ELECTROCHEMICAL PROPERTIES OF Nb3Cl8 IN THE MgCl2-NaCl EUTECTIC AT 471°C

Mohamed Mohamedi, Nobuaki Kawaguchi, Yuzuru Sato and Tsutomu Yamamura
Department of Metallurgy, Faculty of Engineering, Tohoku University, Sendai, 980-77, Japan

ABSTRACT

The electrochemical properties of solutions of Nb3Cl8 in the fused eutectic MgCl2-NaCl eutectic were examined at 471°C by means of cyclic voltammetry and convolution voltammetry. The reduction of Nb3Cl8 to the metal showed a complicated behavior. It was shown that the reduction proceeds mainly via two steps: one electron irreversible step Nb(III)/Nb(II) and two electron reversible step Nb(II)/Nb(0).

INTRODUCTION

The electrochemistry of niobium has been greatly studied in both molten chlorides, chloride-fluoride and fluoride melts. From the literature reviews (1-2) it can be seen that in spite of the numerous studies for obtaining niobium by electrolytic means, the proposed mechanisms still divergent and niobium metal has been obtained essentially in the form of powders or dendrites in molten chlorides with complications due to:
- numerous difficulties due to the low solubility of certain niobium chlorides,
- numerous problems due to electrolyte stability because of volatilization of niobium chlorides of higher oxidation state as well as the disproportionation of intermediate valence niobium chlorides,
- according to the experimental conditions, temperature and current density, the anodic oxidation of niobium metal does not yield the same niobium chlorides.

Considering these problems encountered in molten chlorides, in order to stabilize certain oxidation states of niobium, the latter were complexed with fluoride ions, or the operating temperature was increased. Production of deposits which are coherent and closely adherent has been demonstrated in fluoride melts (3). However the disadvantage of fluorides is that the systems are generally toxic, corrosive and require high working temperatures.
The present paper is concerned with the mechanism of the reduction of \( \text{Nb}_3\text{Cl}_8 \) solution to the metal in \( \text{MgCl}_2\)-NaCl melt in which, to our knowledge, the electrochemistry of niobium has not been investigated. This binary melt presents eutectic at 445°C with 41.5 mol\% (MgCl\(_2\)) - 58.5 mol\% (NaCl) composition (4).

**EXPERIMENTAL**

**Salt preparation**

\( \text{MgCl}_2\cdot6\text{H}_2\text{O} \) was purified according to the procedure described in ref(5). NaCl was purified under dry HCl bubbling into the melt(6). \( \text{Nb}_3\text{Cl}_8 \) was synthesized by chemical transportation reaction from \( \text{NbCl}_5 \) and metallic niobium(7).

**Electrochemical cell and procedure**

A three-electrode Pyrex cell arrangement was used for the electrochemical experiments. The Pyrex crucible (\( \Phi=45\text{mm} \)) served as an electrolyte container. We have chosen to use the cross section of tungsten wire (\( \Phi=0.5\text{mm} \)) sealed in Pyrex tube as a working electrode. Before use, the working electrode was first mechanically polished on emery paper, was washed with distilled water and acetone and then dried. The silver-silver chloride equilibrium was used as the reference for the measurement of the electrode potential. The electrode arrangement was a silver wire (\( \Phi=1\text{mm} \)) dipped into a silver chloride solution in the \( \text{MgCl}_2\)-NaCl eutectic half cell built with a thin Pyrex bulb junction. The silver chloride concentration used was 5mol\%. All the potentials are reported to this reference. The counter-electrode was a graphite rod of 5 mm diameter.

The cell containing the crucible and the electrodes was assembled in the dry box. At this stage, the solvent mixture was introduced into the crucible which was returned to the main cell. Then the cell is removed from the dry-box and placed in a Pyrex transparent furnace and dried completely by heating under vacuum. The temperature in the cell was measured with a Chromel-Alumel thermocouple and kept within 2°C. Atmosphere in the cell was dry argon. The melted mixture was conditioned at the selected temperature for several hours before adding the solute as blocks of frozen \( \text{Nb}_3\text{Cl}_8\)-4NaCl mixture through an air-lock chamber.

**Instrumentation**

The electrolytic reduction of \( \text{Nb}_3\text{Cl}_8 \) solution has been mainly studied by means of cyclic voltammetry and convolution voltammetry. The data acquisition system was composed of a potentiostat/galvanostat HA305, a function generator HB104, an intelligent recorder INR141A for recording transients and a personal computer for data processing. The convolution voltammetry or semi-integral \( m(t) \) is defined by the integral:
\[ m(t) = \frac{d^{-1/2}}{dt^{-1/2}} I(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{I(\tau)}{\sqrt{t-\tau}} d\tau \]  

[1]

Where \( I(\tau) \) is the current measured at the time \( \tau \). The convolution treatment of \( I(t) \) transients was carried out on the basis of Oldham’s G1 and G2 algorithms.

**RESULTS AND DISCUSSION**

**Electrochemical window of the solvent**

The theoretical electrochemical span of the solvent could be computed from thermodynamic data (9). However, the real electrochemical stability domain of MgCl\(_2\)-NaCl was examined by means of voltammetric experiments. A cyclic voltammogram obtained at a tungsten electrode is reported in Fig. 1. The reduction of magnesium ions is easily observed at a potential equal to \(-1.5\text{V/Ag/AgCl}(\text{wave E})\) which is quite close to the theoretical one\((-1.47\text{V/Ag/AgCl})\). Peak E’ which is typical for a stripping of deposit, is observed in the reverse scan. On the anodic side chlorine evolution is seen\((\text{wave F})\).

After the addition of Nb\(_3\)Cl\(_8\), Fig. 2 shows a series of voltammograms recorded for different cathodic reversal potential \(E_2\). Within the narrowest potential window \(+0.2\text{V}\) and \(-0.9\text{V}\), two cathodic peaks were observed with no relevant anodic peaks. The peaks noted A and B are located at \(-0.35\text{V}\) and \(-0.77\text{V}\) respectively. As the reversal potential became more cathodic\((E_2<-1.1\text{V})\) a new redox couple C/C’ was observed at \(-1\text{V}/+0.11\text{V}\). For \(E_2>-1.3\text{V}\) the same cathodic processes remained visible, however, a new peak C” was observed at \(+0.14\text{V}\). The peak A was not visible for \(E_2>-1.4\text{V}\) and a new redox couple D/D’ was evolved at \(-1.4\text{V}/+0.14\text{V}\). The shape of the curve D, and particularly the sharp increase in current is characteristic of the formation of a substance of a constant activity. The cathodic limit E/E’ corresponds to magnesium deposition.

**Analysis in the +0.2V and -1.4V potential range**

On the Fig.3, we report the cathodic evolution of the voltammetric curves as a function of the potential sweep rate recorded in the \(+0.2\text{V}\) and \(-1.4\text{V}\) potential range. Peculiar features of these voltammograms\((\text{Table I and Fig4-6})\) lie in the following:

- Only one reduction peak is observed\((\text{Peak G})\).
- The cathodic peak potential \(E_{pG}\) is dependent upon the potential sweep rate logarithm \(\log v\)(Fig.4), i.e., an increase in the potential sweep rate shifts the \(E_{pG}\) towards negative potentials.
- Figure 5 shows that the dependence of the cathodic peak current \(I_{pG}\) is also complicated.
in that \( I_{p_G} \) is not proportional to the square root of the potential sweep rate. Then values of \( I_{p_G}/\sqrt{v} \) were measured to check for possible chemical reactions coupled to the charge transfer. Constancy of \( I_{p_G}/\sqrt{v} \) would indicate charge transfer with no chemical complication(10). Table I shows that the parameter \( I_{p_G}/\sqrt{v} \) increases as the potential sweep rate increases. This increase can not be due to the ohmic drop since that would tend to decrease the \( I_{p_G}/\sqrt{v} \) parameter(11). When \( I_{p_G} \) is plotted against the potential sweep rate(Fig.6), a linear relation is obtained between the two parameters and the plot passes through the origin.

| \( E_{p_G} \) (V) | \( E_{p_G}/2 \) (V) | \( E_{p_G}-E_{p_G}/2 \) (V) | \( I_{p_G} \times 10^4 \) (A) | \( \sqrt{v} \) (Vs\(^{-1}\)) | \( I_{p_G}/\sqrt{v} \times 10^4 \) (A/(Vs\(^{-1/2}\))) | \( I_{p_G}/\sqrt{v} \times 10^4 \) (A/(Vs\(^{-1}\))) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| -0.96           | -0.66           | -0.30           | -3.0            | 0.2             | -6.70           | -1.50           |
| -1.07           | -0.73           | -0.34           | -6.1            | 0.5             | -8.60           | -1.22           |
| -1.10           | -0.75           | -0.35           | -8.6            | 0.7             | -10.3           | -1.23           |
| -1.10           | -0.77           | -0.33           | -11             | 0.9             | -11.0           | -1.22           |
| -1.14           | -0.80           | -0.34           | -12             | 1.0             | -12.0           | -1.20           |
| -1.20           | -0.85           | -0.35           | -25             | 2.0             | -17.6           | -1.25           |

\( E_{p_G}/2 \) = half peak potential at 0.5\( I_{p_G} \).

The theoretical study of an adsorption step coupled to a charge transfer(10), shows that the reduction current of the adsorbed species becomes predominant at high potential sweep rates, yielding thus an increase of the \( I_{p_G}/\sqrt{v} \) parameter.

Note that the marked constancy of the quantity \( I_{p_G}/\sqrt{v} \) for potential sweep rate >0.2V/s is an inherent feature for adsorption(12-13). In addition the dependence of the peak potential upon the potential sweep rate logarithm suggests that the process is not reversible(12-13).

Laviron(12) indicates, in the case of a totally irreversible adsorption process, that the peak potential varies with the logarithm of the potential sweep rate \( v \) according to the equation:

\[
E_{p_G} = E_0^* + \frac{2.3RT}{\alpha n_F} \log \frac{R T k_0}{\alpha n_F v}
\]  

[2]
where $k^0$ is the standard rate constant, $n$ the overall number of electron transferred, $\alpha$ the transfer coefficient, $n_\alpha$ the number of electrons transferred in the rate determining step and the others symbols have their usual meaning. From the slope of Fig.4, the product $\alpha n_\alpha$ evaluated was found to be equal to 0.62. Assuming $\alpha = 0.5$ this yields to 1.24 electron number.

The peak current is expressed following (12)

$$IP_G = \frac{n_\alpha n F^2 AvT_0}{2.718RT}$$

where $T_0$ is the initial superficial concentration in mol.cm$^{-2}$. This expression was established assuming the potential sweep rate so large that the amount of molecules brought to the electrode by diffusion during the potential sweep is negligible compared to the amount adsorbed, and that the electrode area $A$ can be regarded as constant.

$T_0$ determined from the slope of Fig.6 and using equation 3 was found to be equal to $1.46 \times 10^{-6}$ mol.cm$^{-2}$.

Analysis by semi-integration

The Fig.7 represents a calculated semi-integral of a voltammogram from Fig.3, hysteresis is noticed between the forward and the backward sweeps of the semi-integral. We can therefore conclude that the process is not reversible (14). Furthermore, the return curve crosses the horizontal axis, indicating the formation of an insoluble substance at the electrode (15). Fig.8 shows several cathodic semi-integration curves deduced from the voltammograms of Fig.3. The following facts are established:

- the occurrence of a plateau in the region of cathodic potentials indicates that the diffusion is controlling the process (16). The value of this plateau increases when the potential sweep rate increases.

In the case of a charge transfer under diffusion control when the concentration of the electroactive species at the electrode surface is diminished to virtually zero, the semi-integral function $m(t)$ tends to a limiting value independent of the potential sweep rate, this limiting value is expressed by the following equation:

$$m^* = nFAC_t^* \sqrt{D_t}$$

where $C_t^*$ is the initial superficial concentration in mol.cm$^{-2}$. This expression was established assuming the potential sweep rate so large that the amount of molecules brought to the electrode by diffusion during the potential sweep is negligible compared to the amount adsorbed, and that the electrode area $A$ can be regarded as constant.

$C_t^*$ determined from the slope of Fig.6 and using equation 3 was found to be equal to $1.46 \times 10^{-6}$ mol.cm$^{-2}$.

The peak current is expressed following (12)

$$IP_G = \frac{n_\alpha n F^2 AvT_0}{2.718RT}$$

where $T_0$ is the initial superficial concentration in mol.cm$^{-2}$. This expression was established assuming the potential sweep rate so large that the amount of molecules brought to the electrode by diffusion during the potential sweep is negligible compared to the amount adsorbed, and that the electrode area $A$ can be regarded as constant.

$T_0$ determined from the slope of Fig.6 and using equation 3 was found to be equal to $1.46 \times 10^{-6}$ mol.cm$^{-2}$.

Analysis by semi-integration

The Fig.7 represents a calculated semi-integral of a voltammogram from Fig.3, hysteresis is noticed between the forward and the backward sweeps of the semi-integral. We can therefore conclude that the process is not reversible (14). Furthermore, the return curve crosses the horizontal axis, indicating the formation of an insoluble substance at the electrode (15). Fig.8 shows several cathodic semi-integration curves deduced from the voltammograms of Fig.3. The following facts are established:

- the occurrence of a plateau in the region of cathodic potentials indicates that the diffusion is controlling the process (16). The value of this plateau increases when the potential sweep rate increases.

In the case of a charge transfer under diffusion control when the concentration of the electroactive species at the electrode surface is diminished to virtually zero, the semi-integral function $m(t)$ tends to a limiting value independent of the potential sweep rate, this limiting value is expressed by the following equation:

$$m^* = nFAC_t^* \sqrt{D_t}$$

Electrochemical Society Proceedings Volume 96-7

193

Downloaded on 2019-04-26 to IP 207.241.231.82 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
This equation is valid whether or not the electrochemical system is reversible(16) and demonstrates the proportionality between the initial concentration \( C_\text{s}^* \) of the electroactive species. We have observed that \( m^* \) depends on the potential sweep rate(Fig.8). To our knowledge, this kind of mechanism has not been treated by semi-integration, but we think that the increase of the plateau value with the potential sweep rate is due to the intervention of the adsorption step.

**Analysis in the -0.2V and -1.5V potential range**

Figure 9 shows a typical voltammogram recorded in the -0.2V and -1.5V range. On this figure we recognize the peaks D/D'(see Fig.2) and in addition the peak G(see Fig.3) appears as a shoulder on peak D.

The variations of the anodic and cathodic peak currents D/D' \( I_{pa} \) and \( I_{pc} \) with the square root of the potential sweep rate \( \nu^{1/2} \) shown in Fig.10 are straight lines through the coordinate origin, indicating that the processes are under diffusion-controlled.

The cathodic peak potential slightly moves towards a negative direction with increasing potential sweep rate. It indicates that the cathodic reduction of niobium ions is very close to a reversible process. The electron number can be calculated using the peak potential \( E_{pc} \) and the half peak potential \( E_{pc}/2 \) separation relation in the case of a reversible electrodeposition reaction(17):

\[
|E_{pc} - E_{pc}/2| = 0.77 \frac{RT}{nF} \tag{5}
\]

By applying this equation to peak D, \( n=2.14 \) was obtained. \( E_{pc}-E_{pc}/2 \) was determined by extrapolating the plot of \( E_{pc}-E_{pc}/2 \) to \( \nu =0 \).

The insolubility and the adherence to the electrode of a deposit can be verified on the voltammogram by the fact that the anodic peak current is less than the cathodic one. The peak current ratio \( I_{pa}/I_{pc} \) is lower than unity and assumed the value between 0.5 and 0.57. This is confirmed by the semi-integral curve presented on Fig.11. It can be seen that the reverse semi-integral transient do not cross the abscissa as expected for soluble/insoluble electron transfer(15).

**Discussion**

The plurality of cathodic and anodic peaks observed during the reduction of \( \text{Nb}_5\text{Cl}_8 \) to the metal(Fig.2) shows the high intricacy of the whole electrochemical process. This is the reason why the mechanism could not be elucidated completely. In order to simplify we will consider only the main steps G and D.

According to Safonov *et al.* (18-19) niobium dichloride disproportionates on heating.
to niobium tetrachloride and metallic niobium. K. Zhou et al. (20) concluded that in molten LiCl-KCl that Nb3Cl8 dissociates to Nb(II) and Nb(III) ions, and they are reduced by the steps $\text{Nb}(\text{III}) \rightarrow \text{Nb}(\text{II}) \rightarrow \text{Nb}(0)$.

Lantelme et al. (21) concluded that during the reduction of Nb(III) to the metal an intermediate step occurs during this reaction involving Nb(II) which forms a thin electroactive layer of insoluble cluster compounds at the electrode surface. This agrees with our results, since the cyclic voltammetry and convolution voltammetry confirmed the existence of an adsorption reaction. The electron number involved during step G was found equal to 1.24, thus we can suggest the reduction of Nb(III) ions resulted from the dissociation of Nb3Cl8 to Nb(II) electroactive layer adsorbed on the electrode surface.

The main cathodic peak D is attributed to the formation of niobium metal. The electron exchange during this step was found to be 2.14, it will therefore be assumed that the reaction along the cathodic peak D is:

$$\text{Nb}(\text{II}) + 2e^- \leftrightarrow \text{Nb}(0)$$

It is however certain that the process D/D' corresponds to a superimposition of several processes. This was confirmed by semi-integration which showed the character apparently soluble of the product formed during step D, cyclic voltammetry also showed that the anodic charge involved during step D' was half of the cathodic step D. This suggests that deposited niobium may be dissolved in the melt through a disproportionation reaction.

**CONCLUSION**

The cathodic behavior of Nb3Cl8 was studied by cyclic voltammetry and convolution voltammetry. The results suggest that the mechanism is mainly two reduction steps, the first step is irreversible and the second is close to reversible charge transfer, the following mechanism is then proposed:

$$\text{Nb}_3\text{Cl}_8 + 6\text{Cl}^- \rightarrow \text{Nb}(\text{II})\text{Cl}_4^{2-} + 2\text{Nb}(\text{III})\text{Cl}_5^{2-}$$

$$\text{Nb}(\text{III}) + 1e^- \rightarrow \text{Nb}(\text{II})_{\text{layer}}$$

$$\text{Nb}(\text{II}) + 2e^- \leftrightarrow \text{Nb}(0)$$
AKNOWLEDGEMENT

One of the authors (M.M) is gratefully indebted to Japan Society for the Promotion of Science (JSPS) for the assistance of a post-doctoral fellowship. The authors would like to acknowledge Dr. Zhu and Mr. Kariya for helpful discussions and assistance during the course of the investigation.

REFERENCES

1. L. Arurault, J. Bouteillon and J. C. Poignet, J. Electrochem. Soc., 142, 3351, (1995).
2. E. G. Polyakov, L.P. Polyakova and I. R. Elizarova, Russ. J. Electrochem., 31, 457, (1995).
3. G. W. Mellors and S. Senderoff, J. Electrochem. Soc., 112, 266, (1965).
4. E. M. Levin, C. R. Robbins and H. F. McMurdie, Phase Diagrams for Ceramists, The american Ceramic Society, (1964).
5. T. Ejima, Y. Sato, A. Ando and T. Asakawa, J. Jpn. Inst. Metals, 45, 368, (1981).
6. Y. Sato and T. Ejima, in Molten Salts/1983, M. Blander, D. S. Newman, G. Mamantov, M-L. Saboungi and K. Johnson, Editors, PV 84-2, p121, The Electrochemical Society Proceedings Series, Pennington, NJ (1984).
7. Y. Saeki, M. Yanai and A. Sofue, Denki Kagaku, 40, 816, (1972).
8. K. B. Oldham, J. Electroanal. Chem., 121, 341, (1981).
9. I. Barin, Thermochemical Data of Pure substances, VCH, (1989).
10. R. H. Wopschal, I. Shain, Anal. Chem., 39, 1514, (1967).
11. J. C. Imbeaux, J. M. Saveant, J. Electroanal. Chem., 28, 325, (1970).
12. E. Laviron, Electroanal. Chem. and Interf. Electrochem., 52, 355, (1974).
13. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and applications, John Wiley & Sons, New York (1980).
14. J. M. Saveant and D. Tessier, J. Electroanal. Chem., 65, 57, (1975).
15. D. Renaud, Ph.D Thesis, INP, Grenoble (1985).
16. M. Grenness and K. B. Oldham, Anal. Chem., 44, 1121, (1972).
17. P. Delahay, New Instrumental Methods in Electrochemistry, Interscience, New York (1954).
18. V.V. Safonov, B. G. Korshunov and A.A. Yarovoi, Russ. J. Inorg. Chem., 11, 918, (1966).
19. V.V. Safonov, B. G. Korshunov and S.N. Steblovskaya, Russ. J. Inorg. Chem., 11, 1148, (1966).
20. K. Zhou, T. Takenaka, N. Sato and M. Nanjo, Denki Kagaku, 59, 981, (1991).
21. A. Salmi, Y. Berghoute and F. Lantelme, Electrochimica Acta, 40, 403, (1995).

Fig. 1 Cyclic voltammogram obtained on tungsten electrode at 1 V/s in molten MgCl$_2$-NaCl eutectic at 471°C. Electrode area: 1.96x10$^{-3}$ cm$^2$. 

$I/A$ 

$E/V$ vs Ag/AgCl 

-2 -1.5 -1 -0.5 0 0.5 1 1.5 2 

-0.06 -0.04 -0.02 0 0.02
Fig. 2  Cyclic voltammograms for different cathodic reversal potential at tungsten electrode in MgCl$_2$-NaCl-Nb$_3$Cl$_8$ (<0.07 mol%). T=471°C, v=0.2 V/s 
edtrode area=1.96x10$^{-3}$ cm$^2$
Fig. 3 Cathodic voltammograms recorded at tungsten electrode in the MgCl$_2$-NaCl-Nb$_3$Cl$_8$ system at various potential sweep rate.

$T=471^\circ$C, $[\text{Nb}_3\text{Cl}_8]<0.07$ mol%, $A=0.00396\text{cm}^2$.

Fig. 4 Relation between the $E_{p,G}$ and the logarithm of the potential sweep rate for the voltammograms of Fig.3.
Fig. 5 Variation of the $I_p$ versus $v^{1/2}$ in the same system as Fig. 3.

Fig. 6 Dependence of the $I_p$ on the potential sweep rate for the same system as in Fig. 3.
Fig. 7  Semi-integral curve related to a voltammogram from Fig. 3.

$v=0.2\text{V/s}$

Fig. 8  Cathodic semi-integral curves related to the voltammograms of Fig. 3 for various potential sweep rates.
Fig. 9  Cyclic voltammogram for the reduction of Nb$_3$Cl$_8$ (<0.07mol%) in the MgCl$_2$-NaCl eutectic at 471°C. Potential range -0.2V to -1.5V.

Electrode Area: 1.96x10$^{-3}$cm$^2$, v= 0.1V/s

Fig. 10  A series of voltammograms for various sweep rates: 1, 0.1; 2, 0.2; 3, 0.5; 4, 0.7 and 5, 0.8V/s. [Nb$_3$Cl$_8$] < 0.07mol%, Electrode area: 1.96x10$^{-3}$cm$^2$
Fig. 11  Cyclic voltammogram and its corresponding semi-integral.  
Electrode area=1.96x10^{-3} cm^2, \nu = 0.1 V/s