

ELECTRODEPOSITION OF ALLOYS OR COMPOUNDS IN MOLTEN SALTS AND APPLICATIONS

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Abstract

This article deals with the different modes of preparation of alloys or intermetallic compounds using the electrodeposition in molten salts, more particularly molten alkali fluorides. The interest in this process is to obtain new materials for high technology, particularly the compounds of reactive components such as actinides, rare earth and refractory metals. Two ways of preparation are considered: (i) electrocoating of the more reactive metal on a cathode made of the noble one and reaction between the two metals in contact, and (ii) electrocoating on an inert cathode of the intermetallic compound by coreduction of the ions of each elements. The kinetic is controlled by the reaction at the electrolyte interface. A wide bibliographic survey on the preparation of various compounds (intermetallic compounds, borides, carbides...) is given and a special attention is paid to the own experience of the authors in the preparation of these compounds and interpretation of their results.

Keywords: Electrosynthesis, alloys, intermetallic, compounds, molten salts, alkali fluorides, co-reduction, reactive electrodeposition

1. Introduction

Laboratories of chemical engineering are often interested in high technology processes to prepare coatings of new materials or compounds; most of these compounds

are not easy to obtain by chemical or metallurgical ways. The electrodeposition in molten salts is a specific way to obtain compounds of reactive and refractory elements, such as the refractory metals, the actinides and rare earth metals.

Specially now, the coating of these alloys or compounds are relevant in the following fields, interesting also for our laboratory:

(i) The protection of the vessels in contact with the nuclear fuel; as example, the ref [1] shows that the refractory metal carbides resist to corrosion by liquid plutonium

(ii) Again in the nuclear field, the alloy electrodeposition is involved in the elimination of either fission products (rare earth or minor actinides) or spent fuel (uranium, plutonium) from nuclear wastes [2]. Each of these category of elements are well known to yield easily and at rather high rates alloys or compounds with more noble elements such as nickel or aluminium; obviously the deposition in an alloyed form of these elements proceeds at sensibly more anodic potentials, so that their separation from other reactive elements becomes more easy.

(iii) Certain alloys of refractory metals are promising materials for the making of industrial electrode, suitable for long service life:

- First, it was demonstrated that alloys of Ta and Nb with Nickel ($TaNi_3$ or $NbNi_3$) have an excellent behaviour as anodes with respect of conditions of the oxygen or chlorine evolving in aqueous electrolysis [3,4], due to the lowering of the activity of nickel in the alloy which makes this metal more passive in oxidizing conditions. For the same reasons, these compounds were recently used as cathodes in molten carbonates fuel cells (MCFC) [5]

- Whereas it is stated now that pure refractory metals such as Ta can be used as substrate for DSA (Dimensionally Stable Anodes) for Oxygen evolving in aqueous electrolysis [6,7], owing to the inertness of this metal in oxidizing conditions, tantalum carbides, more corrosion resistant than pure Ta, are expected to be still more efficient substrates [8]. Besides, ref [9] highlights the catalytic activity of these compounds for the NH_3 decomposition

- In the industry of aluminium electrowinning, titanium or zirconium borides are possibly used to protect the carbon cathodes from the electrolyte insertion [10]. Numerous works are dedicated to the preparation of these compounds by electrodeposition in molten salts, either in molten fluorides or in cryolithe media [10-16]

Molten salts are suitable media for electrowinning alloys first owing to specific properties relevant for electroplating in general [17]: high conductivity, good viscosity, high values of Wagner number. Herein, molten alkali fluorides are well known from the sixties to provide smooth coatings of refractory metals [18] and surface alloys [19]. So they are almost exclusively used as solvents for electrocoating in molten salts.

Besides in the particular case of alloy electrowinning where intermetallic diffusion or reactions involving solid elements intervene, the high temperature of using these media is important and enhances sensibly the reactivity of the elements and their diffusion

coefficient when the kinetic is controlled by diffusion.

This article is dedicated to the alloys or compounds electrowinning by two different techniques:

(i) The reactive electrocoating of a reactive element on a noble one used as cathode. In this case the alloy is obtained by reaction of the discharged ion and the cathode material, which is “reactive”.

(ii) The alloy is obtained on an inert cathode by coreduction of ionic precursors. In each case, we will develop first the thermodynamic conditions of obtaining these alloys, then kinetic factors allowing to predict the rate of the process, finally some indications on their applications.

Numerous examples, provided by the literature will be mentioned, certain of them discussed, and a particular accent will be placed on our own results, obtained in our laboratory, concerning the electrochemical synthesis in molten fluorides of compounds of nickel with Ta, Nb, Nd and tantalum carbides.

2. Reactive electrodeposition

2.1. Basic principles - different methods of synthesis

We define by reactive electrodeposition a cathodic system wherein the discharging ions (R^{n+}) or the electrodeposited metal R reacts with the metal of the cathodic substrate to give 3 intermetallic compounds existing in the binary diagram of these elements; let us suppose that two compounds are possible, RN_x and RN_y with $y > x$; we can propose the following path:



Obviously, taking into account the excess of N, this reaction must lead to the more thermodynamically stable compound RN_y :



The overall cathodic reaction is :



The potential of these alloys formation are more anodic than the one of pure metal R electrodeposition (Underpotential Deposition). In most cases the kinetic of the reaction is too low in a moderated temperature range (500-800°C) for yielding layers of

noticeable thickness. Nevertheless, N.C Cook (General Electric) in the sixties published several articles and registered patents on the preparation of numerous surface alloys by the present technique. The process was called *Metalliding* and consisted of a galvanic cell where the anode is the reactive element and the cathode the substrate to be coated with the alloy [19-21].

We have proposed three different modes of preparing surface alloys by reactive electrodeposition [22, 23]:

1- Electrodeposition of the pure reactive metal on the cathode followed by the inter-metallic diffusion of the pair of metals placed into contact, after the electrolysis time; the evolution of the cathode potential during the interdiffusion period allows to record this stage of diffusion, the end of this step being marked by the stabilization of the potential at the “underpotential” of the most stable compound.

2- Electrodeposition at the “underpotential” of the alloy.

3- Metalliding process, by using a galvanic cell, according to the methodology of Cook: Fig.1 shows the principle of the process: the reactive metal dissolves at the anode ($R \rightarrow R^{n+} + ne$) and the cathodic reaction is: $R^{n+} + ne + yN \leftrightarrow RN_y$. As far a difference of chemical potentials between the two electrodes remains, the galvanic cell can feed to the cathode with R^{n+} ions.

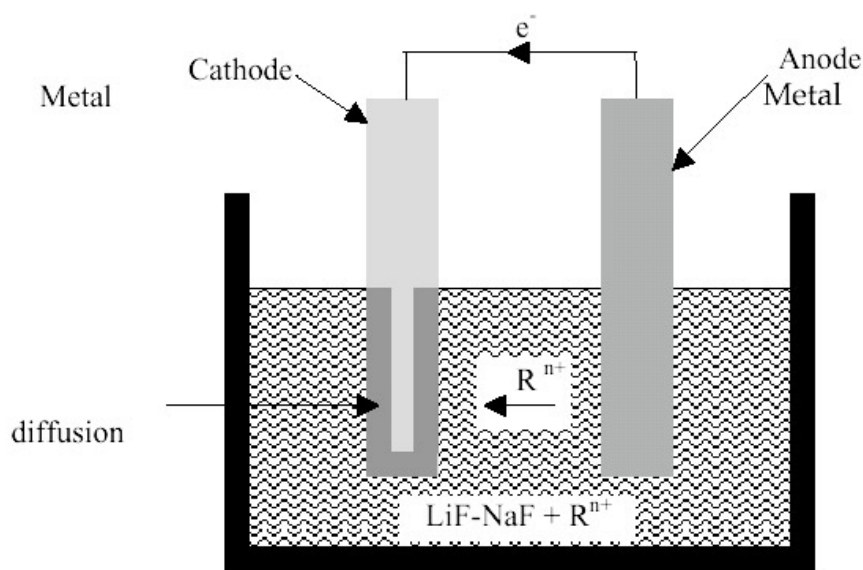


Fig.1: Principle of the metalliding cell used by Cook for the preparation of surface alloys.

2.2. Thermodynamical analysis

The thermodynamic properties of alloys are classically calculated by emf measurement of galvanic cells where one electrode is the pure metal and the other electrode is the alloyed metal. Nevertheless, the preparation of the alloy is often not easy to do by metallurgical method. So, electrochemical method should be preferred if one wants to obtain the alloy “in situ” in the cell where emf measurements are performed.

The most relevant results by this way were first obtained, in molten chlorides by Weppner and Huggins [24-26] for the alloys of lithium with elements such as Bi and Sb. These authors prepared these alloys by electrodepositing small amount of lithium on a Bi or Sb cathode by intermittent galvanic pulses; the electrodeposited metal diffuses rapidly into the cathode and promotes the change of the composition of the alloy; the recording of the cathode potential between the current pulses exhibit a variation with plateaus, each plateau corresponding to a 4 defined compound of the binary diagram. The potential of the plateau referred to the lithium anode is the emf of a cell Sb or Bi / LiCl-KCl, SbCl₃ or BiCl₂/SbLi_x or BiLi_y. The stoichiometry of the compound is determined by the coulometric titration. Gibbs Energy of these compounds can be calculated using the Nernst equation:

$$\Delta_f G^\circ = -nF\zeta = RT \ln a(\text{Li}) \quad (4)$$

Similar results were obtained by Picard and Mottot for the La/Ni system [27] in molten chlorides; the cell was La/LiCl-KCl, LaCl₃/La_xNi; the so-called *Galvanostatic Intermittent Titration Technique* (GITT) allows to identify the successive formations of the compounds of the binary diagram, LaNi₅, La₂Ni₇, LaNi₃, La₂Ni₃, LaNi and the thermodynamic properties of each compound were determined by the measurement of the potential plateau observed when the stoichiometric composition of each compound is reached.

Plateaus of potentials are typical of a biphasic equilibrium between compounds of different compositions; such plateaus can be observed in the transient period after the current pulse when the electrodeposited metal diffuses into the substrate promoting the transient formation on the cathodic surface of the compounds of the binary system.

Thermodynamic data of the binary system nickel/tantalum were computed by this method in our laboratory [23, 28]. First, a Ta coating was deposited in a mixture LiF-NaF-K₂TaF₇ on a nickel cathode and further the potential was recorded versus time after switching off the power.

Fig.2 shows an example of variation of the potential at 950°C of the cathode referred to a pure tantalum electrode observed during the relaxation period: after a first period at E=0 corresponding to pure tantalum on the cathode surface, the potential-time curve exhibits several steps typical of the successive formation of other solid phases on this

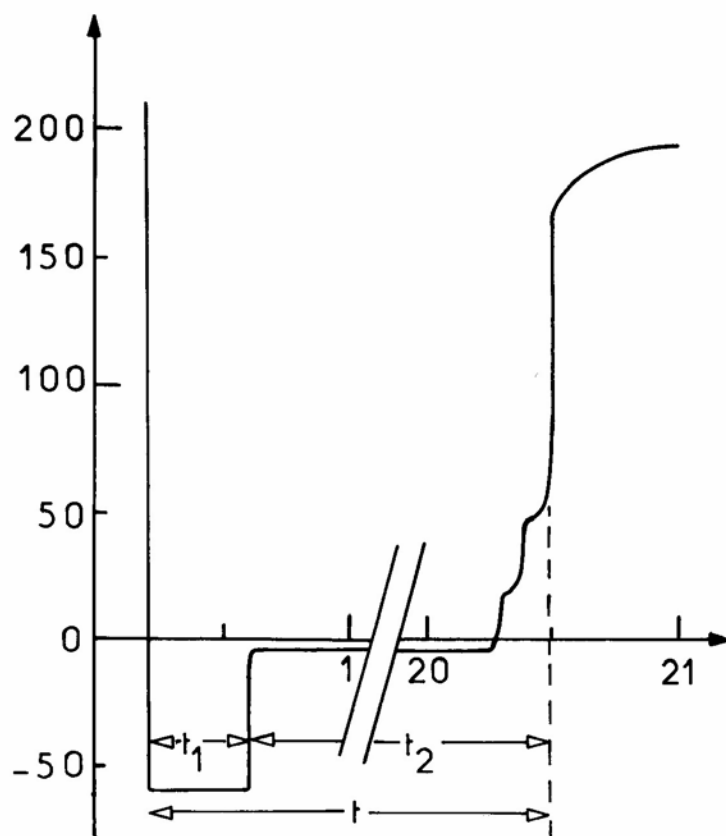


Fig.2: Transient evolution of the potential of a nickel cathode after deposition of tantalum by galvanostatic electrolysis in molten fluorides ($\text{NaF-LiF-K}_2\text{TaF}_7$): $T= 950^\circ\text{C}$; Current density of the electrolysis: 27 mA/cm^2 (taken from [28])

surface; according the binary diagram of the nickel-tantalum system [29], they should be successively: Ta_2Ni , TaNi , TaNi_2 and TaNi_3 . Each potential plateau is associated to the following biphasic equilibria: $\text{Ta}_2\text{Ni}/\text{TaNi}$, $\text{TaNi}/\text{TaNi}_2$ and $\text{TaNi}_2/\text{TaNi}_3$.

The potential values, respectively 20 mV, 45 mV, 200 mV and 245 mV, are the emf of a cell of the type: Ta_xNi , $\text{Ta}_y\text{Ni} / \text{LiF-NaF, K}_2\text{TaF}_7/\text{Ta}$, in which the cathode reaction is:



Each emf is :

$$\xi = \frac{RT}{(y-x)F} \cdot \ln \frac{a^{eq}_{Ta} \left(Ta_y F \right)}{a^{eq}_{Ta} \left(Ta_x F \right)} \quad (6)$$

The plateau at 245 mV connected to the TaNi₃/Ni system (Ta^V + 5 e + 3Ni → TaNi₃) is not visible on this figure, because the process is achieved when the stable phase TaNi₃ recovers the cathode; but we observed this plateau in Refs. [23, 28], at the beginning of the diffusion process by using short times of electrolysis.

Thus, it was possible to calculate, by using Eqs. (4,6), the Gibbs Energy ($\Delta_f G^\circ$) of the compounds and the activity of the reactive metal (Ta) in each of them.

In Refs. [23] and [28], the method is validated by the agreement of calculated ($\Delta_f G^\circ$) of Ta₂Ni and TaNi by this method with literature, while data concerning the other compounds are missing.

Similar phenomena were observed with the titanium-nickel systems by de Lépinay et al [30]. Recently [31], Robin uses the same methodology than us to calculate the free energies of the compounds : Ti₂Ni, TiNi and TiNi₂.

The main conclusions of these works concern the depolarisation occurring for the electrosynthesis of an intermetallic compounds are the following:

(i) Obviously, the depolarisation increases with the content of the compound in reactive element increases.

(ii) The depolarisation can be calculated as being the emf of the cell with a cathode made with the compound and the anode with the reactive element. So, it can be written:

$$E_{CP} = E_R - \frac{\Delta_f G^\circ_{cp}}{nF} \quad (7)$$

where E_{cp} and E_R are the standard potential of depositing respectively the alloy and the pure metal on an inert cathode and $\Delta_f G^\circ_{cp}$ the Gibbs Energy of the compound.

Otherwise, the thermodynamic data, when available, allow the depolarisation to be evaluated. Hence, Kaptay and Kusnetsov used equations similar to (7) to calculate equilibrium potentials of the boride systems in molten salts [32]. Thermodynamic data allow these authors to elaborate so-called *Electrochemical Equilibrium Synthesis* (EES) diagrams where the stability of the compounds of the system B/Me is defined as a function of temperature and the depolarisation term which is the second term of Eq.(5); hence these diagrams display the stability of each compound of systems such as Ti/B in areas delimited by boundary lines given by Eq.(5) computed in the temperature scale adapted to the process of preparing these alloy.

Kaptay elaborated the EES diagram of the ternary system Ti/B/Al at 1000 K in cryolite melts containing alumina, and Ti and boron oxides, combining data from the respective binary system. The goal is to optimize the potential of the carbon cathode for the electrochemical synthesis of titanium boride, used as a protective layer of the carbon cathode for the Hall-Héroult process. Plotting the depolarisation term of the Al/B system as a function of the Ti/B system, the diagram delimits the area of stability in terms of equilibrium potential of each binary compound [33].

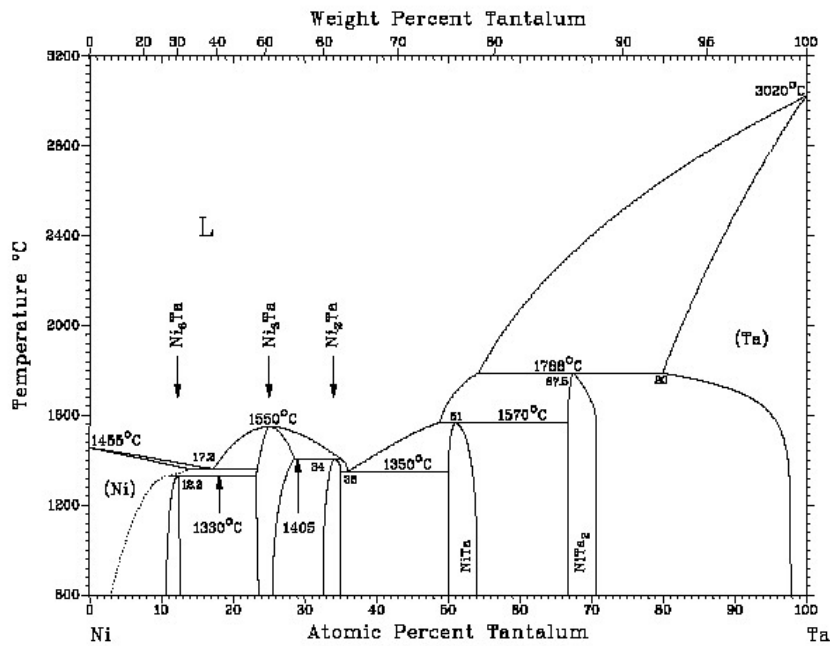


Fig.3: Binary diagram of the system Ta/Ni (taken from [29])

2.3. Applications in the nuclear field

Depolarisation effect by alloy formation may be an additional tool for extracting electropositive elements from molten salts or for separating them from other reactive element. Pyrochemical programs for the treatment of nuclear waste expect to use this route to separate actinides from lanthanides by electrolytic processes in molten salts [34].

Lantelme mentioned that the high reactivity of lanthanum with nickel cathode, prior observed in this article, lead to the efficient elimination of lanthanum from waste by electrolysis in molten salts in the form of liquid La/Ni alloys [35,36]. According to [36], similar treatment can be expected for extracting gadolinium, another major fission product to be separated from spent fuel.

Neodymium is one of most important fission products in nuclear reactors and its extraction from nuclear wastes is an actual problem concerning our laboratory. As this element is a rare earth with a behavior close to La, we expect to extract neodymium by electrolytic process in molten salts; besides, this element gives numerous intermetallic compounds with nickel, as shown on the binary diagram Nd/Ni of Fig. 4.

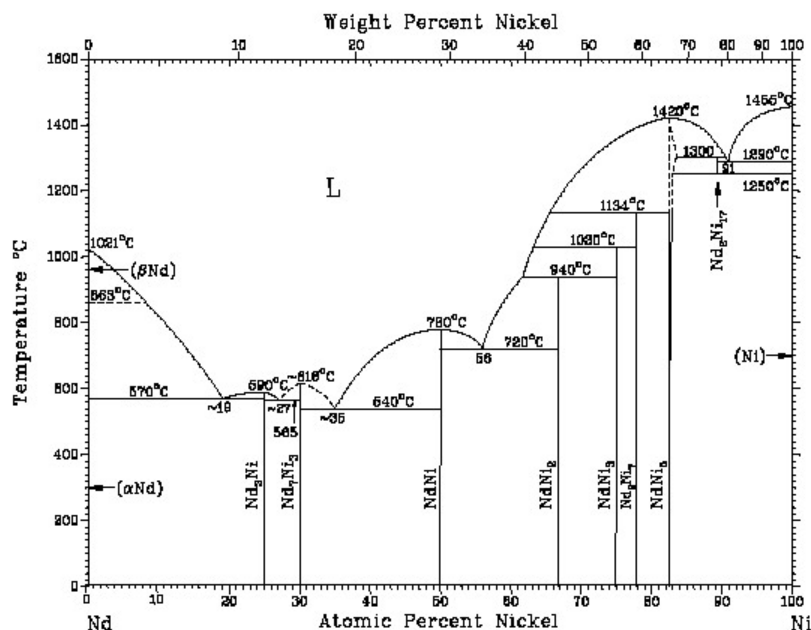


Fig 4: Binary diagram of the system Nd/Ni (taken from [29])

The cyclic voltammetry of the LiF-NdF₃ mixture at 900°C evidences on Fig. 5 the depolarisation effect of the alloy Nd/Ni formation in molten fluorides when the cathodic material is nickel. With an inert cathode (molybdenum) one can observe that at a potential being close to the solvent reduction, a single peak is associated to the pure Nd formation in the cathodic wave of potential scanning ($\text{Nd}^{\text{III}} + 3e \rightarrow \text{Nd}$) and the reoxidation of the deposited metal in the anodic wave. The same voltamogram carried out on a nickel cathode exhibits at more anodic potentials extra peaks associated with the underpotential Nd/Ni alloy formation.

The last reduction peak before nickel being 180 mV more anodic than the reduction on molybdenum, we performed a potentiostatic reduction of the mixture at this potential on a nickel cathode during two hours; Fig.6 shows the SEM micrograph cross-section of the nickel cathode after this treatment; we can observe on this micrograph.

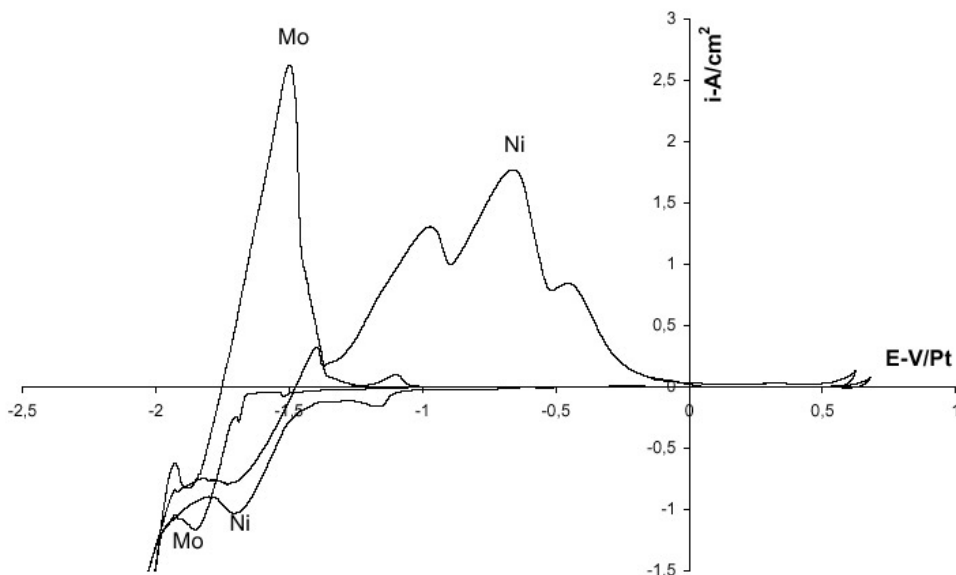


Fig. 5: Cyclic voltammogram of the LiF-NdF_3 mixture at $T= 880^\circ\text{C}$ on a nickel cathode, compared to a molybdenum cathode

(i) The high rate of the intermetallic diffusion Nd/Ni: in a relatively short time, a layer of $300\ \mu\text{m}$ thickness is obtained

(ii) Two phases are observed in the alloy layer: the composition of the outer part, close to the electrolyte interface, determined by EDS, is NdNi_2 while the inner one, in contact with the pure nickel substrate, is identified as NdNi_3 , thus more rich in Nickel. This result highlights that during a transient period, the diffusion of the deposited metal goes with the reaction with the substrate leading to the most stable compound; obviously the compound first synthesized by the potentiostatic electrolysis is NdNi_2 which further reacts with Nickel to give more stable NdNi_3 ; the missing of other compounds still more rich in nickel, Nd_2Ni_7 and NdNi_5 , is questionable and may be due as evidence to low rates of reaction.

2.4. Kinetics of the process

The kinetics of formation of the intermetallic compounds must to be managed for predicting the rate of growth of the alloy layers. Obviously, the process is controlled by the mutual diffusion of the couple of reacting metals and in most cases the processes are

slow, except in the case of examples cited above: Lithium compounds [24-26] and alloys of Rare Earth metals with nickel [27, the present article]. So, Picard et al found [27] high diffusion coefficient in the solid state about 10^{-6} cm²/sec, namely close to values observed in liquid phase, but we can consider that as an exceptional role of the temperature in the kinetic process.

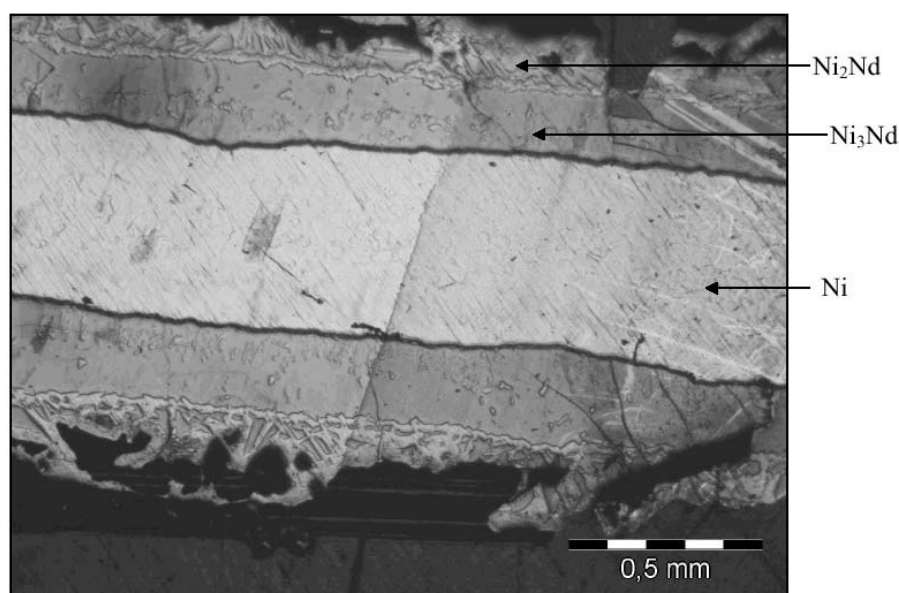


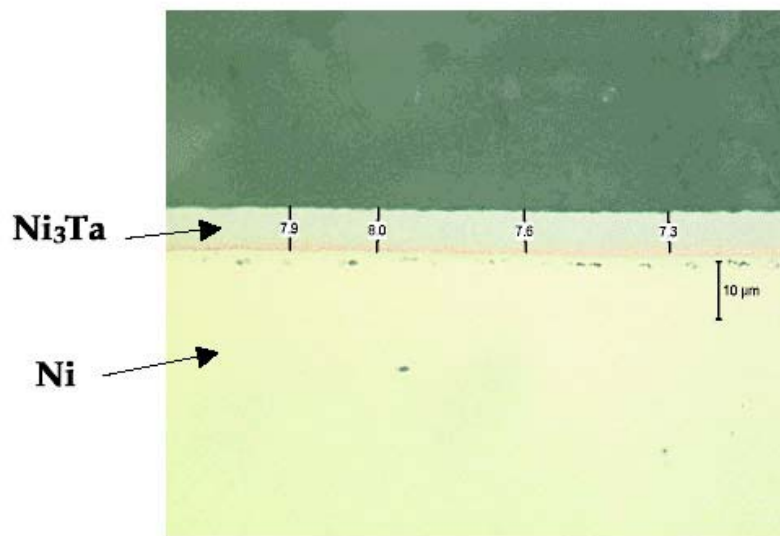
Fig. 6: SEM micrography of a cross section of a nickel cathode after 2h electrolysis of LiFNdF_3 at $T= 880^\circ\text{C}$

Earlier works on Ta/Ni [28] and Nb/Ni [37] systems allowed us to state that the growth of the thickness of the alloy layers obtained by metalliding nickel with tantalum and niobium obeys a parabolic relationship with the duration of the process:

$$X = Kt^{1/2} \quad (8)$$

where X is the thickness of the layer. Similar relationship was found by Bonomi et al in experiments of boriding molybdenum [38]. The values of K are highly depending on temperature obeying to Arrhenius type law.

In earlier works, we used transient techniques to calculate the intermetallic diffusion coefficients involved in the metalliding process. Fig. 7 shows a surface alloy obtained by metalliding nickel with tantalum; we can notice the uniform thickness and the perfect homogeneity of the layer, composed only of the stable phase TaNi_3 . Besides, the surface



*Fig7: Cross section of a nickel tantalum surface alloy after metalliding:
 T = 900°C; time: 2h (extracted from ref [40])*

of the cathode is unchanged by the process, so that only the boundary with nickel is shifted by the intermetallic diffusion. These characteristics lead us to elaborate a kinetic model of diffusion with one moving boundary and within the product of the surface reaction [39]. Fig.8 gives a schematic drawing of the model elaborated in detail in Refs. [22, 23, 28]. Transient techniques were used to calculate the diffusion coefficient. Amperometric measurements during electrolysis at underpotential showed a linear relationship equivalent to Cottrell law between metalliding current and the reciprocal of the square of time; likewise, chronopotentiograms displayed transition times for the alloy formation, linear with the reciprocal of the square of the metalliding current, similarly to Sand's law. The mathematical treatment of these results lead to the following relation between K and the diffusion coefficient, D.

$$K = 4\alpha^2 D \quad (9)$$

Where α is a constant depending on the compositions of the layer at $x = 0$ and $x = X$, namely the limits of the diffusion layer, which can be calculated [39].

Other works in the literature deal with the modelling of the metalliding process: Picard for La/Ni system [27], Bonomi for B/Mo [38] and Lantelme for Pt/Ni [40], all these authors using electrochemical transient techniques to calculate D. The values of D depend highly on the binary systems involved: in cm^2/sec , about 10^{-6} at 720 K for La/Ni, [27], 10^{-14} for Pt/Ni [40] at 870 K, 10^{-10} for Ta/Ni [28] and Nb/Ni [37] at 1000 K.

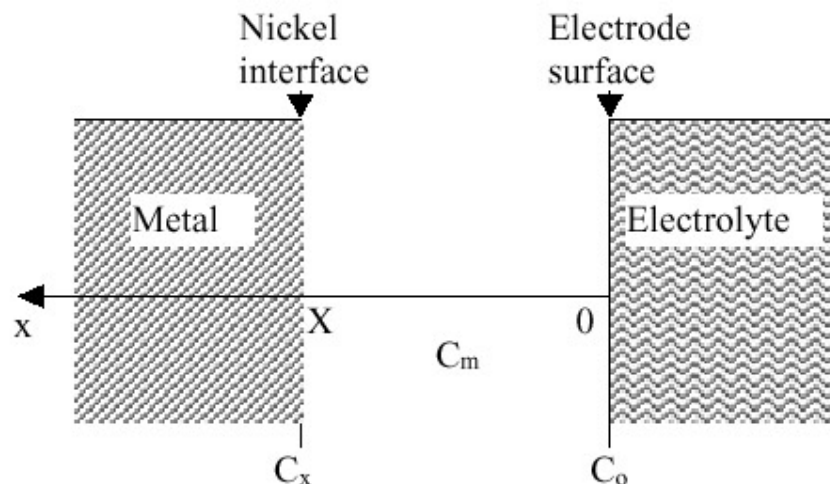


Fig. 8: Graphical representation of the intermetallic diffusion during metallizing process

2.5. Tantalum carbides elaboration by reactive electrodeposition

Layers of tantalum carbide can be now synthesised by chemical vapor deposition of a carbon on a Ta substrate in a temperature range of 1300-1500°C, according to recent work [41]. The carbon prepared by this way is very reactive towards the substrate and 10-20 μm layers of TaC and Ta₂C onto the surface of massive tantalum or Ta coating are obtained in 50 hours of treatment.

Similar treatment of Ta by reactive electrodeposition of carbon alternatively to the CVD process was attempted in our laboratory [42]. The overall process was performed in the temperature range of 700-900°C and consists of two successive stages:

1- Ta coating on usual substrate (steel, copper, ...) in molten fluoride electrolyte : LiF-NaFK₂TaF₇, using a well known technique for about 35-40 years [43]

2- carbon coating onto the Ta coating in an electrolyte LiF-NaF-Na₂CO₃ with a partial pressure of CO₂.

In earlier works [44, 45], we have investigated the electrodeposition of carbon in such media and obtained the following results:

- The electrochemical reduction of carbonate ions in carbon proceeds in one single step exchanging 4 electrons ($\text{CO}_3^{2-} + 4\text{e} \rightarrow \text{C} + 3\text{O}^{2-}$) at potential close to the solvent

reduction. The content in carbonate ions is balanced first by the anodic reaction on a carbon anode ($C + 2O^{2-} \rightarrow CO_2$) and further reaction of O_2^- with CO_2 above the bath.

- The carbon produced at the cathode is amorphous, including both sp^2 and sp^3 links as showed by Raman measurements, all characteristics propitious to a high reactivity. Besides, its nucleation mode is progressive; accordingly, small nuclei of reactive carbon are continuously produced on the cathode. We showed that this electrodeposited carbon reacts spontaneously with the Ta cathode.

The coating of carbon on massive tantalum gives rise in relatively short time (2h) to thin layers of tantalum carbide (about $1 \mu m$) while, as we can see on Fig. 9, larger thickness of the layer are obtained on electrodeposited Ta (about $7-8 \mu m$). Obviously, this difference enables us to suggest the microstructure of the Ta coating promotes a catalytic effect, due to a much more extended area of grains boundaries compared to massive Ta: As evidenced on Fig.9a and its magnification of Fig.9b, the penetration of small grains of carbon supplied by the electrodeposition process proceeds within the grain boundaries and the rate of the reaction increases significantly when the contact between the two elements is enhanced. This work confirms the high reactivity of electrodeposited carbon in molten fluorides the formation of tantalum carbides being proved by a further analysis of the diffused layer (see Ref. [42]).

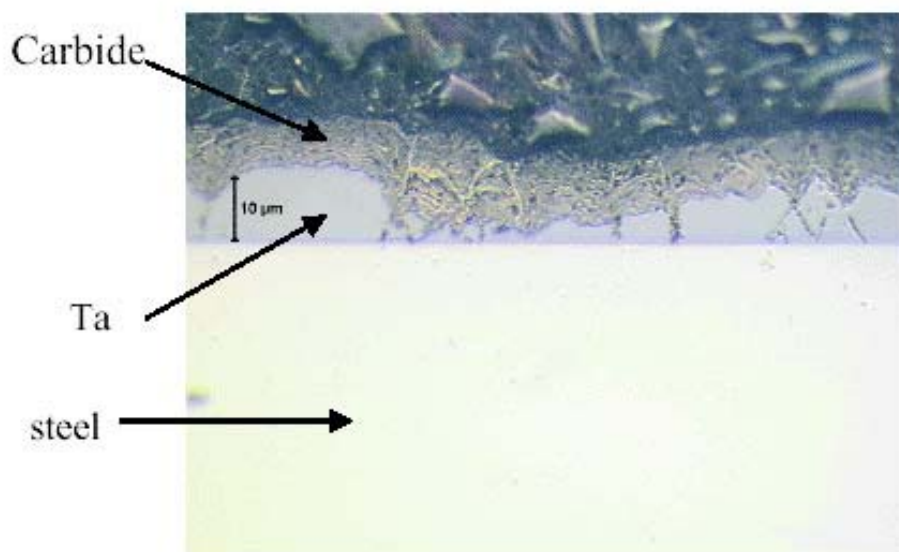


Fig.9a: Optic micrograph of a cross section of an electrodeposited carbon layer in $LiF-NaFNa_2CO_3$ on tantalum coating; $T= 800^\circ C$; electrodeposition of carbon: $i = 5 mA/cm^2$; $t = 2h$.

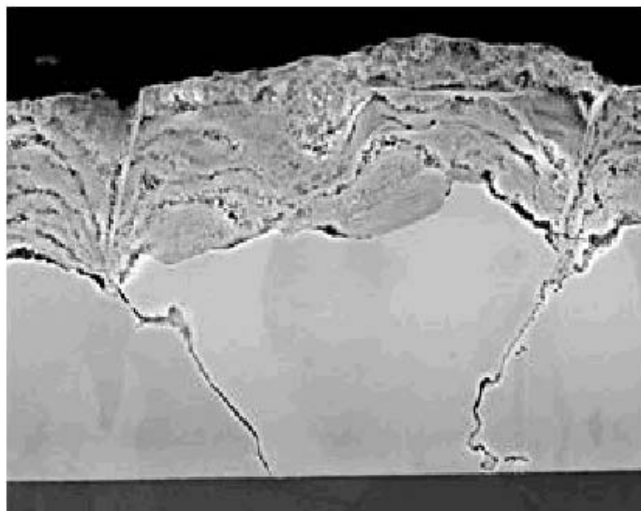


Fig.9b: SEM micrograph of a similar coating than Fig.9 with a larger magnification.

A similar approach in molten oxysalts for obtaining layers of borides and silicides of refractory metals (W, Mo) or oxides (Cr_2O_3) by an electrolytic process in two stages are mentioned in [46]: (1) Deposition of the refractory metal or of the oxide; (2) reactive electrodeposition of B or Si.

3. Coreduction of ionic partners

In spite of the simplicity of implementation, the preceding methodology for surface alloys synthesis is not currently applied for an industrial application. The reasons are special conditions, which should be fulfilled: (i) the cathodic material must be able to react with the electrodeposited metal at moderate temperature; (ii) in most cases the kinetic of the process is too low; (iii) only one composition of the surface alloy is available.

These limitations don't exist in the alternative route, which consist of synthesis of the alloy by simultaneous reduction of the ions of each precursor onto an inert cathodic material. The process is controlled by the diffusion of the electrolyte, thus more rapid in general; nevertheless this control can lead to drawbacks such as the porosity of the coating and dendrites. Furthermore, it can be expected with this procedure to monitor the selectivity of the alloy prepared at the cathode.

Full theoretical principles and practical details of this procedure should be found in a book of Brenner [47].

3.1. Thermodynamic analysis

If we design as above the more reactive precursor by R, the less reactive one by N and the R_xN_y the compound resulting from the co reduction, the electrode process comprises three steps: (1): $x R^{n+} + n e^- \rightarrow x R$; (2): $y N^{p+} + p e^- \rightarrow y N$; (3) : $x R + y N \rightarrow R_xN_y$. the overall process is :



$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 \quad (11)$$

ΔG_3 is the free energy of the alloying reaction, given by equation (7), $\Delta_f G^\circ$.

The equilibrium potential of the system R/ R_xN_y is :

$$E = E_R^\circ + \frac{RT}{nF} \ln \frac{[R^{n+}]}{a_{R_xN_y}} \quad (12)$$

$$\frac{RT}{nF} \ln a_{R_xN_y} = \frac{\Delta G}{nF} \quad (\text{negative}) \text{ is the depolarisation term like expressed in}$$

equation (4) and $E_R^\circ - \frac{RT}{nF} \ln a_{R_xN_y}$ is equivalent to eq. (7). So, measure-

ments of emf of metalliding cells are relevant data for predicting the potential of R and

N coreduction .

Therefore, codeposition of R with a more noble metal allows ions R^{n+} to be reduced at a potential shifted towards positive values, compared to the deposition of pure metal. Nevertheless, the depolarisation effect occurs only if the binary system R-N comprises intermetallic compounds. In the case of complete solubility of the elements in the whole composition scale, the step (3) does not occur and the term ΔG_3 does not exist.

This assumption was verified by a recent investigation in our laboratory dedicated to the electrochemical system niobium-titanium in chloride melts in view of preparation of these metals alloys on inert cathodes [48]. The binary diagram of these metals exhibits complete solubility in all the composition range (see [29]). In this case, we confirmed that each individual electrochemical system is not changed in a mixture of Ti and Nb ions in the fused solvent. The resulting system, analysed by cyclic voltametry and other electrochemical techniques derived from CV, is the sum of both systems without other signal typical for an intermetallic compound. Hence, the alloy is obtained by electrolysis of the melt at the cathode potential of reduction of the more negative element - namely titanium and further reactions in solid phase of electrodeposited elements. The

coatings were in a powder state, because at this potential the deposition of the more noble element Nb is bothered by the electrolyte diffusion which controls the electroreduction of niobium ions.

Otherwise, Polyakova et al observed that the voltammograms of the reduction of mixtures of K_2TaF_7 and KBF_4 in chloride melts exhibit besides peaks of pure Ta and B, extra peaks due to compounds of these elements [49]. Likewise, specific stages of co-reduction were detected on chronopotentiograms (specific plateaus).

Depolarisation effect due to the formation of intermetallic compounds was evidenced in the works of Wendt et al [11,12] on the electrodeposition in fluoride melts of zirconium and titanium borides. Each binary diagram Ti-B and Zr-B includes defined compounds, in particular TiB_2 or ZrB_2 . These authors pointed out on the voltammograms of fluoride solutions (Flinak- K_2TiF_6 and Flinak- K_2ZrF_6) one peak for respectively TiB_2 and ZrB_2 at a potential intermediate between the equilibrium potential of each parent metal.

This depolarisation property can be exploited to extract electropositive elements from molten salts solutions as already expected above with the reactive electrodeposition for the elimination of lanthanides from nuclear wastes. Here the procedure obliges to introduce in the electrolyte a salt of more noble element.

For such extraction applications or other ones (like electrocoating of usual metals with alloys), the codeposition of the intermetallic compound R_xN_y must be the single reduction process at the electrode. That means the deposition of pure N must be avoided; so, the composition of the electrolyte is critical and it has to be calculated in such a way that the equilibrium potential of N is shifted towards negative value, so the following equation is verified:

$$E = E_R^o + \frac{RT}{nF} \ln \frac{[R^{n+}]}{a_R(R_xN_y)} = E_N^o + \frac{RT}{nF} \ln \frac{[N^{p+}]}{a_N(R_xN_y)} \quad (13)$$

Thus, the composition of the electrolyte must obey the following relationship:

$$\frac{[R^{n+}]^x}{[N^{p+}]^y} = \frac{a_R}{a_N} \cdot \exp \frac{nF}{RT} [E_N^o - E_R^o] \quad (14)$$

Furthermore, in the case of several intermetallic compounds, the selectivity of the electrode process for obtaining one of these compounds can be achieved by an electrolyte composition obeying a relation of the type of Eq.(14), adapted to the required compound.

A significant example of selectivity of the codeposition process was dealt with by U. Cohen [50] for niobium-germanium alloys electrowinning in molten fluorides. The

compounds of the binary diagram NbGe_2 , Nb_2Ge_3 , Nb_5Ge_3 or mixtures of these phases were electrosynthesized at controlled potentials, previously determined by cyclic voltammetry and with appropriate Nb/Ge ions ratio in the electrolyte, obeying Eq.(14).

3.2. Electrochemical synthesis of compounds of refractory metals with metalloids (non metals)

The industrial interest of these compounds was emphasized in the beginning of this paper, particularly of titanium diborides for the protection of carbon cathodes in the Hall-Héroult process, and of carbides for corrosion resistance in aggressive media. Likewise, silicides layers should of evidence offer too attractive properties of mechanic and corrosion resistance. The chemical synthesis of these compounds needs high activation energy and a 1500-2000 K temperature range is generally required for obtaining them with a correct kinetic characteristic.

According to relatively recent works and analysis, electrosynthesis should be a promising route alternatively to the chemical synthesis since the work temperature is expected to be sensibly lowered in the electrochemical way; we gave earlier a significant example of this with the preparation of tantalum carbide by reactive electrodeposition.

Russian literature deals with particularly numerous works dedicated to the theory and implementation of the electrosynthesis of this type of compounds in molten oxysalts at moderated temperature (700-900°C), reported in ref [46] and [51]. Hereby [46], the appreciable decrease of the activation energy in the electrochemical process compared to the chemical one should be attributed to: (i) from the supersaturation of dispersion of the elements produced by electrochemistry; (ii) the non equilibrium growth of crystals during electrolysis. Accordingly, the interaction between the metal and the non-metal proceeds on the atomic level, which explains the high reactivity of electrodeposited carbon. This theory seems to complete our own assumption mentioned above on the correlation between the high reactivity of electrodeposited carbon and its amorphous structure or its nucleation mode.

Novoselova et al [46] have combined and exploited *emf* measurements or computations of galvanic cells, using as electrolyte oxides or oxyhalides of both refractory metals and non metals such as boron, carbon and silicium to calculate the energy of decomposition of the electrolyte in metal or non metal and oxygen. Hence, they established a chart of standard potentials of these elements as a function of temperature (equivalently to Ellingham diagrams), useful to predict the ability of electrosynthesis of a binary or even a ternary compound by coreduction of molten oxysalts. The temperature of the process can be adjusted in such a manner that the standard potentials of the partners elements are close, that avoids electroreduction process to be influenced by the composition of the electrolyte in partner ions and the electrolysis parameters.

Otherwise, molten fluorides should be preferred to oxysalts for preparing carbides of

refractory metals; the choice of these media was based on their suitability for electro-coating applications, earlier mentioned in this article. Stern and collaborators published a series of works on carbide electrodeposition in Flinak at 700-900°C: tantalum [52, 53, 56]; tungsten [54, 56]; chromium [55, 56]; titanium, niobium, zirconium [56]. Likewise, Topor and Selman reported obtaining excellent coatings of Mo₂C with a similar processing to Stern [57].

In these works, the respective precursors of refractory metal and carbon are a fluoride complex (e.g., K₂TaF₇) and an alkali carbonate. According to Stern [56], carbonate ions react with the fluoride complex to give a mixed oxide of the alkali metal and the refractory metal (e.g. KTaO₃), with a strong CO₂ release. If this reaction does not go to completion, the carbide layer can be obtained by the simultaneous reduction of remaining precursors. Furthermore, this author mentioned that the reduction of carbonates occurring at a potential more negative than the cathodic limit, carbon should be chemically yielded by chemical reduction of carbonates by the discharged alkali cation and then reacts with the electrodeposited refractory metal.

3.3. Investigation of the electrochemical system Ta/C in molten fluorides

The earlier mechanism, proposed by Stern, is somewhat questionable for us, at least in the particular case of tantalum carbides. It does not take into account the competition between the respective equilibria of (i) decomposition of CO₃²⁻ which releases oxide ions and (ii) the oxifluoride formation, obtained by reaction between oxide ions and the source of Ta, K₂TaF₇. In earlier works, we identified by square wave voltametry in molten fluorides containing TaF₇²⁻ ions and oxide ions at 800°C, coupled with Rosemount spectrometry for the titration of the oxicompsounds, the following reactions at relatively low oxide contents:



These reactions proceed in the right sense and therefore consume the TaF₇²⁻ ions. When the oxide content increases still more, we pointed out successively the formation of an insoluble compound (probably Na TaO₃) and finally a soluble species with 4 oxygen atoms (TaO₄F_y^{3-y}). The oxygenated species were proved to not be electrochemically reduced in Ta.

Taking into account the decomposition of carbonates:



Obviously, in presence of fluorotantalate ions, this reaction is shifted in the right sense. Therefore, mixing carbonate ions and TaF_7^{2-} in molten fluorides results in eliminating both sources of carbon and tantalum from the electrolyte. To keep these sources in the molten electrolyte and thus to achieve the carbides electrodeposition, we attempted to shift the equilibrium (17) in the left sense by setting the bath under overpressure of CO_2 or/and excess of oxide ions. The results are shown on the square wave voltamograms in Figs. 10 and 11, showing respectively the effects of CO_2 overpressure and O^{2-} content on the square wave voltamograms of the electrolyte:

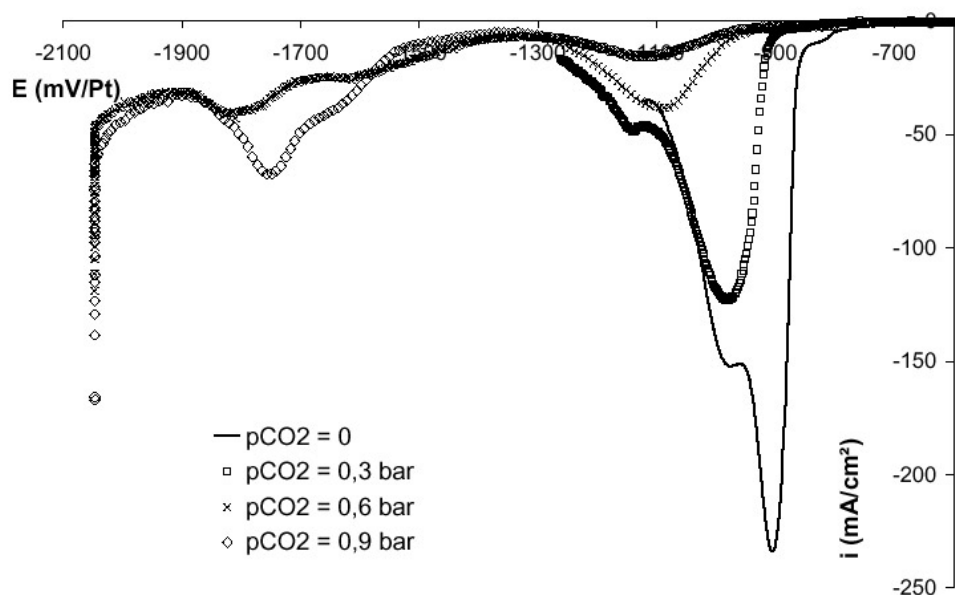


Fig. 10: Influence of the CO_2 overpressure on the square wave voltammogram of the $\text{LiFNaF-K}_2\text{TaF}_7$ containing a few content in oxide ions; WE: Ag; CE: vitreous carbon; reference electrode: Pt; $T= 750^\circ\text{C}$; frequency of the SWV signal: 36 Hz

Initially (Fig.10), the melt includes only K_2TaF_7 in the LiF-NaF solvent with a low content of oxide ions. We point out the reduction process of TaF_7^{2-} (1) and of TaOF_5^{2-} (2), this one at a little more negative potential. A low overpressure of CO_2 generates the formation of carbonate ions in the bath and simultaneously the removal of TaF_7^{2-} (peak 1 is missing), decrease of peak due to TaOF_5^{2-} , a slight increase of other oxifluoride peaks (3 and 4) and the appearance of two peaks (5 and 6) that we attributed to tantalum carbides. This assumption was validated by X-ray analysis of the cathodic product after 10 min electrolysis at the potential of peak 6.

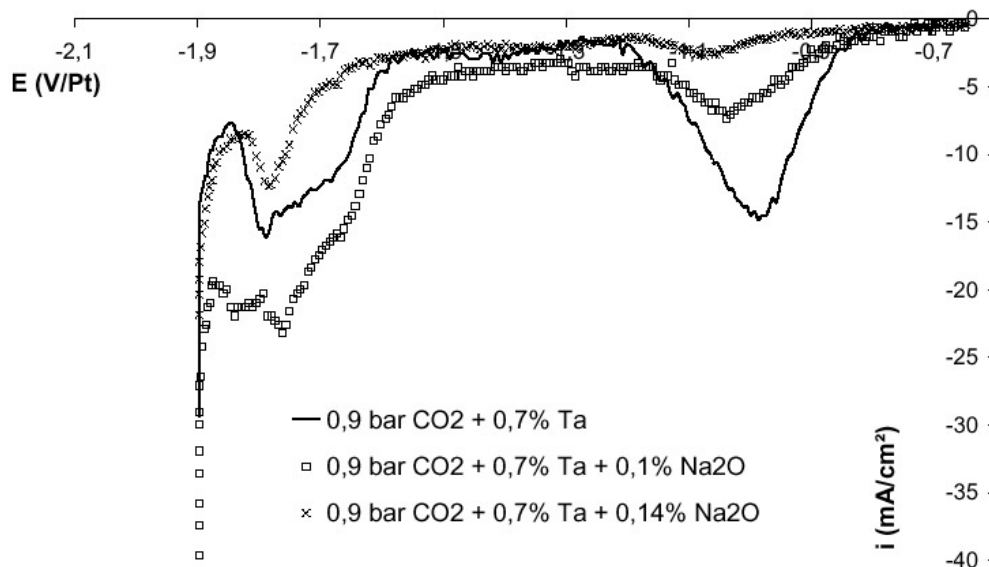


Fig. 11: Influence of the oxide content on the square wave voltammogram of the $\text{LiF-NaFK}_2\text{TaF}_7$ with high overpressure of CO_2 ; WE: Ag; CE: vitreous carbon; reference electrode: Pt; $T=750^\circ\text{C}$; frequency of the SWV signal: 36 Hz

Starting with a bath containing a low content in Ta precursor and a high overpressure of CO_2 , one peak (2) of oxifluoride, TaOF_5^{2-} , and peaks (5) and (6) of carbides are detected on the square wave voltammogram (Fig.11). A first addition of oxide ions lowers the oxifluoride peak while the carbide peaks are increased, due of evidence to the shift of reaction (15) in the left sense. The second addition of oxide ions results in quite complete elimination of oxifluorides and, simultaneously, the decrease of the carbides peaks. Hence, the overall content in Ta is considerably decreased, possibly due to the precipitation of a tantalum oxide occurring for high oxide contents, as settled in our earlier work, described in [59].

Our works seem to demonstrate that (i) tantalum carbides are obtained by simultaneous reduction of each precursor at intermediate potential of the deposition of each element and not by solid reaction between the electrodeposited elements; (ii) overpressure of CO_2 is necessary to succeed the process; these results allow to predict that higher overpressure than 0.9 bar in the electrolysis cell should lead to the formation of pure carbide layers.

4. Conclusion

Electrodeposition of alloys was demonstrated in this review to be favoured by the use of the molten salts media owing to the specific properties of these solvents compared to aqueous media: high conductivity, high throwing power, extended electrochemical window and special reactivity of the electrodeposited elements. These properties may explain that this methodology yields certain compounds used in high technology and difficult to prepare by conventional ways. The most relevant are carbides and borides of refractory metals, excellent candidates to be used as electrode materials in industrial electrolysis.

Thermodynamic data, obtained either by the data banks or by emf measurements in electrolysis cells allow the potential of the electrosynthesis of these compounds to be calculated accurately while by using electrochemical methods, the kinetic parameters of the process can be obtained. We have too emphasized the relevance of binary diagrams for supporting the management of the process.

Two ways of preparation of these compounds were considered: metalliding process (surface alloying on a reactive substrate) and co-deposition of parents metal on an inert cathode. Each methodology according its own limitations or advantages can be selected and implemented as function of the further use of the electrodeposited layer. Our laboratory is actually interested in the preparation of refractory metals carbide layers for the elaboration of electrode materials (DSA, Hall Heroult process...) or the electrodeposition of alloys for the separation between actinides and rare earth (in the frame of the nuclear waste treatment development). Such activities are intensified now and presented in this article.

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