Study of Neodymium Extraction in Molten Fluorides by Electrochemical Co-Reduction with Aluminium

Mathieu Gibilaro, Laurent Massot, Pierre Chamelot, Pierre Taxil

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M. Gibilaro, L. Massot*, P. Chamelot, P. Taxil

Laboratoire de Génie Chimique UMR 5503, Département Procédés Electrochimiques,
Université de Toulouse, 31062 Toulouse Cedex 9
massot@chimie.ups-tlse.fr

Abstract – *This work concerns the co-deposition process of Al-Nd alloys in LiF-CaF_2 medium (79-21% mol.) on tungsten electrode at 860 °C using electrochemical techniques: cyclic and square wave voltammetries and potentiostatic electrolyses. Specific peaks of Al-Nd alloys formation were observed in cyclic voltammograms between the reduction waves of Nd(III) and Al(III), in a fluoride melt containing neodymium and aluminium ions. The difference of potential measured between solvent reduction and the alloys formation allows expecting an extraction efficiency of 99.99% by the use of the co-reduction process. The intermetallic compounds ($Al_{11}Nd_3$, Al_3Nd, $AlNd_2$ and $AlNd_3$) were obtained and characterised by Scanning Electron Microscopy with EDS probe.*
The validity of the process was tested by carrying neodymium extraction in the form of Al-Nd alloy; the extraction efficiency was more than 95%.

INTRODUCTION

This work is dedicated to the simultaneous extraction of a Lanthanide (Ln) and Aluminium, which participates to the pyro-processing of nuclear wastes. Co-reduction of Ln with Al should allow eliminating together fission products and aluminium, providing from a previous treatment of wastes for recovering Actinides by the methodology of reductive extraction. This methodology consists in placing in a molten solution containing the element to be extracted (AnF_3) with a liquid metallic phase containing a reductive agent. The solute AnF_3 is reduced and then transferred into the metal.

According to the thermodynamic calculations of Conocar *et al.* [1], Al is the most promising liquid metal to extract An from the molten solution; the scheme of the extraction is:

$$AnF_{3\,(solution)} + Al_{(metal)} \rightarrow An_{(metal)} + AlF_{3\,(solution)} \quad (1)$$

Further to the An-Ln separation, the excess of aluminium ions must be eliminated with other species of the waste mixture to recycle the molten solvent. For this purpose the simultaneous presence of these metallic ions in the melt lets up to attempt a co-reduction process which should have the advantage of extracting Al(III) and Ln(III) in a single step, yielding Al-Ln alloys.

Therefore the present work is dedicated to the extraction of both Ln and Al elements from molten fluorides solution. The process we used is the co-reduction of Al and Ln ions yielding an alloy of these two metals.

Neodymium is known to be the most concentrated element in the fission products [2]; so the study will be realised with neodymium as lanthanide.

The work described here comprises three parts:

(I) Investigation on the respective reduction mechanisms of Al(III) and Nd(III) in LiF-CaF_2 on tungsten electrode
(II) Investigation on the co-reduction of the mixture AlF_3-NdF_3 and observations of the products of the co-reduction
(III) Trial runs of quantitative extraction of Al and Nd by Al(III) and Nd(III) co-reduction.

EXPERIMENTAL

- The cell consisted of a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled inside by circulating water. The inner part of the walls was protected against fluoride vapours by a graphite liner containing the experimental crucible. The experiments were performed under an inert argon atmosphere (U-

grade: less than 5 ppm O_2), previously dehydrated and deoxygenated using a purification cartridge (Air Liquide). The cell was heated using a programmable furnace and the temperature was measured using a chromel-alumel thermocouple. A more detailed description of the device can be found in previous papers of our laboratory such as the one referred in [3].

- The electrolytic bath consisted of the eutectic LiF/CaF_2 (SDS 99.99%) mixture (79/21 molar ratio). Before use, it was dehydrated by heating under vacuum (3.10^{-2} mbar) from the room temperature up to its melting point (762 °C) for 72 h. For providing aluminium and neodymium ions, aluminium fluoride AlF_3 (SDS 99.95%) and neodymium fluoride (SDS 99.99%) powders were introduced into the bath through a lock chamber under argon gas atmosphere.

- Electrochemical equipment: all electrochemical studies and electrolyses were performed with an Autolab PGSTAT 30 potentiostat/galvanostat controlled by a computer using the research software GPES 4.9.

- Electrochemical techniques: cyclic voltammetry, square wave voltammetry and potentiostatic electrolyses were used for the investigation of the aluminium-neodymium co-reduction process.

- Characterisation of reduction products: after electrolysis runs, cathode surface was examined by Scanning Electron Microscopy (LEO 435 VP) equipped with an EDS probe (Oxford INCA 200) for determining the composition of the alloys.

- *(I) Analytical setting*

For investigations on electrochemical behaviour of the fluoride baths, we used the following cell components:
Tungsten wire (1 mm diameter) was used as working electrode. The surface area of the working electrode was determined by measuring its immersion depth in the bath after withdrawing from the cell. The auxiliary electrode was a vitreous carbon rod (3 mm diameter) with a large surface area. Potentials were referred to a platinum wire (0.5 mm diameter) immersed in the molten electrolyte, acting as a quasi-reference electrode $Pt/PtO_x/O^{2-}$ [4]. This reference is reliable when the composition of the electrolyte remains unchanged, like in analytical experiments.

- *(II) Extraction setting*

Compared with the previous setting, the extraction experiments need specific arrangements:

1- The reference electrode is a nickel 1 mm diameter wire immersed in a mixture of LiF-CaF_2-NiF_2 (1 mass %), placed in a boron nitride basket. This reference electrode was proved to be reliable in molten fluoride baths [5]. Moreover, the insulation from the electrolytic bath guarantees the invariability of its potential with the change of composition of the electrolyte.

2- The anode made of vitreous carbon was isolated in a graphite compartment containing LiCl-LiF-CaF_2 eutectic mixture. The anodic reaction was the chlorine release; the electrode compartmentalisation avoids gas and fluoride media mixing and reoxidation of Al-Nd compounds catholically formed.

3- The working electrode was a tungsten plate with a large surface area (3 cm²).

RESULTS AND DISCUSSION

Co-Reduction Principle

The simultaneous reduction of two or several ions on an inert cathodic material was widely described by Brenner [6] and more recently by Taxil *et al.* [7].

In the case of two metallic ions, R^{n+} and N^{p+} where R is the more reactive precursor, N the less reactive and R_xN_y the alloy formed by co-reduction, the co-reduction process occurs in three steps:

$$(1)\ xR^{n+} + ne^- = xR$$
$$(2)\ yN^{p+} + pe^- = yN$$
$$(3)\ xR + yN = R_xN_y$$

The overall process is:

$$xR^{n+} + yN^{p+} + (n+p)e^- = R_xN_y \qquad (2)$$

The equilibrium potential of the system R/R_xN_y can be expressed as:

$$E_{R^{n+}/R_xN_y} = E^0_{R^{n+}/R} + \frac{RT}{nF}\ln\left[\frac{a_{R^{n+}}}{a_{R\,(in\ R_xN_y)}}\right] \qquad (3)$$

$$E_{R^{n+}/R_xN_y} = E_{R^{n+}/R} - \frac{RT}{nF}\ln\left[a_{R\,(in\ R_xN_y)}\right] \qquad (4)$$

Where $E_{R^{n+}/R}$ the equilibrium potential of pure R element, T the absolute temperature in K, n the number of exchanged electron, F the Faraday constant (96 500 C) and a_R(in R_xN_y) the activity of R in the intermetallic compound R_xN_y.
As a_R in R_xN_y is less than one, it can be deduced that $E_{R^{n+}/R_xN_y} > E_{R^{n+}/R}$.

So, the co-deposition of R with a more noble metal allows R^{n+} ions to be reduced at a potential shifted towards more positive values, compared to the pure metal deposition: this "depolarisation effect" is similar to one observed when the reduced element reacts with the cathode material [8]. Nevertheless, the depolarisation effect is significative only if the binary system R-N can form intermetallic compounds.

After showing the results obtained in our laboratory on the respective electrochemical behaviour of Al and Nd in fluoride solutions, we will investigate the behaviour of these elements together in molten fluorides in order to define accurately the potential of formations of intermetallic compounds.

Previous Results on NdF_3 and AlF_3 Reduction Mechanism

Cyclic voltammograms

The NdF_3 electrochemical reduction on inert electrode was investigated in our laboratory by Hamel [9] and Nourry [10].

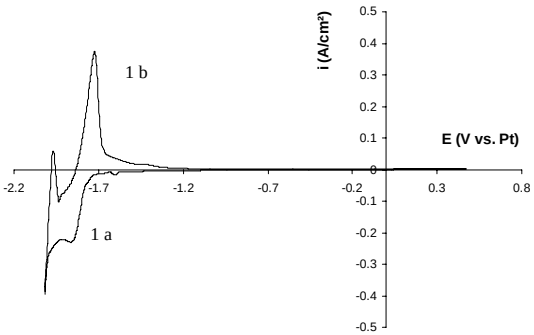

Fig. 1: Cyclic voltammogram of the LiF-CaF_2-NdF_3 (2 10^{-4} mol.cm^{-3}) system at 100 mV.s^{-1} and T = 860 °C. Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt

On the cyclic voltammogram of the LiF-CaF_2-NdF_3 (C^0 = 1.10^{-4} mol.cm^{-3}) system at 860 °C on inert Mo electrode at 100 mV.s^{-1} shown in Fig. 1, the peak (1 a) at -1.9 V vs. Pt is attributed to Nd(III)/Nd reduction. The peak (1 b) observed in reverse scan (stripping peak) is typical of the anodic dissolution of the electrodeposited metal. So, we can assume that neodymium metal is deposited in a single step by reduction of Nd(III) ions into Nd(0) as:

$$Nd(III) + 3e^- = Nd \qquad (5)$$

Like NdF_3, AlF_3 electrochemical behaviour was studied by our team in [8]. On the cyclic voltammogram of LiF-CaF_2-AlF_3 (C^0 = 1.82 10^{-4} mol.cm^{-3}) presented in Fig. 2, plotted at 860 °C and 100 mV.s^{-1}, a single peak is observed in the cathodic run at around -1.25 V vs. Pt. This peak is associated with an oxidation peak (stripping peak) at around -1 V vs. Pt.

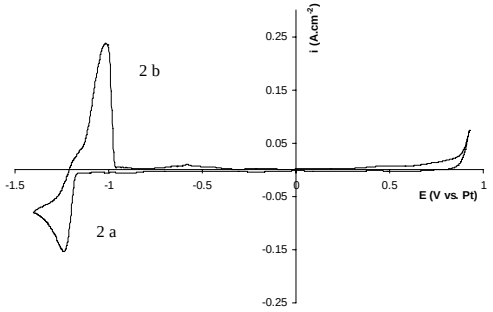

Fig. 2: Typical cyclic voltammogram of the LiF-CaF_2-AlF_3 (1.8 10^{-4} mol.cm^{-3}) system at 100 mV.s^{-1} and T = 860 °C. Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt.

The Al(III) reduction mechanism is assumed to be:

$$Al(III) + 3e^- = Al \qquad (6)$$

Then, the influence of the scan rate on the peak intensity was considered to verify the Berzins Delahaye relationship for a soluble/insoluble system [11]:

$$I_p = -0.61 \times nFSC^o \left(\frac{nF}{RT}\right)^{1/2} D^{1/2} v^{1/2} \qquad (7)$$

where S is the electrode area in cm^2, C^o the solute concentration in mol.cm^{-3}, D the diffusion coefficient in $cm^2.s^{-1}$, F the Faraday constant (96500 C), n the number of exchanged electrons, v the potential scanning rate in V.s^{-1} and T the temperature in K.

The linearity of Ip versus $v^{1/2}$ was proved for both metallic ions so the electrochemical reduction process of Nd(III) and Al(III) is diffusion-controlled.
The slope of this linear equation is found to be:
- for neodymium ions:

$$\frac{I_p}{S \times v^{1/2}} = -0.7866\ A.s^{1/2}.V^{-1/2}.cm^{-2} \qquad (8)$$

at T = 860°C and $C^o = 2\times10^{-4}$ mol.cm^{-3}

- for aluminium ions:

$$\frac{I_p}{S \times v^{1/2}} = -0.4228\ A.s^{1/2}.V^{-1/2}.cm^{-2} \qquad (9)$$

at T = 860 °C and $C^0 = 1.82\ 10^{-4}$ mol.cm^{-3}

Square wave voltammetry

To determine exchanged electron number, we used the square wave voltammetry which is an accurate method for this purpose [12]. In this method, derived from cyclic voltammetry, the scanning of potential proceeds stepwise with superimposition, on each step of the staircase, of two potential pulses, direct and reverse, with equal values. Plotting the differential intensity measured at each step between the successive pulses versus the potential associated to each electrochemical reaction provides a Gaussian shaped peak. In the case of a reversible system, mathematical analysis of the peak yields a simple equation associating the half-width of the peak ($W_{1/2}$) and the number of electrons exchanged:

$$W_{1/2} = 3.52\frac{RT}{nF} \qquad (10)$$

Fig.3 shows that the square wave voltammogram of NdF_3 in LiF-CaF_2 exhibited a single peak. Accordingly, measuring the half-width of the half peak can perform the calculation of n.

Using this methodology, the average value of $W_{1/2}$ is 114 mV; according to Eq. (9), the result for n is close to 3 (2.88).
This result allows the diffusion coefficient of Nd(III) ions to be calculated, at 860°C so we find $D = 1.61\ 10^{-5}$ cm².s^{-1}.

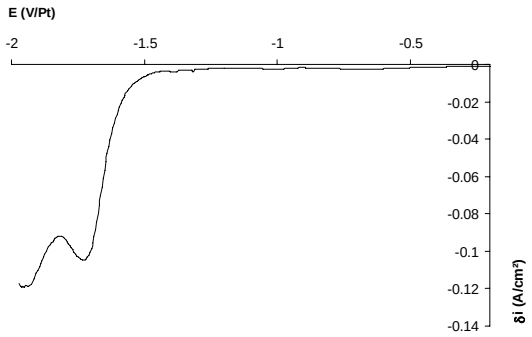

Fig. 3: Square wave voltammogram of LiF-CaF_2-NdF_3 (2 10^{-4} mol.cm^{-3}). Frequency: 9 Hz; T = 860 °C; Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt.

A typical square wave voltammogram of the system LiF-CaF_2-AlF_3 ($C^0 = 1.82\ 10^{-4}$ mol. cm^{-3}) is shown in Fig. 4 at T = 860 °C and f = 9 Hz. The curve exhibits one peak at about -1.2 V vs. Pt which corresponds to the $E_{p/2}$ of the cyclic voltammogram.

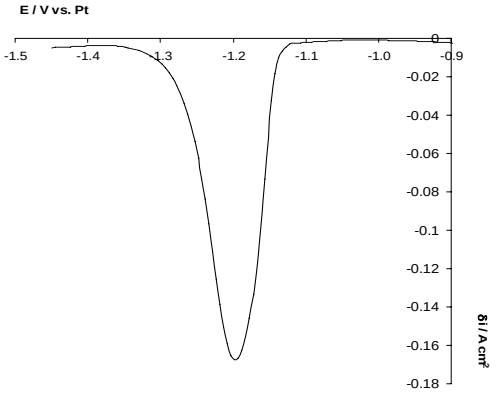

Fig. 4: Square wave voltammogram of LiF-CaF_2-AlF_3 (1.82 10^{-4} mol.cm^{-3}). Frequency: 9 Hz; T = 860 °C; Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt.

Measuring $W_{1/2}$ ($W_{1/2:}$ 112mV in this figure) gives as described in Eq. (10) an average value for the number of electrons exchanged of 3.06 ± 0.1.

The diffusion coefficient $D_{Al(III)}$ was calculated according previous results and Eq. (9); its value is $5.59\ 10^{-6}$ cm².s^{-1} at T = 860 °C.

Investigation of the LiF-CaF_2-AlF_3-NdF_3 System

According to Eq.(4), the equilibrium potential shift of neodymium metal deposition in the anodic sense is expected for the co-reduction of Al and Nd ions into a binary Al-Nd compound where the activity of each element is less than one.

Experiments were carried out on an inert tungsten electrode at 860 °C and with the analytical setting described in (I) of the Experimental part; the electrochemical behaviour of the Al-Nd system was investigated by cyclic voltammetry and square wave voltammetry. The same metallic ions concentrations than in the individual studies above were used: [Al(III)] = 1.8 10^{-4} mol.cm^{-3} and [Nd(III)] = 2 10^{-4} mol.cm^{-3}.

Square wave and Cyclic voltammograms of the mixture is presented in Fig. 5 and 6 respectively.

- First, the AlF_3 NdF_3 mixture was studied by square wave voltammetry on W electrode at 860 °C at a signal frequency of 9 Hz; Fig. 5 evidences that in addition to Al(III) peak (2 a) and Nd(III) peak (1 a), new co-reduction peaks (3 and 4 a) observed between (2 a) and (1 a). Furthermore, we notice an increase of the current density is observed on peaks (2 a) and (1 a), corresponding to pure metals deposition, probably due to the superimposition of alloys peaks.

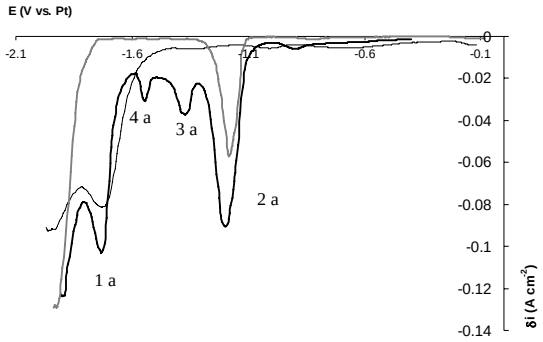

Fig. 5: Square wave voltammogram of the LiF-CaF_2-AlF_3-NdF_3 system (respectively 1.8 10^{-4} and 2 10^{-4} mol.cm^{-3}) at 9 Hz and T = 860 °C. Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt.

- Then, cyclic voltammetry on W electrode at 860 °C and the voltammogram (Fig. 6) confirms the same distribution of peak potentials.

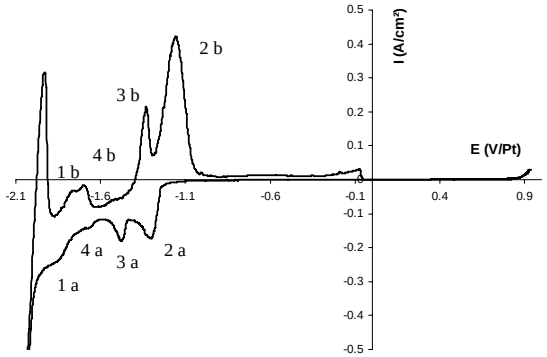

Fig. 6: Cyclic voltammogram of the LiF-CaF_2-AlF_3-NdF_3 system (respectively 1.8 10^{-4} and 2 10^{-4} mol.cm^{-3}) at 100 mV.s^{-1} and T = 860 °C. Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt.

Short potentiostatic electrolysis runs during 1200 s were performed on a tungsten electrode to prove that Al-Nd alloys could be produced in LiF-CaF_2 by co-reduction of the respective ions. Just after each run, the alloyed electrode was quenched by a rapid withdrawing from the cell. Then, an EDS analysis, joined to the SEM observation of the sample cross section, allowed us to determine all the composition phases observed on micrographs.

- E_p = -1.33V vs. Pt: this peak (2 a) is at the same potential than the one observed on Fig. 2 for the reduction of Al(III) into Al with only aluminium fluoride in the bath. It can be noted that the peak intensity is higher when both Al and Nd ions are presenting the bath. The product of this electrolysis, presented in Fig. 7, exhibits only one intermetallic compound formed at the cathode, $Al_{11}Nd_3$, instead of pure Al as expected from Fig. 2. We can first note that the alloy is no adherent to the tungsten electrode. This observation leads us to conclude that at this potential, Al(III) is co-reduced with Nd(III), that explains the higher peak current density peak (2 a) observed in Fig. 5 for similar contents in Al(III).

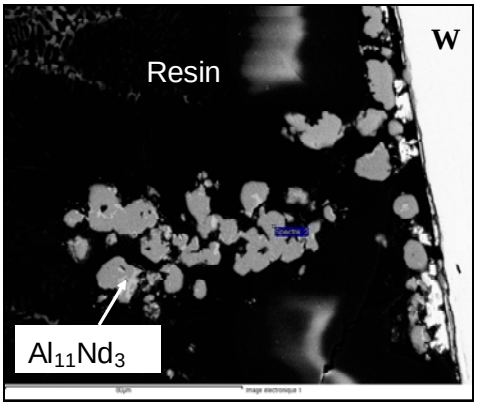

Fig. 7: Micrograph of the cross section of a tungsten wire after electrolysis. Experimental conditions: T = 860 °C, E = -1.33 V vs. Pt, t = 1200 s.[2]

- E_p = -1.88 V vs. Pt: the Nd(III)/Nd system of Fig. 1 is again observed on Fig. 6 (peaks 1 a and 1 b) with a similar enhancement of the peak. At this potential of pure neodymium deposition observed in Fig. 1, the electrolysis yields in Fig. 8 an intermetallic Al-Nd compound on the tungsten surface. The EDS analysis allows determining that the product is $AlNd_3$. Once again, this result explains the increase of the cathodic current density observed in Fig. 5 for the Al-Nd co-reduction and suggests a superimposition of peaks of Al-Nd co-reduction and pure Nd deposition.

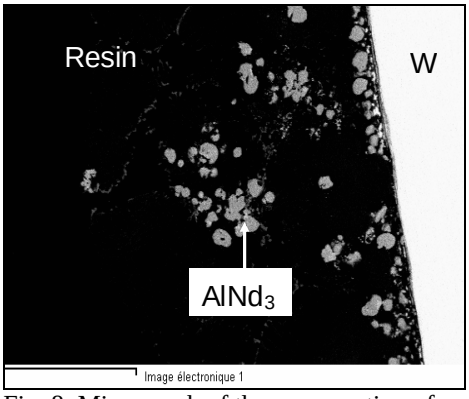

Fig. 8: Micrograph of the cross section of a tungsten wire after electrolysis. Experimental conditions: T = 860 °C, E = -1.88 V vs. Pt, t = 1200 s.

- E_p = -1.49V vs. Pt: the first additional reduction peak (3 a), comprised between the respective reduction potentials of Al(III) into Al and Nd(III) into Nd, should be attributed to the aluminium-neodymium co-reduction. Its re-oxidation peak is observed at E = -1.34 V vs. Pt (3 b). The electrolysis carried out at this intermediate potential between those of pure metal electrodeposition leads to cathodic product shown in Fig. 9. EDS analyses prove that the composition is uniform: Al_3Nd

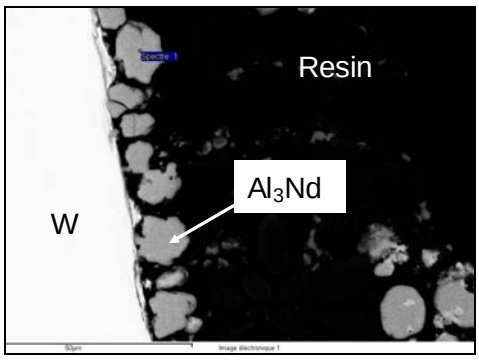

Fig. 9: Micrograph of the cross section of a tungsten wire after electrolysis. Experimental conditions: T = 860 °C, E = -1.49 V vs. Pt, t = 1200 s.

- E_p = -1.69V vs. Pt: the second additional reduction peak (4 a) is more cathodic and should be attributed to the aluminium-neodymium co-reduction. The re-oxidation peak are observed at E = -1.68 V vs. Pt (4 b). The short electrolysis performed on tungsten electrode is presented in Fig. 10 and yields to a poorly adherent alloy to the electrode surface: $AlNd_2$.

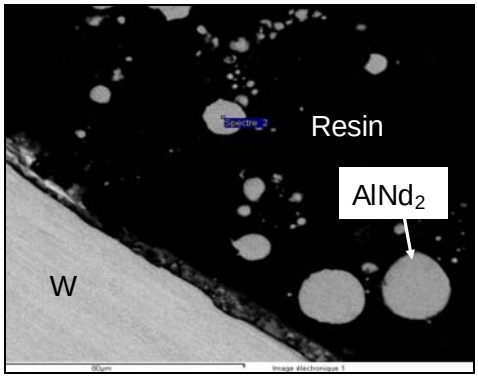

Fig. 10: Micrograph of the cross section of a tungsten wire after electrolysis. Experimental conditions: T = 860 °C, E = -1.69 V vs. Pt, t = 1200 s.

Through these preliminary observations, it can be concluded that the Al-Nd alloys co-deposition can be performed from a molten solution containing the respective metallic ions reduced together at the cathode in a potential range between depositions of each pure metal.

As a general conclusion of these experiments:

(I) the aluminium-neodymium co-reduction on tungsten electrode can yield Al-Nd compounds, non adherent on the substrate and which are thus released in the bath.

(II) The composition of the alloys is depending on the potential of the cathode; we observe that more the electrolysis potential is cathodic, higher is the neodymium content in the intermetallic compound, as expressed in Eq. (4) where the depolarisation term is a function of the neodymium activity in the Al-Nd alloys.

Electrolytic Extraction of Neodymium Ions by Co-Reduction

The following part of the work will concern the extraction of Nd(III) by co-reduction with Al(III) ions.

Experimental Conditions

The extraction was realised on tungsten electrode in LiF-CaF_2 media at T = 860°C. The initial concentrations in metallic ions were: [Al(III)] = 2.6 10^{-4} mol.cm^{-3}; [Nd(III)] = 7.5 10^{-5} mol.cm^{-3}.

The experimental setting is described in the Experimental part (II) with a specific reference electrode and anodic compartment. Unlike to the preceding part of this work, extraction process implies the change of the composition therefore we had to replace, as reference of potentials, the platinum wire by a NiF_2/Ni reference electrode isolated from the bath, to guarantee a more stable potential during long time electrolyses.

The electrolysis potentials were chosen by drawing on a W wire a cyclic voltammogram; this potential was the co-reduction peak (3a). Then, potentiostatic electrolysis was performed on a tungsten plate as cathode. Finally, an after-electrolysis voltammogram is recorded to observe the extraction progress, correlated to the electrochemical signal decrease.
These stages are repeated as a long as an electrochemical signal, provided by the melt in the electrochemical window of the fluoride solvent, can be detected by cyclic voltammetry.

Neodymium Aluminium Co-Reduction: Extraction Process

Electrolyses were performed on a tungsten plate during 3 hours and a record of the current versus time is plotted in Fig. 11.

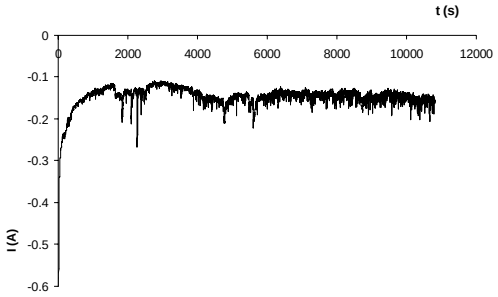

Fig. 11: Cathodic current on tungsten electrode during potentiostatic electrolysis versus time. Experimental conditions: T = 860 °C, S = 3 cm², E = -1.5 V vs. NiF_2/Ni.

The disturbances of the current signal noted at this figure can be explained by the detachment of the alloy at the cathode surface. As it was observed above, the electrodeposited alloys are non adherent. Two steps can be supposed:

(I) the growth of the alloy phases increases the surface, thus the current

(II) the alloy phase is released in the bath and the surface goes back to its stationary value.

As mentioned above, the process was followed by drawing periodically cyclic voltammograms of the solution. Such typical voltammograms are presented in Fig 12 where only the cathodic part is showed. A significant decrease of the current density on the cyclic voltammetry is observed, correlated to the decrease of Al(III) and Nd(III) ions concentration in the bath during the extraction process. Electrolyses were performed during 50 hours to obtain a cathodic current density value approaching zero.

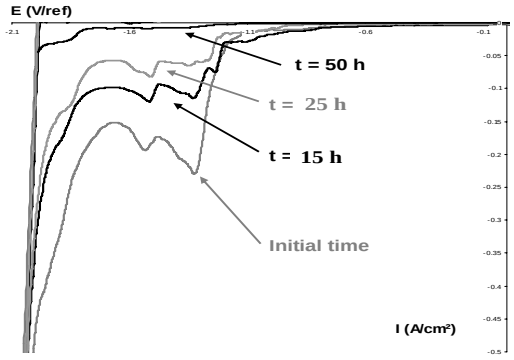

Fig. 12 : Cathodic current density evolution during electrolysis measured by cyclic voltammetry. Experimental conditions: T = 860 °C, v = 100 mV.s^{-1}; Working electrode: W; Counter electrode: vitreous carbon; Reference electrode: NiF_2/Ni.

According to the comparison of the current, measured on the Fig. 12, at the end of the extraction process and at the one at the beginning of the process, the extraction efficiency was estimated to be at least 95% in neodymium.

CONCLUSION

The possibility of preparing Al-Nd compounds by co-deposition was evidenced on the cyclic voltammogram of the Al-Nd fluoride solutions: specific electrochemical systems for the co-reduction of Al(III) and Nd(III) ions were identified in the potential range between pure Al and Nd metals deposition. Each of the four reduction waves observed are correlated to Al-Nd intermetallic compounds, further identified with SEM observation and EDS analysis after a short electrolysis run: $Al_{11}Nd_3$, Al_3Nd, $AlNd_2$ and $AlNd_3$ were obtained on a tungsten electrode. At increasing cathodic potential, these compositions are in agreement with Equation 5 where more the electrolysis potential is cathodic, higher is the neodymium content in the alloy.

So, these preliminary experiments have shown that it is possible to extract both neodymium and aluminium ions present in the melt at potential comprised between the equilibrium potentials of each metal. Furthermore, a new experimental setting for the extraction has been developed and tested successfully and lead to an extraction efficiency of Nd(III) estimated to be at least 95 %.

This work has shown that a novel process for lanthanides extraction based on the co-reduction between Al(III) and Nd(III) ions can be proposed. This method presents the advantage to eliminate simultaneously the two metallic ions in order to recycle the fluoride solvent. Indeed this co-reduction process can be extended to other electrochemical systems. Thus, in a more general aspect, this work lets to expect a promising route for preparing intermetallic compounds involving aluminium and lanthanides.

REFERENCES

1. O. CONOCAR, N. DOUYERE, J. LACQUEMENT, *J. Nucl. Mater*., **344**, 136-141 (2005)
2. J.P. ACKERMAN, *Ind. Eng. Chem. Res.*, **30**, 1, 141-145 (1991)
3. P. CHAMELOT, P. TAXIL, B. LAFAGE, *Electrochim. Acta*, **39**, 17, 2571-2575 (1994)
4. A. D. GRAVES, D. INMAN, *Nature*, **208**, 481-482 (1965)
5. P. TAXIL, Z. QIAO, *J. Chim. Phys.*, **82**, 1, 83-86 (1985)
6. A. BRENNER, *Electrodeposition of alloys*, Vol. 1, Academic Press, New York, pp. 362-367
7. P. TAXIL, P. CHAMELOT, L. MASSOT, C. HAMEL, *J. Min. Met*., **39**, 1-2, 177-200 (2003)
8. M. GIBILARO, L. MASSOT, P. CHAMELOT, P. TAXIL, Submitted article in *J. Alloy Compd*
9. C. HAMEL, P. CHAMELOT, P. TAXIL, *Electrochim. Acta*, **49**, 4467-4476 (2004)
10. C. NOURRY, *PhD thesis*, "Extraction Electrochimique des Lanthanides des Milieux Fluorures Fondus par Formation d'Alliage", Toulouse (2007)
11. T. BERZINS, P. DELAHAY, *J. Am. Chem. Soc.*, **75**, 555 (1953).
12. M.S. RAMALEY, L. KRAUSE, Anal. Chem., **41**, 1365-1369 (1969)