

## **STUDY OF THE Mg–Nd ALLOY OBTAINED BY ELECTROLYSIS IN MOLTEN OXIFLUORIDE MEDIA**

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### **Abstract**

*Mg–Nd alloys have been produced by electrolysis of the molten mixture  $\text{LiF–NdF}_3\text{–MgF}_2$  using  $\text{Nd}_2(\text{CO}_3)_3$  and  $\text{MgF}_2$  as raw materials. An electrolysis cell was designed having the anode made of super dense graphite and the cathode made of molybdenum metal. The quasi-binary system  $(\text{NdF}_3\text{–LiF})_{\text{eutectic}}\text{–MgF}_2$  was investigated and the liquidus line was determined using thermo-differential analysis. The solubility of  $\text{Nd}_2(\text{CO}_3)_3$  in the  $\text{LiF–NdF}_3\text{–MgF}_2$  system was investigated by the carbothermal technique.*

*Keywords:* Mg–Nd alloys, molten salts, electrolyte, electrolysis, solubility

### **1. Introduction**

Due to their physico-mechanical properties, which are superior compared to common alloys, the demand for Mg–Nd alloys is increasing continuously. Users of these alloys include, among others, the airspace and car industry, thanks to their reduced weight and

increased corrosion resistance.

The common methods for the production of such alloys, pyrometallurgy and electrolysis from molten chloride media, have several problems such as metal losses and discontinuity of the process, high costs and difficult-to-control composition of the alloy produced (pyrometallurgical method). As for the electrolytic process, low current efficiency (50–55 %) and pollution caused by the evolution of chlorine at the anode are typical disadvantages of it.

All that can be eliminated by the electrolysis of neodymium oxide (carbonate) in molten fluoride media. This method has the following advantages:

- High current and energy efficiencies, due to the high electroconductivity of the electrolyte and to the very low solubility of metallic *Nd* in  $NdF_3$  [1].
- Environment friendly technology ( $O_2$  is evolved at the anode instead of  $Cl_2$ ).

One of the disadvantages of this technology is the relatively low solubility of raw material,  $Nd_2O_3$ , in molten salts, and especially a very small rate of the oxide dissolution in the electrolyte. The dissolution kinetics of the oxide is an important factor for current efficiency of the *Nd*-electrolysis.

The possibility to produce rare earth alloys by molten salt electrolysis has been investigated by some researchers. In the 1960's Morrice et al. investigated the electrolytic preparation of neodymium metal from its oxide [2]. The electrolysis was conducted in a thermal gradient cell in which the metal was electrowon in the high temperature zone and dripped from the molybdenum rod cathode to the frozen scull situated at the bottom of the cell.

Chambers et al. investigated electrolysis from chloride [3] and oxide-fluoride media to produce neodymium metal.

Ohashi described a cell for commercial electrolysis of  $Nd_2O_3$  in a fluoride electrolyte [4], and Tamamura reported on commercial production of *Nd-Fe* alloys by the electrolysis of  $NdF_3$  [5].

The production of *Mg-Nd* alloys by electrolysis in oxi-fluoride media has been studied in the present work. In order to establish the proper electrolyte, the quasi-binary diagram  $(NdF_3-LiF)_{eutectic}-MgF_2$  was investigated. Also, the solubility and dissolution kinetics of  $Nd_2(CO_3)_3$  in the ternary electrolyte were studied.

In electrolysis experiments with  $Nd_2(CO_3)_3$  and  $MgF_2$  additives, *Mg-Nd* alloys have been obtained by co-depositing *Nd* and *Mg* onto a molybdenum cathode.

## 2. Experimental

The following reagents were used for the experiments:

- *LiF*: Merck production, pa purity, re-crystallized twice under *Ar*.
- *NdF<sub>3</sub>*: Merck production, pa purity, calcinated at 600 °C for 6 hours.

- $MgF_2$ : Merck production, pa purity, calcinated at 600 °C for 6 hours.
- $Nd_2(CO_3)_3$ : Merck production, pa purity, dried at 150 °C for 6 hours.

### **2.1. Determination of the quasi-binary diagram**

#### **$(NdF_3-LiF)_{eutectic}-MgF_2$**

The quasi-binary system  $(NdF_3-LiF)_{eutectic}-MgF_2$  was investigated in order to determine the melting point of the mixture used as electrolyte in the experiments. This investigation was done by means of thermo-differential analysis performed on a Derivatograph type C apparatus. This kind of apparatus works at temperatures up to 1600 °C, with 10 °C/min heating rate, and it uses  $Al_2O_3$  as reference material. Due to the high corrosion action of molten fluorides, a special crucible for samples made of super dense graphite was used. Also, an inert gas flow (*Ar*) was constantly fed to protect the furnace and other components of the apparatus.

The samples were heated at a high heating rate and only values of temperature measured at cooling of the samples, when the mixture is homogenous, were taken into account.

### **2.2. Determination of $Nd_2(CO_3)_3$ solubility in $NdF_3-LiF-MgF_2$**

Due to the very low rate of  $Nd_2O_3$  dissolution in the electrolyte, a series of experiments was conducted to assess the solubility of  $Nd_2(CO_3)_3$  in the ternary system  $NdF_3-LiF-MgF_2$ . Two electrolyte compositions were used for these measurements. Their chemical composition is presented in Table 1. The solubility of  $Nd_2(CO_3)_3$  in  $LiF-NdF_3-MgF_2$  mixtures was determined by measuring the total content of oxygen in the samples, using the carbo-thermal analysis. During carbo-thermal analysis thermal decomposition of chemical species presented in the sample is taking place in a special graphite crucible at 2400°C, and subsequently, infrared determination of the evolved *CO* and *CO*<sub>2</sub> is performed with an EXHALLOGRAPH–BALTZERS–EAO 220 apparatus. In order to avoid the mechanical extraction of undissolved oxide a special graphite filter (pore 4 quality, produced by “Svensk Specialgraphit AB”, Sweden) was used during the sampling procedure.

The experimental set-up for solubility measurements is presented in Figure 1. The crucible, made of super dense graphite with a diameter of 50 mm and height of 60 mm, was kept (for protection) in a metallic (*Ni*) crucible. The cover of the furnace permits to install the feeding tube, the sampling tube, the tube for inert atmosphere (*Ar*) as well as the stirring apparatus (100 rpm, propeller made of super dense graphite).

The sampling device consists of a metallic tube (*Ni*) with a diameter of 10 mm and

length of 400 mm. At one part, the tube was screwed for fixing the graphite filter by means of a metal (*Ni*) sleeve. The seal was assured using a metal O-ring made of copper. The graphite filter road was cut thin at 2.5mm height. The connection with a vacuum pump was assured by means of a flexible tube.

Table 1. Chemical composition of electrolytes

No.	NdF <sub>3</sub>		LiF		MgF <sub>2</sub>	
	% mol	% wt	% mol	% wt	% mol	% wt
	E1	21.26	64.92	71.34	28.08	7.4
E2	20.53	62.82	68.92	27.18	10.55	10

### 2.3. Sampling and analysis procedure

There were five series of experiments performed in five batches, for five temperatures (800 °C, 850 °C, 900 °C, 950 °C and 1000 °C) for each electrolyte composition. For each temperature, samples were taken at different time. To do that, the sampling device was used. It was introduced into the furnace just up to the melt surface.

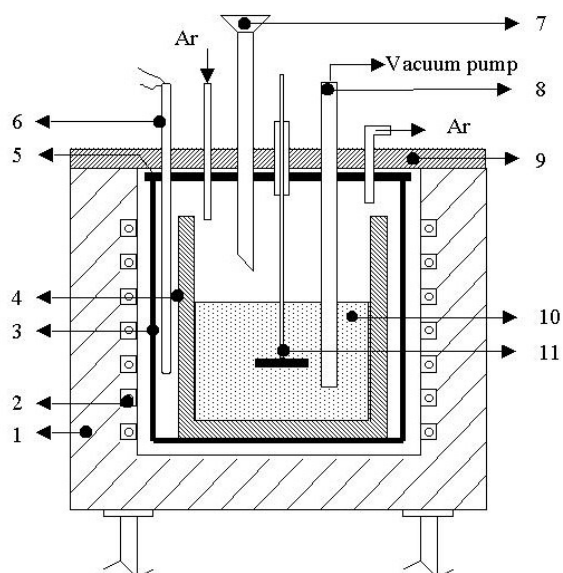
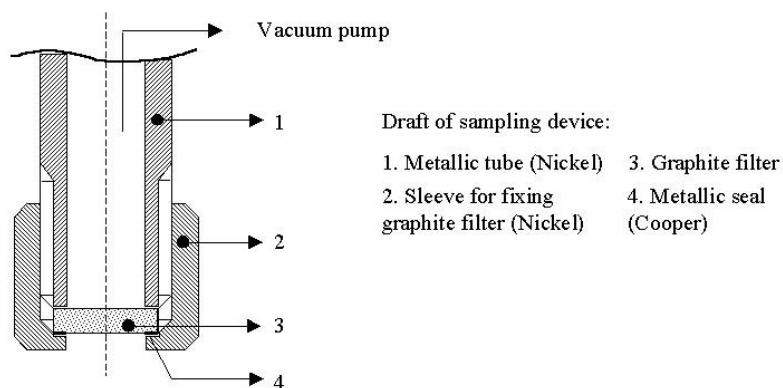
The weight of a sample was 1.5 g (0.5 cm<sup>3</sup>) and the time needed to extract one sample was 5 minutes. After each sampling, the sleeve for fixing the graphite filter as well as the filter itself, were changed. For fast cooling, the sampling device with the sample was immediately placed in a metal box with inert atmosphere (*Ar*). The samples were put into tightly closed capsules (made of super dense graphite) used later for oxygen analysis by EXHALLOGRAPH; these capsules were stored under *Ar* in the same metal box.

### 2.4. Electrolysis experiments for Mg–Nd alloys production

The draft of the electrolysis cell is illustrated in Figure 2. The cell crucible was made of silicon oxy-nitride, a material resisting very well the corrosion action of molten fluorides. The anode, made of super dense graphite, has a special shape that improves the possibility to evolve anode gases. The cathode made of metallic *Mo* is placed at the bottom of the cell. The anode-cathode distance can be modified during electrolysis process, thanks to the anode tube fixed with a screw on the cover of the cell. The anode tube was also used for feeding the  $Nd_2(CO_3)_3$  and  $MgF_2$  during electrolysis process.

A resistance furnace (CARBOLITE type) with temperature electronic control ( $\pm 1$  °C) was used to heat the cell up to the operating temperature. In order to prevent oxidation of the cell materials, dry *Ar* was fed continuously inside the furnace and the cell.

The working and technological conditions for the electrolysis were as follows:



The experimental installation

- |                           |                        |
|---------------------------|------------------------|
| 1. Electric furnace       | 7. Feeding tube        |
| 2. Electrical heating     | 8. Sampling device     |
| 3. Metallic crucible (Ni) | 9. Asbestos cover      |
| 4. Graphite crucible      | 10. Melt               |
| 5. Metallic cover         | 11. Stirring apparatus |
| 6. Thermocouple           |                        |

Figure 1. Draft of the experimental set-up for solubility measurements

temperature: 850 °C; voltage: 4–4.2 V; amperage: 10 A; anodic current density:  $D_A=0.45$  A/cm<sup>2</sup>; cathodic current density:  $D_C=3.9$  A/cm<sup>2</sup>; Nd/Mg feeding ratio: 6; feeding period: every 30 min; total time of electrolysis: 6 hours; raw materials used in the process:  $Nd_2(CO_3)_3$  and  $MgF_2$ ; composition of the electrolyte (in mol. percent):  $NdF_3 - 21$ ,  $LiF - 72$ ,  $MgF_2 - 7$ ; total  $Nd_2(CO_3)_3$  fed: 160 g; and total  $MgF_2$  fed: 40 g.

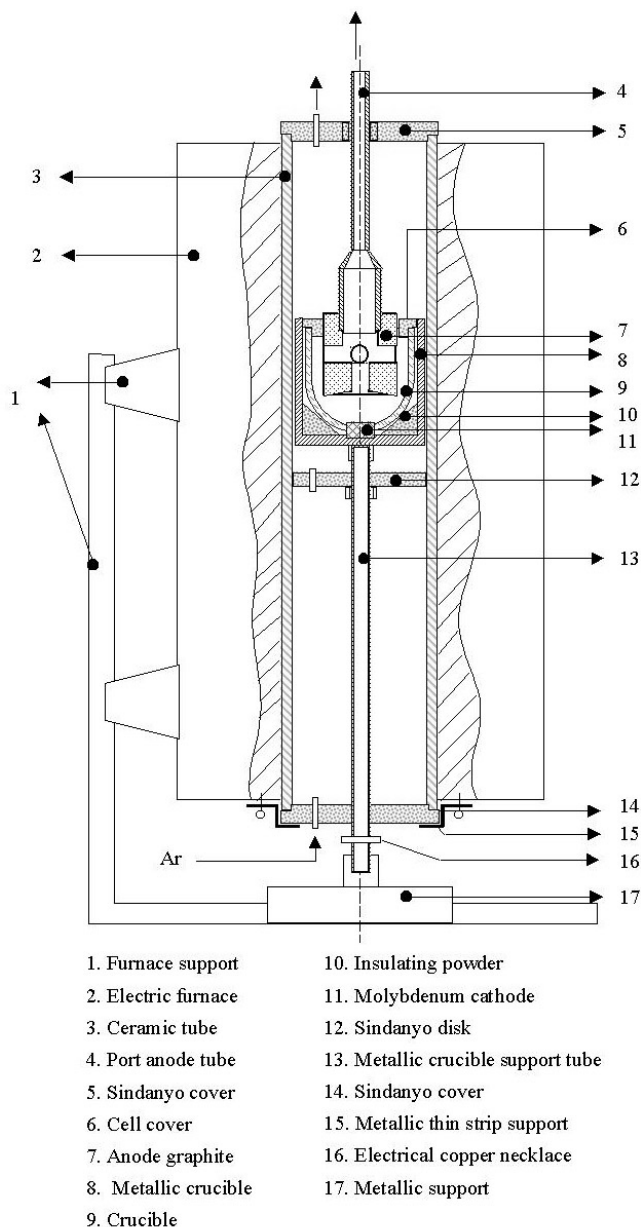


Figure 2. Draft of the electrolysis installation.

## Results

The results of the thermo-differential analysis for the quasi-binary diagram  $(NdF_3-LiF)_{eutectic}-MgF_2$  are presented in Table 2. The liquidus and the solidus lines for the ternary system can be seen in Figs. 3 and 4 respectively, and the quasi-binary diagram in the investigated area (up to 14.75 mol %  $MgF_2$ ) is illustrated in Figure 5.

In Table 3 and Figures 6 and 7, the results of the  $Nd_2(CO_3)_3$  solubility studies as well as the dissolution kinetics in the two electrolytes investigated are presented.

Table 2. Thermo-differential analysis data

No.	Chemical composition						Exp. temp. ( $^{\circ}C$ )
	$NdF_3$		LiF		$MgF_2$		
	% mol	% wt	% mol	% wt	% mol	% wt	
1	22.71	69.11	76.22	29.89	1.07	1	724 – 640
2	22.24	67.72	74.58	29.28	3.18	3	717 – 660
3	21.74	66.32	72.97	28.68	5.29	5	705 – 652
4	21.26	64.92	71.34	28.08	7.40	7	692 – 651
5	21.02	64.22	70.53	27.78	8.45	8	690 – 658
6	20.77	63.52	69.72	27.48	9.51	9	689 – 655
7	20.53	62.87	68.92	27.18	10.55	10	684 – 653
8	20.05	61.43	67.30	26.57	12.65	12	684 – 655
9	19.58	60.04	65.67	25.96	14.75	14	677 – 653

For the electrolysis experiments, after 6 hours of electrolysis 61 g of  $Nd-Mg$  alloy was obtained. The composition of the alloy was (wt. %):  $Nd$  80.4,  $Mg$  19.2,  $O$  0.4. Current efficiency (calculated for  $Nd-Mg$  alloys) was 63.8 %, and  $Nd$  total extraction degree ( $e$ ) was 83.17 %, where:

$$e = \frac{Nd_{alloy} + Nd_{final\ electrolyte}}{Total\ Nd\ fed}$$

The composition of the electrolyte at the end of the electrolysis process was (in mole percent)  $NdF_3$  22.1,  $LiF$  71.2,  $MgF_2$  6.7. It can be seen that the electrolyte composition is practically not changing during the electrolysis, compared to the initial state.

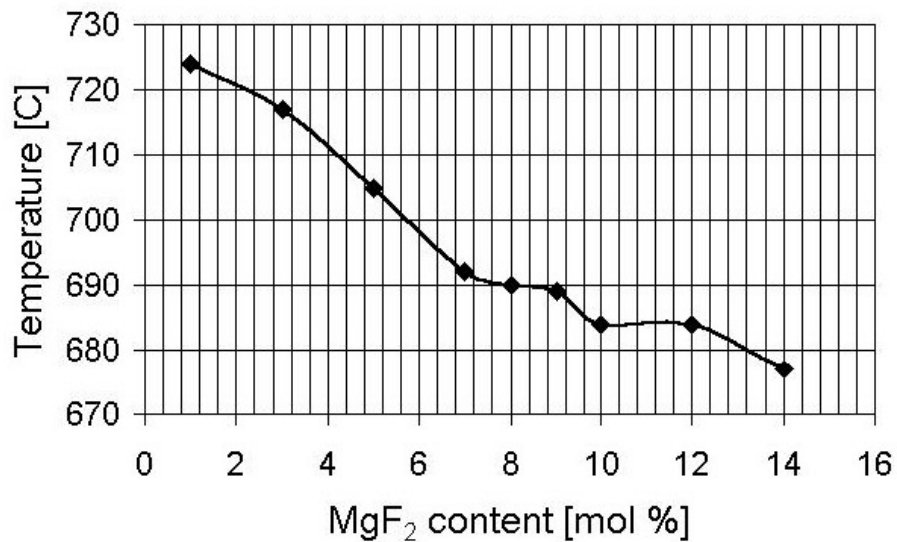


Figure 3. Liquidus temperature versus  $MgF_2$  content in  $(NdF_3-LiF)_{eutectic}-MgF_2$  system

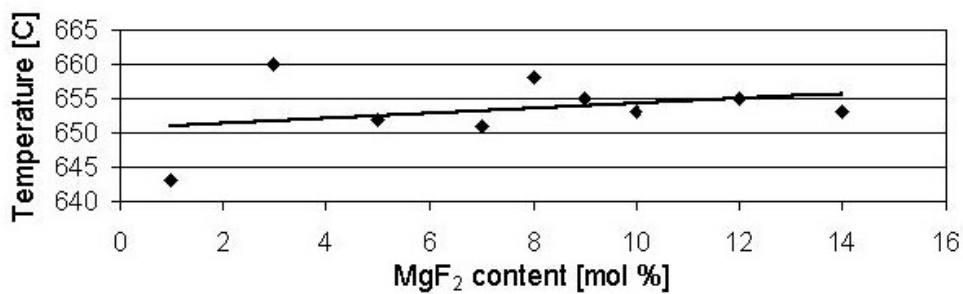


Figure 4. Solidus temperature versus  $MgF_2$  content in  $(NdF_3-LiF)_{eutectic}-MgF_2$  system



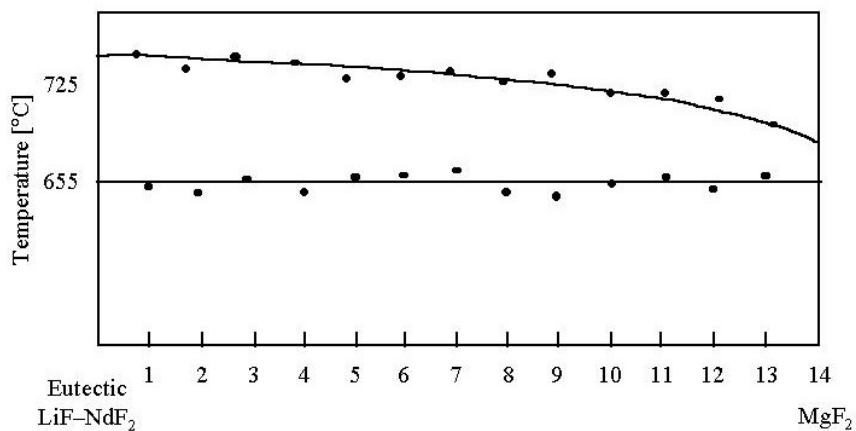


Figure 5. Part of a quasi-binary diagram  $(\text{NdF}_3\text{-LiF})_{\text{eutectic}}\text{-MgF}_2$ .

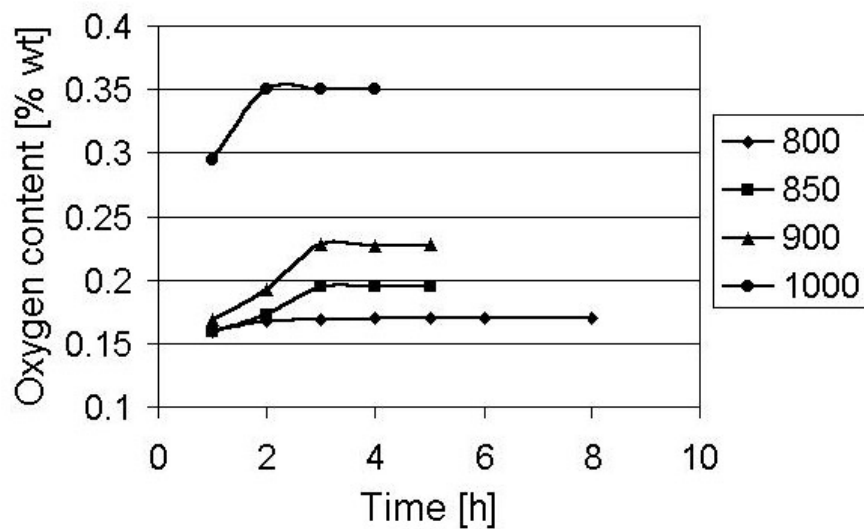


Figure 6. Measured oxygen content for system E1 at different temperatures.

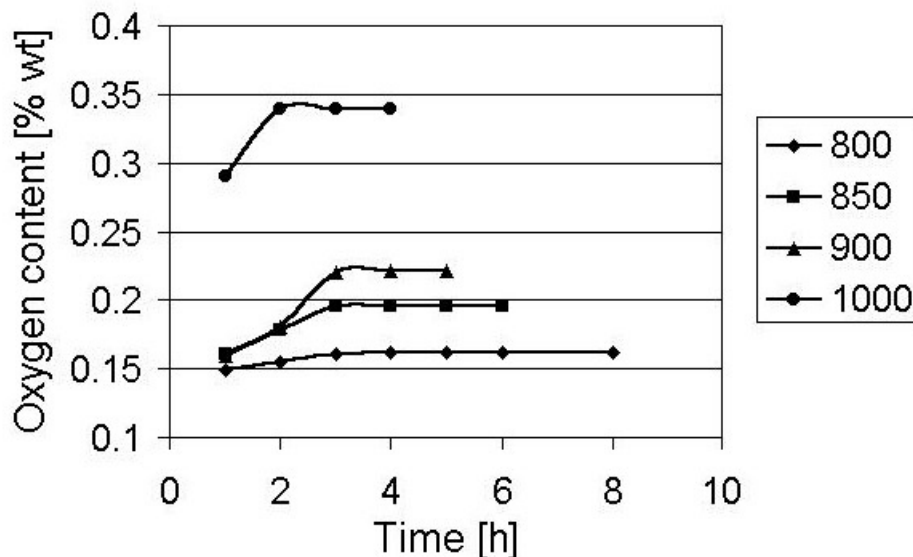


Figure 7. Measured oxygen content for system E2 at different temperatures.

## Discussion

The presence of  $MgF_2$  in the electrolyte is very favorable for the electrolysis process as it increases the fluidity and the electric conductivity of the molten mixture. On the other hand, it is a raw material for the  $Mg$  electrodeposition. As can be seen from Figures 3–5, the liquidus temperature of the ternary system  $NdF_3$ – $LiF$ – $MgF_2$  decreases slowly with increase in the  $MgF_2$  content of the electrolyte.

It is well known that the melting point of an electrolyte must be lower than the melting point of metal (or alloy) deposited at the cathode but close enough to it. In this way, the losses of electrolyte caused by overheating of the bath can be avoided, and simultaneously, the metal (alloy) can be obtained in the liquid phase, with important technological advantages for the electrolysis process. As one can see from Table 2, the electrolyte compositions investigated have liquidus temperatures below 720 °C. Taking into account the melting point of  $Nd$ – $Mg$  alloys (which is below 800 °C up to 95 wt. %  $Nd$ ), an electrolyte with 7–11 mol. %  $MgF_2$  can be used successfully for the  $Nd$ – $Mg$  alloys production by co-deposition.

The solubility of  $Nd_2(CO_3)_3$  in the electrolytes is comparable to the  $Nd_2O_3$  solubility in the same systems ( $Nd_2O_3$  solubility was investigated in previous works). The

Table 3.  $Nd_2(CO_3)_3$  solubility in the electrolytes studied

Temp °C	Total oxygen content (wt %)								Equilibrium				
	Holding time [h]								Time to reach equilibrium [hours]	Oxygen		Concentration $Nd_2O_3$	
	1	2	3	4	5	6	8	mol %		wt %	mol %	wt %	
E1	800	0.158	0.167	0.168	0.171	0.171	0.170	0.170	4	0.011	0.170	0.235	1.191
	850	0.159	0.172	0.195	0.195	0.195	-	-	3	0.012	0.095	0.270	1.364
	900	0.198	0.192	0.228	0.226	0.227	-	-	3	0.014	0.228	0.308	1.557
	1000	0.294	0.351	0.351	0.351	-	-	-	2	0.021	0.351	0.491	2.454
E2	800	0.149	0.154	0.161	0.161	0.162	0.161	0.168	4	0.011	0.162	0.224	1.133
	850	0.160	0.178	0.196	0.196	0.195	-	-	3	0.012	0.196	0.271	1.373
	900	0.159	0.181	0.221	0.221	0.222	-	-	3	0.013	0.220	0.306	1.542
	1000	0.290	0.338	0.339	0.338	-	-	-	2	0.021	0.339	0.473	2.374

Obs. The initial content of dissolved oxygen in the electrolyte was 0.015 wt %.

solubility increases with temperature and also with the content of  $NdF_3$  in the electrolyte; the maximum value of solubility is 2.454 wt % at 1000 °C. As for the dissolution kinetics of  $Nd$ -carbonate in the electrolytes, this is much better than that of the oxide; the time needed to reach equilibrium is less than 3 hours. This fact is very important because the major problems for the electrolysis process are low oxide solubility and especially slow oxide dissolution rate. The improvement of the dissolution kinetics using  $Nd_2(CO_3)_3$  as raw material for the electrolysis is due to the in-situ oxide formation and to the local agitation linked to the evaluation of gases ( $CO$ ,  $CO_2$ ) at the electrolyte surface, and also to better dispersion of the fed powder.

The electrolysis experiments have shown that the production of  $Mg-Nd$  alloys by co-deposition is feasible. The chemical composition of the electrolyte before and after electrolysis process was approximately the same and the purity of the obtained alloy confirms the stability of the electrochemical process. The current efficiency is superior to that for electrolysis in molten chlorides, and it probably can be improved by using larger electrolysis cells. Continuous feeding of the raw materials will improve electrolysis parameters and diminish mechanical losses.

## Conclusions

1. High purity  $Mg-Nd$  alloys can be obtained by electrochemical co-deposition of  $Nd$  and  $Mg$  in molten fluoride media.
2. The ternary system  $NdF_3$  21 mol% -  $LiF$  72 mol% -  $MgF_2$  7 mol% used as electrolyte exhibits remarkable chemical stability during the electrolysis process and allows to obtain high purity  $Mg-Nd$  alloys.
3. The dissolution kinetics of  $Nd_2O_3$  in the electrolyte can be improved by using  $Nd_2(CO_3)_3$  as raw material for electrolysis.
4. For anodic current densities up to 0.45 A/cm<sup>2</sup> no anodic effects were detected. These results are encouraging in the light of improving the efficiency of the electrolysis process.
5. Determination of the anode gases composition is needed in order to find out if the process is environmentally friendly. From this point of view  $MgO$  could replace  $MgF_2$  as raw material for  $Mg$  electrodeposition.

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