STUDY ON ELECTROWINNING OF INTERMETALLIC COMPOUNDS
TANTALUM-NICKEL AND NIIOBIUM-NICKEL IN MOLTEN LiF-NaF

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ABSTRACT
A study of the mechanism of the electrochemical reduction of K2 TaF7 or K2 NbF7 on a nickel electrode in molten LiF-NaF allows the range of potentials to be defined where Nb-Ni or Ta-Ni alloys are formed. Further static potential measurements in a galvanostatic intermittent electrolysis allow the intermetallic compounds to be identified in each case and the Gibbs energy of the Ta-Ni compounds. Then surface alloys are prepared by electrolysis at a controlled positive potential; only NbNi3 and TaNi3 stable phases are detected in the bulk of the layer. A parabolic law of growth is stated, involving the intermetallic diffusion coefficient D and a parameter α depending on solid composition at the boundaries of the layer; values of both α and D were estimated after combination of electrochemical measurements and diffusion equation.

INTRODUCTION
Nickel is known to give very corrosion-resistant alloys with refractory metals such as tantalum and niobium. So, these materials can be used as insoluble anodes in chlorine or oxygen gas production [1,2]; if we consider the high melting point of Ta and Nb (respectively 3,000 °C and 2,500 °C), the metalliding process is an advantageous mean of obtaining these compounds since the temperature range involved here is moderate (800 - 1,100 °C). This technique was firstly developed by COOK [3]; in this particular case, it consists of the electrochemical reduction of tantalum or niobium ions combined with the diffusion of the deposited elements in the nickel substrate [4,5].

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In addition of the practical aim of the work, we intend to obtain fundamental data concerning the solid compounds which are formed and the intermetallic diffusion in each system; today, only few investigations over this subject, based on conventional techniques of the solid state science have been carried out. Electrochemistry in molten salts have been shown to be a powerful technique in this field since the measured current and potentials during the electrodeposition process are very sensitive to the diffusion of the anodic metal element [6,9].

In this work, the use of electrochemical techniques leads to the estimation of thermodynamic values concerning the formation of tantalum-nickel compounds and of kinetic parameters concerning the intermetallic diffusion into both systems.

EXPERIMENTAL PART

Technical

The cell consists of a refractory steel lid placed in a regulated furnace and provided with a vacuum supply and an argon gas circuit. The device was described elsewhere (fig. 1).

The melt is previously dehydrated by a slow fusion under vacuum followed by argon gas bubbling during 16 hours. Then all the experiments are performed under argon atmosphere.

For the electrochemical part, a multipurpose installation was used, based on a TACUSSEL PRT 20-10X potentiostat monitored by a periodical triangular signal generator TACUSSEL Model GSTP: voltammograms, chronoamperograms and chronopotentiograms were recorded with a X-Y recorder, and a TACUSSEL recorder type EPLI. The micrographic analysis was performed by means of an electronic microscope and X-ray microprobe.

Salts

The electrolytic bath consists of a solution of K2 TaF7 or K2 NbF7 in the eutectic melt LiF- NaF (freezing point 650°C).

As a single valence (V) is noted for tantalum ions in the fluoride melt, two valences are to be considered in the case of niobium solutions, according to the following equilibrated reaction:

\[ \text{Nb} + 4\text{Nb}^V \rightleftharpoons 5\text{Nb}^{IV} \] (1)
In order to get good cathodic efficiencies in the electrodeposition process, a valence of niobium ions close to 4 is required; a further addition of metallic niobium of the bath displaces the equilibrium (1) in the right hand and leads to an average valence approximately equal to 4.2.

**Electrodes**

Tantalum and niobium foils [3 x 1.5 x 0.05 cm] are used as counter electrode and reference electrode. The working electrode is either a nickel and molybdenum wire (diameter 0.1 cm) or nickel sheets (3 x 0.5 x 1 cm). All these metals were provided from ALPHA INORGANICS (purity 99.9%).

**PRELIMINARY THERMODYNAMIC MEASUREMENTS**

Electrochemical techniques allow one to identify the formation of the tantalum-nickel compounds.

**Voltammetric curves**

The reduction of the Ta F7" ions at 1 050 °C was carried out by cyclic voltammetry alternatively with molybdenum and nickel as working electrode. A typical voltammogram is shown on fig. 2; since only the second metal gives alloys with tantalum at this temperature [10] it is concluded that:

1. the nucleation step, observed in both cases, is located at negative potentials with respect to the Ta reference electrode.

2. the peaks and plateaus at positive potentials observed in the case of a nickel cathode are characteristics of the intermetallic compounds formation.

**Potentials of formation of the tantalum-nickel compounds**

The accurate determination of these potentials is available by means of an intermittent galvanostatic electrodeposition of tantalum on a nickel cathode. During the off-times, the diffusion of electrodeposited Ta occurs and promotes a change in the composition of the external layer. On fig. 3, the evolution of the static potential of the nickel electrode (potential during the off-time) exhibits several definite plateaus; each plateau is characteristic of a biphased equilibrium which takes place at the surface of the electrode [11]:

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The phases diagram of the tantalum-nickel system includes the following compounds: Ta$_2$Ni, TaNi, TaNi$_2$, and TaNi$_3$ [12]. According to fig. 3, they are supposed to be formed at respectively 20, 45, 200, and 245 mV versus the Ta reference. The reaction (2) is associated to a cell, the e.m.f. of which would be expressed as:

$$\mathcal{E} = -\frac{RT}{5yF} \ln \frac{a_{Ta} [Ta (x+y) Ni]}{a_{Ta} [Ta (x) Ni]}$$

(3)

5 is the number of electrons exchanged in the discharge of tantalum ions, and $a_{Ta}$ is the activity of the refractory metal in the intermetallic phase.

The values of the GIBBS free energy of each plateau, deduced from the potentials of the plateaus are given in Table I. The values for TaNi$_3$ and TaNi$_2$ agree with those calculated from the emf measurements of NESTERENKO [13] and LYAKISHEV [14] using solid galvanic cells. No other measurements are reported for TaNi and Ta$_2$Ni.

The weight of the diffused refractory metal per surface unity $\frac{m}{S}$ is shown to be proportional to the square root of the metalliding treatment on fig. 5. According to an X-ray analysis, performed with the microprobe on several samples, the composition of the layer is uniform and corresponds to TaNi$_3$ and NbNi$_3$ compounds. Since, the other compounds of each system are metastable.
It is to be noted that the other compounds are quantitatively formed in the case of techniques such as diffusion welding involving an overpressure exerted on the couples of metals [16,17]. In our experiments, the metastable compounds Ta₂Ni, TaNi, Ta₂Ni, on one hand [5] and NbNi on the other hand [4] appear only during transient phenomena.

The preceding results allow us to determine the thickness of the layer, by means of the following equation:

\[ X = \frac{\Delta m}{S} \cdot \frac{1}{W \rho} \]  

(4)

where \( X \) is the thickness of the layer, \( W \) the massic fraction of the refractory metal in the alloy and \( \rho \) the density of the alloy.

The growth of the layer obeys a parabolic relationship:

\[ X^2 = K t \]  

(5)

The values for \( K_{Ta} \) and \( K_{Nb} \) are given in the first line of tables II and III, respectively.

DETERMINATION OF THE INTERMETALLIC DIFFUSION COEFFICIENT

The theoretical treatment of metalliding is to be included into the general problem of an unsteady state diffusion with moving boundary [18]: the motion of the nickel interface is only due to the intermetallic diffusion and the rate of the process is controlled by the flux of the diffusing species, termed by \( J \), at this boundary:

\[ J = - \delta \left( \frac{\partial C}{\partial x} \right) \]  

(6)

\( \delta \) is the intermetallic diffusion coefficient, \( c \) the composition of the alloy layer, \( x \) the abscissa in the layer \( (x = 0 \text{ at the liquid interface}) \). The process is described by the FICK's second equation.

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

(7)

The appropriate boundary conditions are the following:

\[ t = 0 \quad c = 0 \quad x > 0 \]  

(8)

\[ t > 0 \quad c = C \quad x = 0 \]  

(9)

\[ t > 0 \quad c = 0 \quad x = \infty \]  

(10)

The solution of equation (7) leads to the following expres-
sion of C and J:

\[ C = C_0 \text{erfc} \frac{x}{2(\sqrt{Dt})^{1/2}} \tag{11} \]

\[ J = \frac{C_0 \sqrt{D}}{(\pi t)^{1/2}} \exp \left[ -\frac{x}{2(\sqrt{Dt})^{1/2}} \right] \exp (-a^2) \tag{12} \]

So, the theoretical expression of the metalliding current density, taking account of equation (5) is:

\[ i = \frac{n F D^{1/2} C_0}{(\pi t)^{1/2}} \exp (-a^2) \tag{13} \]

\[ \text{[n is the number of electrons exchanged (5 for Ta and 4 for Nb)]} \]

\[ \text{with} \quad a = \frac{1}{2} \left( \frac{K}{D} \right)^{1/2} \tag{14} \]

\( a \) is a dimensionless parameter depending on Co, Cx and Cm which are respectively the composition of the layer at \( x=0 \), \( x=X \) and the average composition [19].

The evolution of the metalliding current, observed on fig. 4 follows the theoretical expression, as it is shown on figs. 6 and 7: on fig. 6, equation [13] is verified, in the case of niobium, at various temperatures. In each run, the potential of the cathode is close to zero. So, the composition of the external layer is supposed to be saturated in niobium \( (Co = Co_s) \). It is stated elsewhere that \( Co_s \) corresponds to the NbNi compound \( (Co_s = 0.051 \text{ at. g./cm}^3) \) [4].

Fig. 7 shows in the case of tantalum the dependence of the slope of the straight lines, \( i = f(t -1/2) \), on the potential of the cathode i.e. on Co.

An increase of the slope is observed when the potential is decreased, meaning that the external composition in tantalum is increased. A maximum is reached when the potential is about 10 mV: thus for this potential, Co is close to the saturated value, \( Co_s \), corresponding to the Ta2 Ni compound \( (Co = 0.068 \text{ at. g./cm}^3) \) [5].

The slopes of the straight lines, for \( Co = Co_s \), termed by \( p^SNb \) and \( p^STa \) are given in the second line of tables II and III.

The combination of equations (13) and (14) gives:

\[ \exp (-a^2) = \frac{2 \pi \frac{1}{2} p^S}{a n F Co K^{1/2}} \tag{15} \]

From equation (15), the parameters for Ta and Nb are availa-
ble. These values, which are given in the third line of tables II and III confirm that this parameter does not depend on temperature. The intermetallic diffusion coefficient, determined from equation (14) obeys ARRHENIUS law (values on the fourth lines of tables II and III):

\[
\text{DNb} = 1.3 \times 10^{-4} \exp \left[ -\frac{16700}{T} \right] \text{cm}^2 \cdot \text{sec}^{-1} \quad (16)
\]

\[
\text{DTa} = 1.1 \times 10^{-6} \exp \left[ -\frac{10400}{T} \right] \text{cm}^2 \cdot \text{sec}^{-1} \quad (17)
\]

**CONCLUDING REMARKS**

- The experimental values of \( \alpha \) can be compared with other more theoretical ones which are available as follows. According to DANCKWERTS [16], the expression of the moving rate of the nickel interface is the following:

\[
\frac{dX}{dt} = B \left[ -D \frac{C}{x} \right] x = X + Cx \frac{dx}{dt} \quad (18)
\]

\( B \) is a proportionality constant between the thickness of the layer and the mass of diffusion species crossing the interface. It is clear that \( B = 1/\wp \) [equation (4)] and that \( 1/\wp = Cm \). Then, after combination of equations (5), (19) and (18), we obtain:

\[
\frac{Co - Cx}{Cm - Cx} = \frac{1}{2} \text{erf} \alpha - \alpha \exp (\alpha^2) \quad (19)
\]

and

\[
\frac{Co}{Cm} = \frac{1}{\tau^{-1/2} \exp (-\alpha^2) + \text{erfc}} \quad (20)
\]

Eq. (19) shows the dependence of \( \alpha \) on \( Co \), \( Cx \) and \( Cm \). Eq. (20) allows to determine \( \alpha \). \( \alpha \)Nb and \( \alpha \)Ta are found to be respectively 0.85 and 0.92. As the order of magnitude is similar, the agreement with the experimental values can be considered satisfactory.

- Nevertheless the mathematical treatment which is used in this work fails on one point: the composition of the layer, given by equation (11) involves an uniform variation of the composition of the layer which is not confirmed by the Xray analysis. On the other hand, the expression of the metalling current, related to the flux, which is given by equation 13, leads to coherent results. Thus, the structural arrangement leading to the compounds Ta Ni3 and Nb Ni3 is supposed to have no effect on the rate of the
process.

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| Compound | $\zeta$ (mV) at 950°C | $\Delta G$ (kcal/mole) | $\Delta G$ (kcal/mole) | $\Delta G$ (kcal/mole) |
|----------|-----------------|-----------------|-----------------|-----------------|
| Ta Ni$_3$ | $\sim 245$ | $-28.2$ | $-26 \pm 6.8$ | $-31.7$ |
| Ta Ni$_2$ | 200 | $-25.7$ | $-22.9 \pm 6.4$ | $-28.9$ |
| Ta Ni | 45 | $-15.4$ | $-$ | $-$ |
| Ta$_2$ Ni | 20 | $-8.8$ | $-$ | $-$ |

Table I: GIBBS free energy of Tantalum Nickel compounds

| $t$ °C | 850 | 900 | 940 | 1 000 | 1 050 |
|--------|-----|-----|-----|-------|-------|
| $K_{Nb}\cdot 10^{10}$ (cm$^2$.sec$^{-1}$) | 0.58 | 1.12 | 1.93 | 3.46 | 6.91 |
| $p^a_{Nb}$ (A. sec$^{1/2}$) | 0.061 | 0.068 | 0.098 | 0.115 | 0.165 |
| $\alpha_{Nb}$ | 0.54 | 0.62 | 0.58 | 0.65 | 0.65 |
| $D_{Nb}\cdot 10^{10}$ (cm$^2$.sec$^{-1}$) | 0.50 | 0.73 | 1.43 | 2.04 | 4.09 |

Table II: Determination of kinetic parameters of the intermetallic diffusion Niobium-Nickel

| $t$ °C | 850 | 950 | 1 050 |
|--------|-----|-----|-------|
| $K_{Ta}\cdot 10^{10}$ (cm$^1$.sec$^{-1}$) | 1.3 | 2.6 | 5.9 |
| $p^a_{Ta}$ (A. sec$^{1/2}$) | 0.094 | 0.150 | 0.23 |
| $\alpha_{Ta}$ | 0.70 | 0.68 | 0.68 |
| $D_{Ta}\cdot 10^{10}$ (cm$^2$.sec$^{-1}$) | 0.65 | 1.42 | 2.98 |

Table III: Determination of kinetic parameters of the intermetallic diffusion Tantalum-Nickel
Fig 1: The experimental cell:
a: Refractory steel lid; b = nickel crucible; c = nickel liner; d = counter electrode; e = working electrode; f = reference electrode; g = thermocouple; h = addition of solute set up; i = electrode fittings; J = vacuum connection; → Argon: → water cooling circuit
Fig 2: Voltammogram of the LiF-NaF-K2TaF7 at 1050° C on different cathode materials (Reference: tantalum foil; potential sweep: 2 mV per sec.)

Fig 3: Determination of the potentials of biphased equilibria of the tantalum nickel system by a galvanostatic intermittent electrolysis (t = 1050° C; i = 16 mA cm⁻², duration of each pulse: 10 sec.)
Fig 4: Typical current-time observed during the metalliding of nickel with niobium (t = 1 050° C ; s = 3. 6 cm²)

Fig 5: Linear relationship between Δm and the square root of time for metalliding of nickel with refractory metals at several temperatures
a) with tantalum
• Electrodeposition-diffusion technique
• Potentiostatic or galvanic technique
b) with niobium
Fig 6: Typical linear relationship between the metalliding current density and the reciprocal square root of time in the case of niobium-nickel alloy formation at various temperatures.

Fig 7: Typical linear relationship between the metalliding current density and the reciprocal square root of time in the case of tantalum-nickel alloys formation at various potentials (temperature 950° C).