltammograms and by plotting a I_a^1/I^1 versus time curve (Fig. 3). Termination of the reduction process was assumed when the I_a^1/I^1 ratio was unity, i.e. when the wave corresponding to $Nb^{V} \rightarrow Nb^{IV}$ has shifted completely to the anodic region.

The rate of the process at constant temperature was established as being independent of the initial concentration and the length of the process. Figure 4 depicts a plot of the rate of the reaction as a function of temperature where K_{red} is expressed in g K_2NbF_7 reduced per unit time. The experimental values of the rate constants for the process lie on a straight line when plotted on the basis of log K_{red} versus $1/T$ coordinates (Fig. 5). The activation energy for the oxidation–reduction process depicted in eqn. (2) was calculated as 9.69 kcal mol^{-1}. The rate for the $Nb^{V} \rightarrow Nb^{IV}$ process at constant temperature was dependent on the fluoride ion concentration; thus, if hexa-coordinate Nb^{V} fluoro complexes are added to the melt, they are not reduced irrespective of the length of time the melt is maintained at constant temperature. The redox reaction is also completely suppressed by the addition of an excess (5–10 wt.%) of fluoride ions to the melt.

The experiments show that dissolution of metallic niobium in CsCl–KCl–NaCl–K_2NbF_7 melts proceeds with formation of Nb^{IV} according to eqn. (1) and is accompanied by a side oxidation–reduction reaction [eqn. (2)] whereby the weight losses expected from eqn. (1) are reduced. The reaction equilibrium expressed in eqn. (1) is shifted completely to the right,

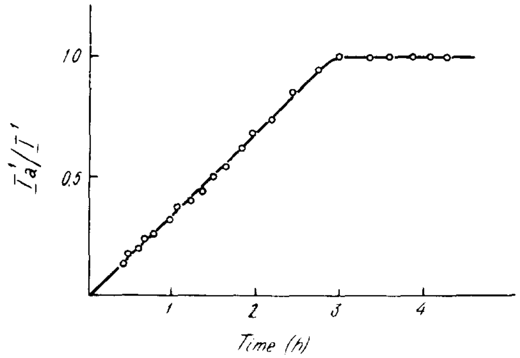


Fig. 3. Plot of I_a^1/I^1 versus time in a CsCl–KCl–NaCl–K_2NbF_7 melt. Temperature, 1073 K; $m_{melt} = 50$ g; $m_{K_2NbF_7} = 0.716$ g.

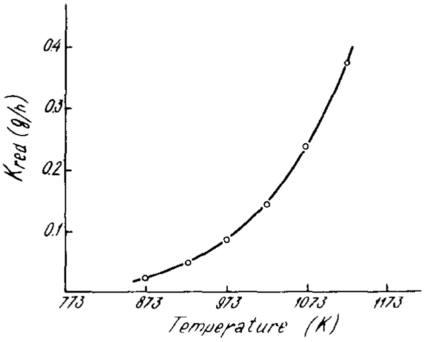


Fig. 4. Plot of the rate constant for $Nb^V \rightarrow Nb^{IV}$ reduction expressed according to eqn. (2) versus temperature.

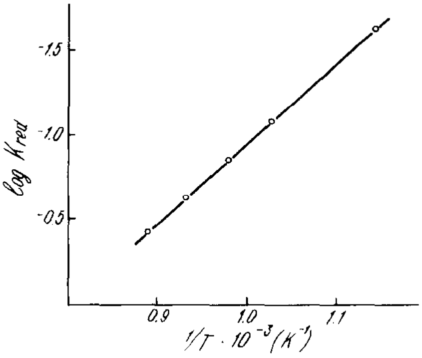


Fig. 5. Influence of temperature on the logarithm of the rate constant for $Nb^V \rightarrow Nb^{IV}$ reduction expressed according to eqn. (2).

as evidenced by a complete shift of the cathodic wave corresponding to $Nb^V \rightarrow Nb^{IV}$ reduction to the anodic region.

These results indicate that the rate of the $Nb^V \rightarrow Nb^{IV}$ process is influenced not only by the type of alkali metal cation in the melt but also by the proportion between the concentration of the different types of cations present. This may be explained by one type of outer-sphere cation ensuring a minimum activation energy for electron transfer to Nb^V while a different type of outer-sphere environment ensures the greatest stability for the Nb^{IV} complex. As demonstrated by Volkov and Zasukha [9], the activation energy for electron transfer via an outer-sphere cation decreases in the alkali metal cation series from Li^+ to Cs^+ and, hence, the presence of Cs^+ in the melt ensures the highest $Nb^V \rightarrow Nb^{IV}$ transfer rate. Equally, the rate of the reverse process decreases in proceeding from caesium to lithium. Purely ionic interactions between outer-sphere cations and hexafluoride Nb^{IV} complexes in the same series must lead to an increase in the stability of the latter.

The influence of covalent interactions on hexafluoride Nb^{IV} complexes is easily demonstrated by theoretical group analysis of the interaction between the atomic orbitals of alkali metal cations and the highest occupied molecular orbital (HOMO) as well as the lowest unoccupied MO (LUMO) of Nb^V hexafluoride complexes [9]. The HOMO and LUMO symmetry is known to be t_{1g} and t_{2g}, respectively [10]. Analysis of the tetrahedral, octahedral and cubic outer-sphere environment of the Nb^V hexafluoride complex shows that convergence of the HOMO and LUMO (and, consequently, an increase in the stability of the Nb^{IV} hexafluoride complex) occurs in the first and in third cases, the stability of the Nb^{IV} complex increasing in the presence of outer-sphere cations in the series Cs^+ to Li^+.

In our case, the greatest electron-transfer rate is achieved when the outer-sphere environment of the Nb^{IV} complex is derived from Cs^+ cations, whereas the maximum Nb^{IV} complex stability is achieved in the presence of Na^+ outer-sphere cations. The resulting Nb^{IV} formation rate should depend on the proportion of the concentration of these cations in the melt. An absence of one of these cations from the melt must lead to a decrease in the $Nb^V \rightarrow Nb^{IV}$ transition rate as observed experimentally. The zero-order reaction relative to the initial niobium concentration in the melt can probably be explained by the fact that the limiting step in the reaction is the exchange process between Cs^+ and Na^+ ions in the outer sphere of Nb^{IV} complexes which depends mainly on the ratio of the concentration of these cations in the system.

Further research is needed to gain an insight into the processes involved in the $Nb^V \rightarrow Nb^{IV}$ transition. In particular, it is unclear as to whether the preliminary formation of an activated Nb^V complex (fluoride–chloride, for example) is necessary for electron transfer, as well as whether fluoride ion oxidation occurs directly or in two stages involving intermediate chloride ion oxidation.

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