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# Electrochemical Reaction Processes of Niobium Ions in FLINAK melt

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**Abstract:** To investigate the mechanism and influence of oxide and niobium metal on the electrodeposition of niobium, the electrochemical reaction mechanisms of niobium ions in LiF-NaF-KF eutectic (FLINAK) melt at 973 K was studied by chronopotentiometry, chronoamperometry and cyclic voltammetry. The electrochemical reduction process of Nb(V) ($K_2NbF_7$) in FLINAK melt relates to the complex anions. A two-step electrochemical reduction with disproportionate and catalytic reactions is proposed. The metallic niobium in $K_2NbF_7$-FLINAK melt can reduce the catalytic reaction. The influence of oxide ($Na_2O$) on the electrochemical processes of Nb(V) in $K_2NbF_7$-FLINAK-$O^{2-}$ melts without and with niobium metal present was also studied. When oxide present in $K_2NbF_7$-FLINAK melt, a much stable oxyfluorocomplex ion is formed. Cyclic voltammetry showed that the reduction potential of oxyfluoro-complex ion is more negative than that of fluorocomplex ion ($NbF_6^{2-}$). The electrochemical stability of $NbOF_6^{3-}$ is higher than those of $NbF_7^{2-}$ and $NbF_6^{2-}$. An optimum composition for a coherent niobium metal coating on low-carbon steel is found to be 2.7%$K_2NbF_7$-0.5~2.0%$Na_2O$-FLINAK in molar fraction. The cathodic current density is about 90 mA/cm$^2$.

**Key words:** electrochemistry; molten Salt; FLINAK; niobium reduction

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The cathodic process mechanism of niobium reduction from chloride-fluoride and fluoride melts has been studied in detail [1~4], but there seems still to be some disagreement concerning the reduction mechanism. Essentially, three types of models have been put forward to explain the electrochemical data. These include three-step [Nb(V) → Nb(IV) → Nb(I) → Nb(0)] [2], two-step [Nb(V) → Nb(IV) → Nb(0)] [3,5] and [Nb(V) → Nb(III) → Nb(0)] [6,7]. As shown in reference [5], the formation of oxofluoride complexes changes the reduction mechanism of Nb(V) completely. Their results indicate an one-step discharge of the Nb(V) mono-oxofluoro complex.

Niobium [1] as well as other refractory metals were first demonstrated by Senderoff, *et al.*[2] to be capable of electroplating in coherent and dense coating from molten fluoride solvents. As can be understood there are many factors which influence the properties of the deposited metal layer. Mellors, *et al.*[1] discussed the importance of essentially pure fluoride melts to obtain coherent refractory metal coatings. Mixed chloride-fluoride systems were found to produce only dendrites, powders or sometimes alloy layers covered with powders [1]. According to Mellors, *et al.*'s opinion, the deposition of coherent deposit from molten salts requires a complex anion which is available in the electrolyte with the correct thermodynamic stability for reduction. A prereduction of Nb(V) with niobium metal present was suggested by Senderoff, *et al.* for niobium electroplating from molten fluorides. These observations indicate how important the oxide content and niobium metal in melt may be during electrochemical reduction and deposition of niobium species. This paper presents some results obtained on the electrodeposition of niobium from LiF-NaF-KF eutectic (FLINAK) melt.

## 1 Experimental

$K_2NbF_7$ and $Na_2O$ were obtained from LAFA and Aldrich, and used without further purification. The chemical analysis results of $K_2NbF_7$ are Nb, (30±1)%; K, (26.8±0.3)% and F, (42.9±0.8)% compared with calculated values Nb, 30.6%; K, 25.7% and F, 43.7% in mass fraction. $Na_2O$ was analyzed by titration with hydrochloric acid to be 98% in mass fraction. The analytical grade alkali fluorides (LiF, NaF and KF) from Merck was purified by slow recrystallizaton and zone-refine technique. The cooling rate was kept at 3 K/h. The oxide content of purified FLINAK melts was determined by electrochemical titration technique to be (0.05 ± 0.02)% in molar fraction [8].

The experimental setup used for electrochemical measurement and electrodeposition was described previously [9]. The electrochemical measurements were carried out at (973 ± 0.5) K under argon (99.99% in mass fraction) atmosphere. The pressure of argon in furnace chamber was kept at (120 ± 5) kPa by an automatic pressure regulator. The container for the melts is a glassy carbon crucible. A Pt wire (0.5 mm in diameter) was taken as a working electrode. Its vertical depth in molten salts was controlled by a screw micrometer, and the certain electrode surface area (0.04 $cm^2$) was obtained. The counter electrode for electrochemical measurement is a platinum foil. A Ni/$NiF_2$ electrode and a Pt wire electrode were used as reference and quasi-reference electrodes [10].

For an electrochemical experiment, the mixture of LiF, NaF, KF and other chemicals contained in glassy carbon crucible was evaluated to a pressure of about 3 Pa at 473 K to remove residual water, oxygen and others. Then an argon atmosphere in the furnace chamber was established. At argon atmosphere, the temperature was raised to and kept at 973 K. The electrochemical measurements were obtained by means of Galvanostat/potentiostat apparatus.

For an electrodeposition experiment, a flow of argon at room temperature for 1 h and during heating to the experimental temperature of 973 K was initially kept. When this temperature was reached, a change to overpressure ((120 ± 5) kPa) was carried out. All melts for electrochemical measurements and plating were premixed at 973 K for 4 h. A low carbon steel rod (0.5 mm in diameter) was used as substrate (cathode). The anode was niobium metal foil (99.99% in mass fraction, 1 mm in thickness) from Goodfellow. When the electrodes dipped into the melt, the chemical reaction between Nb(V) and the niobium metal anode took place before the electrochemical reduction for 3 h. In all case, the electrolysis time was 3 h, and the cathodic current density was (94 ± 18) mA/$cm^2$. The area of the electrodes in contact with the melt depended on the depth of the electrodes in the melts. The amount of melt used for each experiment was in the range of 22 g (depending on the composition).

To investigate the chemical reaction between Nb(V) and niobium metal, sheets of niobium metal (approximately 4 $cm^2$ in area) were used for reduction experiments with varying $Na_2O$ content. The niobium metal was placed in the crucible together with the chemicals at room temperature, then heated to 973 K and kept under argon atmosphere for 10 h. The number of grams of niobium metal dissolved was determined from the mass loss, and the average oxidation state of niobium was calculated.

## 2 Results and Discussion

### 2.1 $K_2NbF_7$ in FLINAK melt

(1) Chronopotentiometry

A cathodic current single pulse (step and off) technique was employed to investigate the electrochemical reduction mechanism. To measure the potential during current step and off is more effective than only during current step. The curves of potential ($\varphi$) with time ($t$) at various cathodic current steps for Nb(V) in FLINAK melt is shown in **figure 1**.

At too low (−2 mA) and high (−7 mA) cathodic current step, in the part of current off, the plateau of the potential is not very clear. At high cathodic current step, there is a typical peak of electrocrystallization in step part.

There are two potential plateaus in current off part for −5 and −5.5 mA steps. These two plateaus could be produced in two ways: (a) consecutive and (b) parallel charge transfer processes [11]. In consecutive charge transfer process, the relation of transient time ($\tau$) with electron number ($n$) of the electrochemical reac-

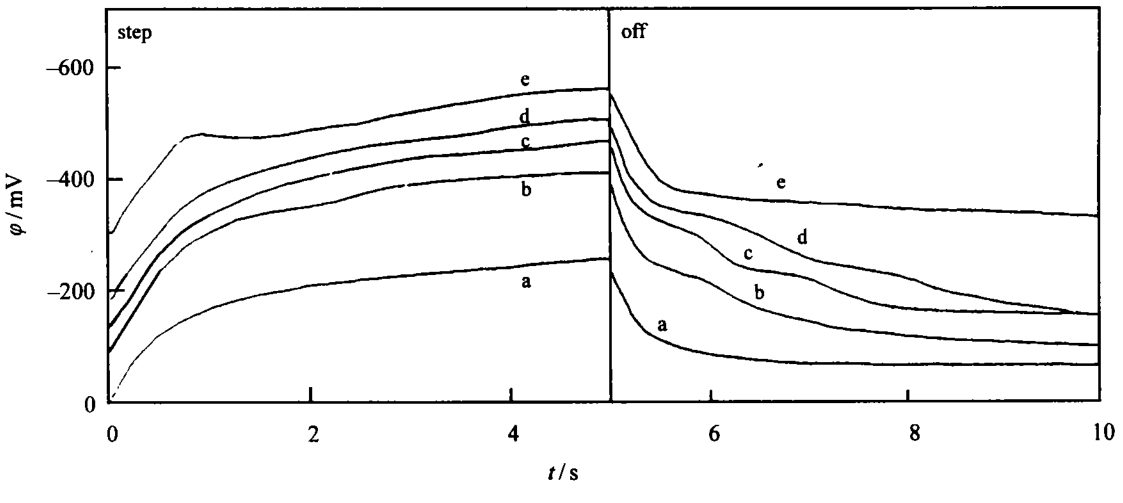

Figure 1 $\varphi - t$ curve for cathodic current single pulse (step and off). The melt is $0.1K_2NbF_7$-FLINAK (in molar fraction) at 973 K; the current step (0 ~ 5 s) is a, −2 mA; b, −4 mA; c, −5 mA; d, −5.5 mA and e, −7 mA; and in 5 ~ 10 s, the current is off.

tion is as

$$(\tau_2/\tau_1+1)^{1/2}=n_2/n_1+1 \tag{1}$$

The ratio of $\tau_2/\tau_1$ only depends on the ratio of $n_2/n_1$.

For a parallel charge transfer process, the rate of $\tau_2/\tau_1$ depends not only on the ratio of $n_2/n_1$, but also on the concentrations of the reactant species. For −5 and −5.5 mA steps, the ratio of $\tau_2/\tau_1$ are 1.00/1.20 and 1.75/1.22, respectively. The results show that the reaction process is not a consecutive charge transfer process. These two potential plateaus are due to the anodic reaction of solution and adsorption (or electrocrystallization) species of niobium atoms ($Nb_{sol}$ and $Nb_{ads}$) in the melt.

For −4 mA step, there are two plateaus in current step and off process, respectively. One plateau potential during current off is reaching the potential of second plateau of −5 and −5.5 mA steps. For this potential plateau, the transient time is 1.18, 1.20 and 1.22 s for −4, −5 and −5.5 mA steps, respectively. According to the chronopotentiometric equation

$$E=E_{\tau/4}+\frac{RT}{nF}\ln\left[\left(\frac{\tau}{t}\right)^{1/2}-1\right] \tag{2}$$

the electron number ($n$) can be calculated from the slope of $E$— $\ln\left[\left(\frac{\tau}{t}\right)^{1/2}-1\right]$ plot [12]. For these three cases, the electron number is obtained to be around 4. The reaction related to this plateau potential is anodic reaction of $Nb_{sol}$, $Nb_{sol} \rightarrow Nb(IV)+4e^-$. The reaction related to another plateau potential is $Nb(IV) \rightarrow Nb(V)+4e^-$. For small current step, only this mono-electron reaction was observed.

Therefore, the redox process of Nb(V) ($K_2NbF_7$) in FLINAK melt is concluded as follows:

(a) cathodic current step process,

$Nb(V)+e^- \rightarrow Nb(IV)$,

$Nb(IV)+4e^- \rightarrow Nb_{sol}$ and/or $Nb_{ads}$.

(b) current off process,

$Nb_{sol} \rightarrow Nb(IV)+4e^-$,

$Nb_{ads} \rightarrow Nb(IV)+4e^-$,

$Nb(IV) \rightarrow Nb(V)+e^-$.

(2) Chronoamperometry

The chronoamperometry is also a conventional method to study the electrocrystallization and redox process. The typical plots are shown in **figures 2**. At high cathodic potential step (−325 mV), an electrocrystallization process is involved. For a low potential step (−250 mV), no obvious electrocrystallization is observed. For this case, it is suitable to study the reduction process of Nb(V) in the melt. From figure 2 (b) curve, three kinds of plots ($I-t^{1/2}$, $Q-t^{1/2}$ and $I-t^{-1/2}$) can be obtained. They are shown in **figure 3**.

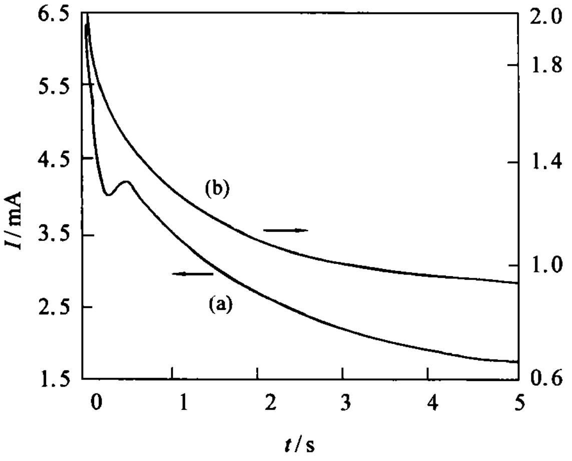

**Figure 2 Chronoamperometric curve ($I-t$) of 0.1% $K_2NbF_7$ (in molar fraction) in FLINAK melt. The potential step is (a) −325 mV and (b) −250 mV *vs.* Ni/Ni(II).**

The relation of current ($I$) with $t^{1/2}$ is linear in short time. It is shown that the process is controlled by charge transfer. For a long time, another linear relation of $Q$ (charge) with $t^{1/2}$ is obtained (see figure 3(b)). According to chronocoulometry, the function of $Q$ and $t^{1/2}$ is linear for a diffusion control process [13]:

$$Q=2nFC_0\pi^{-1/2}D^{1/2}t^{1/2} \tag{3}$$

Therefore the reduction reaction of Nb(V) in the melt is a mixed control process. The process is controlled by charge transfer at initial stage, then by mass diffusion.

In order to study the reduction mechanism of Nb(V) to niobium atom, the third plot ($I-t^{-1/2}$) is made and shown in figure 3(c). From the figure, an ECE mechanism is proposed. For ECE mechanism [11],

$$I=FAC_0\pi^{-1/2}D^{1/2}[(n_1+n_2)-n_2\exp(-kt)]\,t^{-1/2} \tag{4}$$

When measuring time is very short, equation (4) can approximately be written as

$$I=FAC_0\pi^{-1/2}D^{1/2}n_1t^{-1/2} \tag{5}$$

The slope of $I-t^{-1/2}$ curve depends on the electron number $n_1$ and other parameters. The curve of $I-t^{-1/2}$ is varied due to the second electrochemical reaction ($n_2$). At a very long time,

$$I=FAC_0\pi^{-1/2}D^{1/2}(n_1+n_2)\,t^{-1/2} \tag{6}$$

the slope is related to the electron number $n_1$ and $n_2$.The chemical reaction (C) is a disproportionate reaction of $NbF_6^{2-}$ in fluoride melt.

$5NbF_6^{2-} \Leftrightarrow 4NbF_7^{2-}+Nb+2F^-$.

According to chronopotentiometric and chronoampe-

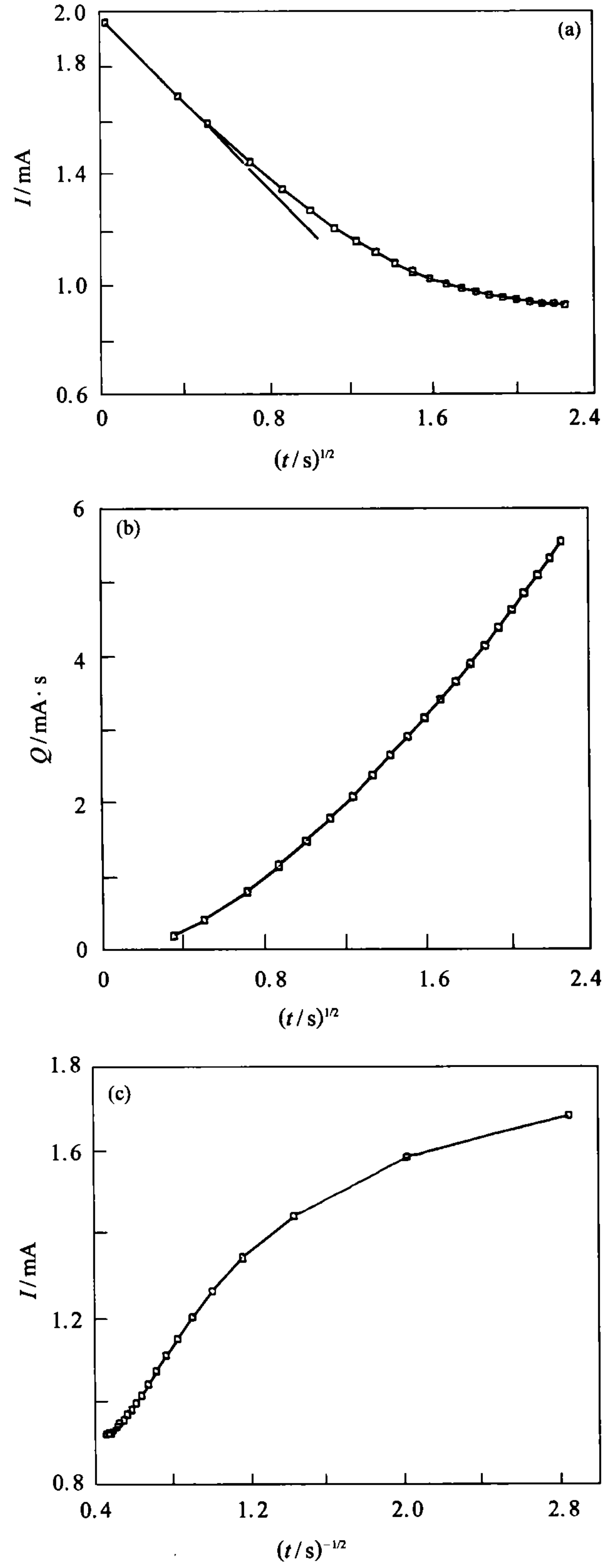

Figure 4 Plots of $I-t^{1/2}$, $Q-t^{1/2}$ and $I-t^{-1/2}$ from figure 2 (b) curve.

rometric results, the ECE reaction process is concluded as

E: $NbF_7^{2-} + e^- \rightarrow NbF_6^{2-} + F^-$,

C: $5NbF_6^{2-} \Leftrightarrow 4NbF_7^{2-} + Nb + 2F^-$,

E: $NbF_6^{2-} + 4e^- \rightarrow Nb + 6F^-$.

(3) Cyclic voltammetry

The cyclic voltammogram as an "electrochemical spectrum" is very useful to study and to determine the electrochemical mechanism. A typical cyclic voltammogram was shown in **figure 4**. One loop is found in cathodic branch. It means that an elecrocrystallization process is involved in reduction process of Nb(V) in FLINAK melt. For a reduction mechanism of Nb(V) in FLINAK melt, peak A is analyzed in detail. The plots of $I_p^c - v^{1/2}$ and $I_p^c/v^{1/2} - v$ of peak A at various sweep rates are shown in **figure 5**. At low sweep rate, the reaction process could be taken as a reversible charge transfer process from the plot of $I_p^c - v^{1/2}$. The electron number can be obtained at the sweep rate of 0.2 and 0.1 V/s at 973 K according to

$$E_p^c - E_{p/2}^c = \frac{-2.20RT}{nF} \qquad (7)$$

The calculated electron number ($n$) is reaching to 4. Therefore, peak B could be a mono-electron reaction. From the relationship curve of $I_p^c/v^{1/2} - v$ of peak A and electrochemical reaction mechanism diagnosis, a catalytic reaction is confirmed to accompany the electrochemical reaction. The reduction process of Nb (V) ($K_2NbF_7$) in FLINAK melt at 973 K is concluded as

$NbF_7^{2-} + e^- \rightarrow NbF_6^{2-} + F^-$,

$5NbF_6^{2-} \Leftrightarrow 4NbF_7^{2-} + Nb + 2F^-$,

$NbF_6^{2-} + 4e^- \rightarrow Nb + 6F^-$,

$Nb + 4NbF_7^{2-} + 2F^- \Leftrightarrow 5NbF_6^{2-}$.

## 2.2 Role of niobium

From the discussion above, a metallic niobium is used to reduce the dissolution of niobium deposited on

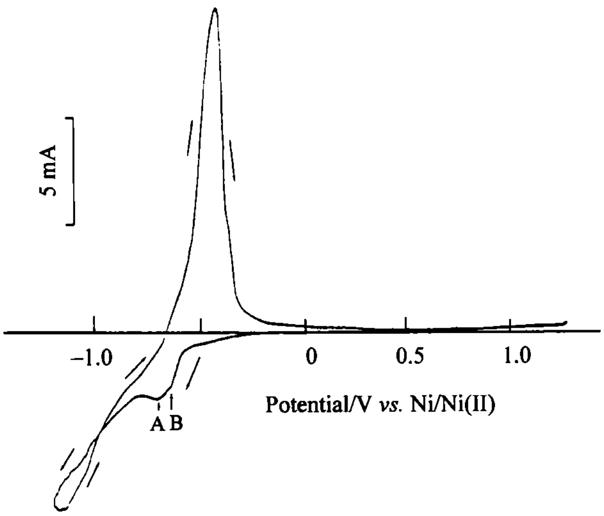

Figure 4 A typical cyclic voltammogram of 0.175% $K_2NbF_7$ (in molar fraction) in FLINAK melt. The sweep rate is 0.2 V/s.

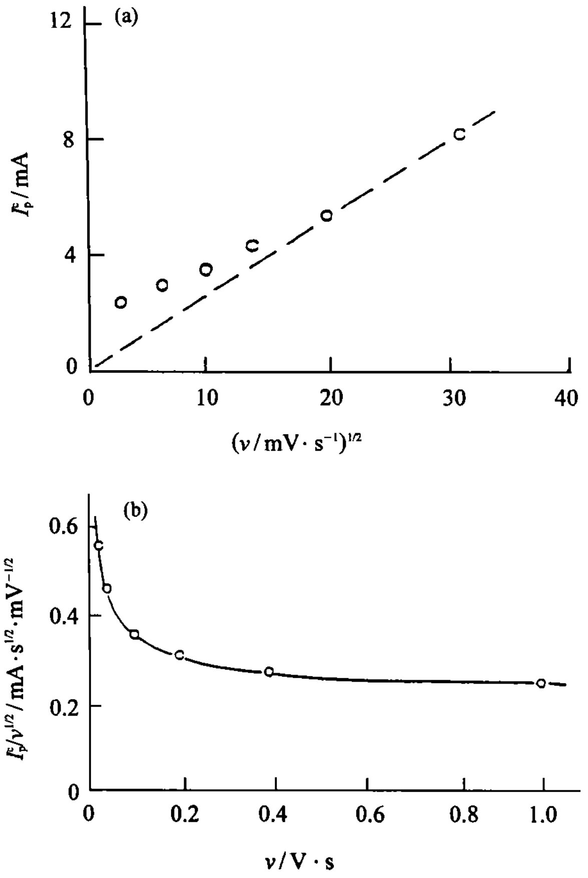

**Figure 5 Plots of $I_p^c - v^{1/2}$ and $I_p^c/v^{1/2} - v$ for 0.175% $K_2NbF_7$-FLINAK (in molar fraction) electrolyte without Nb present.**

the substrate. **Figure 6** is a typical voltammogram of Nb(V) ($K_2NbF_7$) in FLINAK melt with niobium metal present. From the figure, much different plots of $I_p^c - v^{1/2}$ and $I_p^c/v^{1/2} - v$ with Nb(V) in FLINAK melt without niobium metal present are obtained (see **figure 7**). The relation of $I_p^c/v^{1/2}$ with $v$ is linear which indicates that the catalytic reaction (equations (3) – (14)) is greatly decreased. The main role of niobium metal present in $K_2NbF_7$-FLINAK melt is pre-reduction of $NbF_7^{2-}$ and to reduce the dissolution of deposited niobium (catalytic reaction).

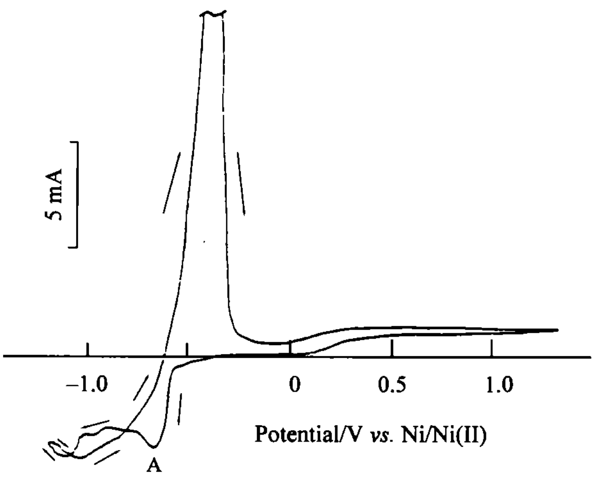

**Figure 6 A typical cyclic voltammogram from 0.15% $K_2NbF_7$ (in molar fraction) in FLINAK melt with Nb present. The scan rate is 0.2 V/s.**

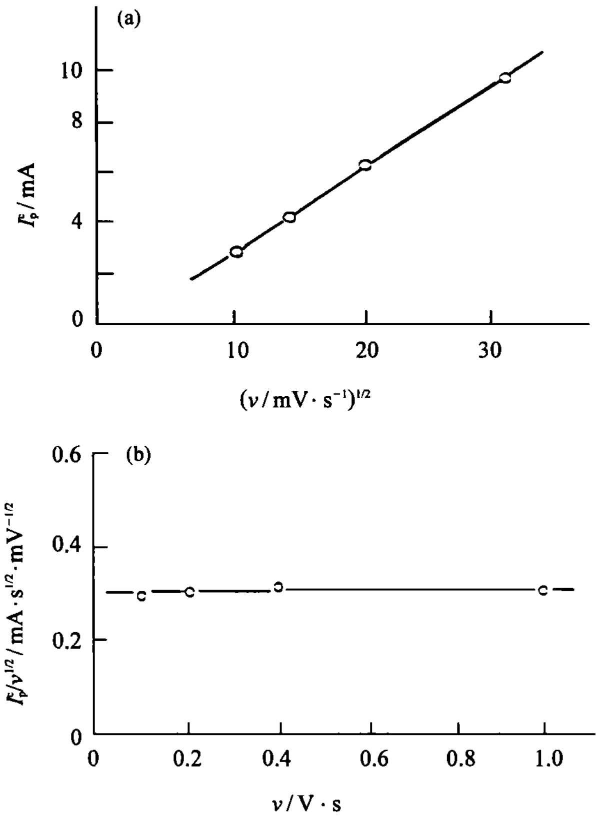

**Figure 7 Plots of $I_p^c - v^{1/2}$ and $I_p^c/v^{1/2} - v$ for 0.15% $K_2NbF_7$-FLINAK (in molar fraction) electrolyte without Nb present.**

## 2.3 Influence of oxide

From IR [14] and Raman [15] spectroscopic results, the oxide can transform the complex ion of Nb(V) in FLINAK melt. Now, an electrochemical investigation is carried out to study the reduction mechanism and the electrochemical stability of Nb (V) in FLINAK-$O^{2-}$ melt without and with niobium metal present.

When the molar ratio of $O^{2-}$ to Nb(V) is less than 1, a typical voltammogram with various switch potentials was shown in **figure 8**. In figure 8(a), one peak and a split wave are observed at cathodic reduction branch. In reversal scan, a clear anodic peak and a shoulder related to fluoride and oxide are found. When the switching potential is smaller [−0.75V to 1.25V *vs.* Ni(II)/Ni], only one reduction peak and one anodic peak are observed [see figure 8(b)]. It can be explained by a parallel charge transfer reaction mechanism. When the amount of oxide is less than that of Nb(V) in FLINAK melt, Nb(V) exists both as a fluorocomplex anion, $NbF_7^{2-}$ and an oxyfluorocomplex anion, $NbOF_6^{3-}$. The oxyfluorocomplex anion is formed undergoing the chemical reaction of oxide ($O^{2-}$) and $NbF_7^{2-}$:

$$NbF_7^{2-} + O^{2-} \Leftrightarrow NbOF_6^{3-} + F^-.$$

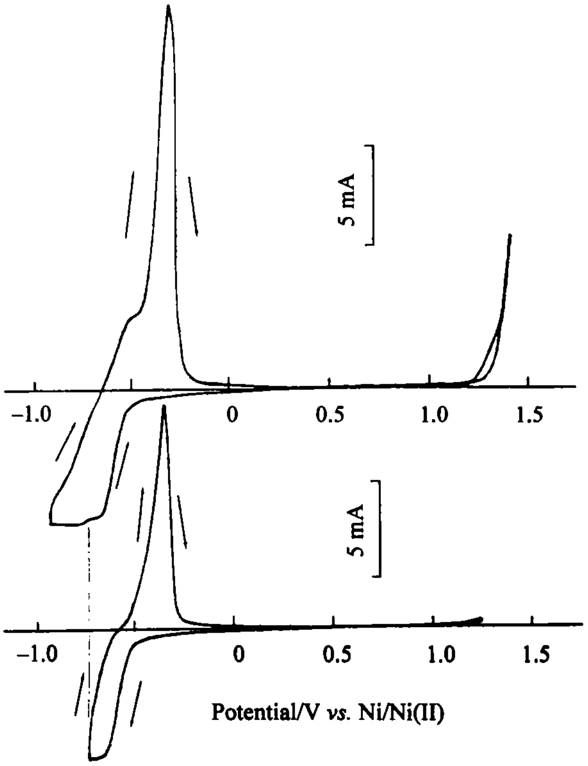

**Figure 8 Cyclic voltammograms of 0.25%$K_2NbF_7$-0.15$Na_2O$-FLINAK (in molar fraction) for various potential ranges. The sweep rate is 0.2 V/s; the potential ranges are (a) form −0.95 to 1.45 V and (b) from −0.75 to 1.25 V, respectively.**

The reaction between $NbF_7^{2-}$ and $NbOF_6^{3-}$ is not an electrochemical redox process. Therefore, the reduction reactions of $NbF_7^{2-}$ and $NbOF_6^{3-}$ are not consecutive charge transfer reaction. They are a parellel charge transfer reaction for $NbF_7^{2-}$ and $NbOF_6^{3-}$. **Figure 9** shows the cyclic voltammograms of 0.30% $K_2NbF_7$-FLINAK melts in molar fraction with niobium metal present and added $Na_2O$ at various concentrations. The peak potential of Nb(V) reduction is shifted to more negative potential with the increasing of oxide content. At higher oxide content, the shape of the voltammogram is similar to no niobium metal present. It means that the most of $K_2NbF_7$ had been reacted with oxide to form niobium oxyfluorocomplex and/or dioxyfluoride. The comparison of figure 8(a) with (b) shows that the reduction of $NbOF_6^{3-}$ is at more negative potential than $NbF_7^{2-}$. From electrochemical aspects, $NbOF_6^{3-}$ is more stable than $NbF_7^{2-}$ and $NbF_6^{2-}$. It can be confirmed by the chemical reaction of Nb(V) in FLINAK-$O^{2-}$ melt with niobium metal present (see **figure 10**). The average oxidation state is reaching to 5. **Figure 11** gives the relation of anodic peak current with $Na_2O$ content. The reduction of Nb(V) in FLINAK melt depends greatly on the molar ratio of $Na_2O$ to $K_2NbF_7$. The reduction of $NbOF_6^{3-}$ is given as

$$NbOF_6^{3-} + 5e^- \rightarrow Nb + O^{2-} + 6F^-,$$

which is controlled by chemical dissociation of $NbOF_6^{3-}$. The electrochemical reaction rate of Nb(V) in FLINAK melt is decreased due to the addition of oxide when the molar ratio of $Na_2O$ to $K_2NbF_7$ is less than 1. When the ratio is more than 1, the electrochemical reaction rate is greatly reduced due to much stable dioxyfluoro-complex ion ($NbO_2F_4^{3-}$) formed.

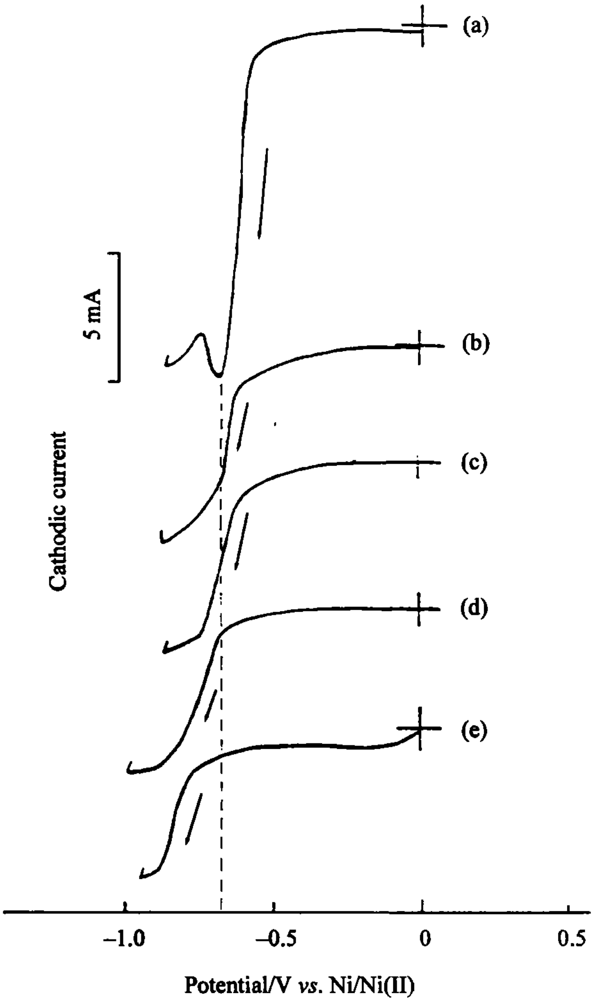

**Figure 9 Cathodic branches of cyclic voltammograms of 0.30% $K_2NbF_7$-FLINAK melt with Nb metal and various of $Na_2O$ added: (a) 0, (b) 0.2%, (c) 0.3%, (d) 0.5% and (e) 0.6% in molar fraction.**

## 2.4 Electrodeposition

Taking into account the influence of oxide on the chemical and electrochemical behaviours of niobium ion in molten fluorides, the electrolyte compositions with oxide present were studied. The current efficiency and the characteristic colour of niobium complex in solidified melt vary with oxide content and the molar ratio of $Na_2O$ and $K_2NbF_7$. A coherent and dense coating is obtained when oxide presents in FLINAK melt. The optimum composition for niobium electrodeposition is 2.7%$K_2NbF_7$-(0.5 – 2.0)%$Na_2O$-FLINAK in molar fraction. For a galvanostatic electroplating, the desirable cathodic current density is 90 $mA/cm^2$. When

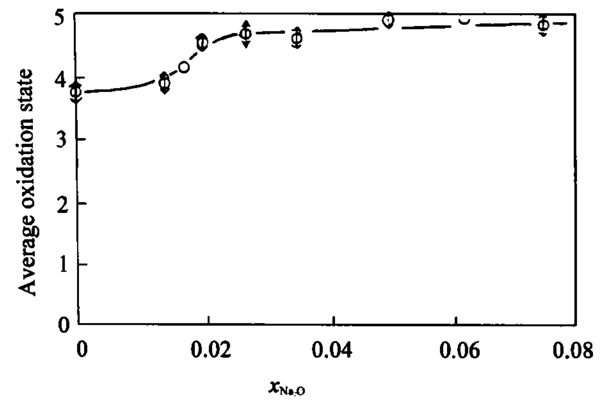

**Figure 10 Average oxidation states of Ni in 2.7%$K_3NbF_7$-FLINAK (in molar fraction) melts with oxide present.**

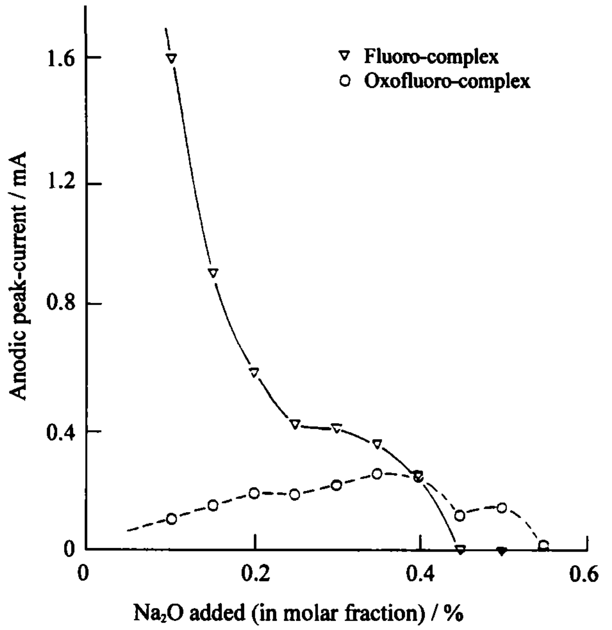

**Figure 11 Effect of oxide ($Na_2O$) on anodic peak-current. The concenttration of $K_2NbF_7$ in FLINAK melts is 0.25% in molar fraction and the sweep rate is 0.2 V/s.**

without oxide added, umbrella-like niobium deposit could be found at the boundary of the cathode (substrate) and the surface of the melt.

## 3 Conclusions

The electrochemical reduction process of Nb (V) depends on the complex ions of Nb(V) in the melt. The reduction reaction of fluorocomplex ion ($NbF_7^{2-}$) is as

$$NbF_7^{2-} + e^- \rightarrow NbF_6^{2-} + F^-,$$

$$5NbF_6^{2-} \Leftrightarrow 4NbF_7^{2-} + Nb + 2F^-,$$

$$NbF_6^{2-} + 4e^- \rightarrow Nb + 6F^-,$$

$$Nb + 4NbF_7^{2-} + 2F^- \Leftrightarrow 5NbF_6^{2-}.$$

When oxide presents in molten alkali fluorides melt, the reduction reaction of an oxyfluorocomplex ion is much different with fluorocomplex ion. The oxyfluorocomplex ion ($NbOF_6^{3-}$) is much stable than fluorocomplex ions ($NbF_7^{2-}$ and $NbF_6^{2-}$) in chemical and electrochemical opinion. In pure fluorides melt, the catalytic and disproportionate reactions are involved in the electrochemical reduction reaction process. The catalytic reaction can be reduced by the pre-reduction of $NbF_7^{2-}$ with metallic niobium. The present of oxide in fluoride melts reduces the catalytic and disproportionate reactions. A suitable amount of oxide present in FLINAK melt is available with correct chemical and electrochemical stability for the electrodeposition of niobium. A typical composition for a coherent niobium metal coating on low-carbon steel was found to be 2.7% $K_2NbF_7$-(0.5–2.0)%$Na_2O$-FLINAK in molar fraction at 973 K.

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