PREPARATION OF NEOXYMIUM-IRON MASTER ALLOYS FROM NEOXYMIUM (III) SALTS AND METALLIC IRON IN MOLTEN CHLORIDE - FLUORIDE MIXTURES
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ABSTRACT
Four years ago, the need for neodymium showed a steep increase because of the development of neodymium – iron – boron magnets with very high magnetic properties. Today, metallic or alloyed neodymium is mainly manufactured using the calciiothermic reduction technique. Here the results are presented of our lab-scale investigations into a promising route: low melting point master neodymium – iron alloy electrowinning from NdCl₃-based melts using consumable iron cathodes. A comparison between this method and the calciiothermic preparation is given.

INTRODUCTION
The first permanent magnets, Alnicos (aluminum – nickel – iron alloys) were developed in the 1930’s. About twenty years later, ferrites (compounds of iron and barium or strontium oxides) appeared on the market. These two kinds of magnets have a maximum energy product (BH max) of about 5 M Gauss – Oersteds (MGOe). More than twenty years later (in the 1970’s) rare earth and cobalt magnets made their appearance. Their strength is four times higher than Alnicos and ferrites, and they have a Curie temperature in the range of 600–800°C. Finally, in 1983, General Motors and Sumitomo Special Metals publicly revealed the new possibilities offered by neodymium – iron – boron (Nd₂Fe₁₄B) magnets, which have very high BH max (∼50 MGOe) but a low Curie temperature (close to 300°C) (1 – 6).

The need for metallic neodymium, which was only a few hundreds kg in 1983, increased up to 50 T last year and is forecast to be 800 – 1100 T by 1990, a figure that should double by 1996.

Today, metallic or alloyed neodymium is mainly produced by using the calciiothermic reduction route (7 – 12). The purpose of this paper is to report the results of our lab-scale investigations into another route for obtaining low melting point master neodymium – iron alloys whose compositions are close to the eutectic point, 88 wt % Nd (13) (see Fig. 1). This technique is based on electrolysis of NdCl₃ containing melts using consumable iron cathodes. A comparison of these two routes indicates that the electrolytic process is a very promising preparation technique.

EXPERIMENTAL
Reagents.
The products used for calciiothermic reductions and electrolysis
are grouped in Table 1, where suppliers and purity of the compounds are summarized. NdCl$_2$-6H$_2$O, CaCl$_2$-2H$_2$O and lithium halides were dehydrated and dried by heating under reduced pressure. Their maximum water content was \( \sim 1 \) wt %. Other products were used in their commercially available form.

Electrolysis operating procedure.

The experiments were carried out in either alumina or glassy carbon crucibles placed in an Inconel-made reactor. Heating was carried out by means of an electric furnace. Two types of electrodes, vertical or horizontal, were investigated, as shown in Fig. 2. The anode was a graphite rod, and the consumable cathodes were iron rods. The anode-cathode distance depended on the runs. The electrolytic bath was made up of a mixture of the neodymium chloride to be electrolyzed and alkaline halides.

Values of the cathodic current density (ccd) were 100 – 250 A.dm$^{-2}$, and the voltage was 4– 10 volts. For each electrolysis operation, the metal produced was recovered after hot pouring into a cast iron ingot mold.

Calciothermic reduction operating procedure.

Iron chips, calcium grains, neodymium fluoride and anhydrous calcium chloride to constitute the loading were intimately mixed together.

The amount of CaCl$_2$ added was adjusted so as to obtain, after reduction, a CaCl$_2$-CaF$_2$ molten slag. The amount of the reducing metal (Ca) was above the stoichiometric quantity, and the amount of iron depended on the desired composition of the alloy to be produced.

The mixture described above was introduced into a tantalum crucible (whose capacity was approximately one liter) placed at the bottom of an Inconel-made reactor, itself placed in an electric-resistance furnace. After reducing pressure (1 cm Hg), the temperature was raised to 1000–1100°C. Then the reaction was conducted at this temperature, under atmospheric pressure, in an inert gas atmosphere (argon) maintained throughout the reduction. During heating, two phases were formed in the reaction medium: a metallic phase constituted by the rare earth-iron alloy, on top of which floated a CaCl$_2$-CaF$_2$ slag. After a reaction time ranging from 30 min to 2 hours, the alloy was separated from the slag by hot pouring into a cast iron ingot mold.

RESULTS AND DISCUSSION

Solubility of metallic neodymium in various molten alkaline halide + neodymium (III) chloride mixtures.

The solubility of neodymium in chloride melts is a complex process involving both physical dissolution as a metal fog, and chemical dissolution according to the following equilibrium:

\[
\text{Nd} + 2 \text{NdCl}_3 \rightleftharpoons 3 \text{NdCl}_2
\]

We take into account the overall solubility by defining it as the weight loss of a metal sample occurring when it is immersed in the melt.

Effect of NdCl$_3$ content and temperature in pure chloride melts.

It is first to be noted that neodymium "dissolves" in a melt which does not contain NdCl$_3$ because of a metal dispersion phenomenon.
After 3 hours, we observed that 2 wt % metal dissolves in a BaCl\textsubscript{2} (78 wt %) - NaCl bath at 940°C. Metal solubility strongly depends on NdCl\textsubscript{3} content in the melt. At 800°C, for example, solubility equal to 7 wt % in a melt containing 30 wt % NdCl\textsubscript{3} is at least tripled when NdCl\textsubscript{3} content reaches 80 wt %. Moreover, temperature has a great influence on solubility: solubility (7 wt % at 800°C) becomes unacceptable (∼22 wt %) beyond 1000°C, which is close to neodymium's melting point. These results explain why Kurita (14) obtained only yields lower or equal to 20 % for the electrowinning of neodymium from a NdCl\textsubscript{3}–KCl bath.

Benefit due to the presence of alkaline fluorides and lithium salts. Our experiments have shown that solubility is always lower in chloride-fluoride media than in pure chloride melts when temperature is less than 1000°C. For example, solubility is equal to 4 wt % at 800°C in a chloride-fluoride bath containing 30 wt % NdCl\textsubscript{3}, that is, twice lower than in pure chloride melts (7 wt %). This effect of fluoride salts may be explained by their complexing role, causing the oxidation state + III of neodymium to stabilize. This, in turn, leads to the disproportionation of neodymium (II) (displacement of equilibrium [I] to the left), thus decreasing the "chemical" solubility.

We also observed that lithium salts give a similar effect; compared with melts without lithium, solubility is always lower in melts containing LiCl or LiF. The major impact of lithium salts will be seen in electrolysis yields.

Impact on the choice of electrolytic bath composition. Our experimental results described above can be summarized as follows: (i) metal solubility strongly depends on neodymium (III) content of the bath; (ii) whatever the bath composition, neodymium solubility steeply increases when temperature reaches 1000°C; (iii) for a given neodymium (III) content of the bath, solubility is higher in pure chloride melts than in chloride-fluoride melts. Thus, for the electrowinning of neodymium – iron alloys, chloride-fluoride baths containing lithium salts with a low amount of neodymium chloride are preferable to pure chloride melts in order to minimize the yield loss due to metal solubilization.

Neodymium – iron alloy electrowinning on consumable iron cathodes. The master alloy under study was the eutectic neodymium – iron composition (88 wt % Nd – 12 wt % Fe), which melts at 640°C (see Fig. 1); it can be electrolyzed at a low enough temperature for neodymium solubility to remain sufficiently low.

Effect of several operating parameters on metal yield. In the following, the metal yield $R_M$ designates the ratio of the neodymium obtained with respect to the neodymium in the NdCl\textsubscript{3} introduced in the electrolytic bath. In addition, the duration of electrolysis $t$ is given with respect to $t_d$, which is the time theoretically required for reduction of all the NdCl\textsubscript{3} at 100% current efficiency $R_{E_F}$.

Fig. 3a indicates the effect of temperature on the metal yield of alloys electrowon on consumable vertical cathodes in a melt containing 25 wt % NdCl\textsubscript{3}, and Fig. 3b gives the corresponding neodymium content of these alloys. It is observed that the metal yield reaches 75 %
at 850°C, \( R_M \) becomes very low (\( \approx 25\% \)) for temperatures close to 1000°C, at which metal solubility is predominant. In the temperature range from 800 to 1000°C, the electrowon metal composition can be deducted from the Nd/Fe phase diagram (Fig. 1). On the contrary, when temperature is lower than 800°C, a Nd/Fe alloy is difficult to obtain because of the decreasing of the diffusion rate of neodymium into iron.

The influence electrolyzing time on metal yield and current efficiency has been studied by electrolyzing neodymium chloride at 850°C on horizontal iron cathodes in the melt described above. Values of ccd have been respectively 220 to 250 A.dm\(^{-2}\). Depending on the runs, the recovered nodules titrated 85 to 88 wt % neodymium. An analysis of Fig. 4, which specifically gives the metal yield - current efficiency - electrolysis time relationship, shows that aiming at high productivity (high metal yield) leads to weak current efficiency. In order to optimize the batch operating conditions, by reaching a compromise between productivity and energy consumption, we have considered the cumulative yield \( R_c \), defined as the product of \( R_M \) and \( R_e \). We can see from Fig. 4 that \( R_c \) presents a maximum for an electrolysis time \( t = 1.5t^* \).

For this set of experiments a metal yield of 75 % and a current efficiency of 50 % are obtained.

Concerning Nd/Fe electrowinning from a NdCl\(_3\) 25 wt % - LiCl - LiF bath at 850°C with an electrolysis time of 1.5 \( t^* \), we have observed that there is practically no ccd dependence of the metal yield when the anode-cathode distance is sufficiently large.

It has been considered desirable to confirm that using a lithium bath for neodymium - iron electrowinning is advantageous. A NdCl\(_3\) 25 wt % - LiCl - LiF bath has been used as a reference. Other bath compositions have been chosen containing 25 wt % of neodymium chloride. Electrolysis has been carried out at 800°C on vertical iron cathodes, with a ccd of 100 A.dm\(^{-2}\). Their electrolysis time \( t \) was equal to 1.5 \( t^* \). Fig. 5 positively shows that replacement of LiCl by NaCl is unfavorable as metal yield falls when the amount of LiCl in the bath decreases. \( R_M \) which is equal to 70% with a melt containing LiCl only, falls to 22% with a NaCl - containing bath. However, it is preferable to replace LiCl completely with KCl rather than NaCl, as the metal yield is almost twice as high (Fig. 6). The role of the kind of fluoride salt used in LiCl-based melts (Fig. 7) has been analyzed, and it is shown that metal yield decreases as follows:

\[ \text{LiF} > \text{NaF} > \text{CaF}_2 \]

Electrolysis carried out on horizontal cathodes at 850°C with NdCl\(_3\)-LiCl-LIF baths containing varying amounts of NdCl\(_3\) (ccd : 250 A.dm\(^{-2}\); \( t = 2t^* \)) unequivocally demonstrated (Fig. 8) that metal yield falls when NdCl\(_3\) content goes over 40 wt %. Between 20 and 35 wt%, \( R_M \) has a nearly constant value of 80 - 84 %.

Comparison of the electrolytic process and calcium reduction to obtain neodymium - iron alloys.

Typical example of a calciothermic reduction of NdF\(_3\) in the presence of iron chips. By using the following loading : 27.5 g of iron chips, 101.0 g of Ca grains, 281.4 g of NdF\(_3\) and 382.2 g of anhydrous...
CaCl₂, 188.0 g of neodymium iron alloy has been recovered with a composition of 87.4 wt % Nd, 12 wt % Fe and almost 0.6 wt % Ca, with a metal yield equal to 81 % (15). In general, metal yields were always better than 80 %.

**Electrolysis compared with chemical reduction.**

Both preparation methods make it possible to produce the desired master alloy, with a good purity level as is seen in Table 2. Yet, the main impurities are different in each case. Electrowon alloys generally contain 0.2 wt % Al (due to a slight corrosion of the crucible) and 0.2 wt % Cl. Calciothermic alloys have an average calcium level of 0.4 wt %. This can, however, be decreased to 200 ppm by distillation in a HF furnace at 1300°C under reduced pressure. Metal yields are quite similar (> 80%).

**CONCLUSION**

Operating conditions for optimum efficiency are now known for both processes. In particular, the halide/metal percentage of conversion (or yield) is virtually the same in both cases, and contamination of the alloy by the crucible is slight. In conclusion, the respective features and advantages of the two processes have been compared. Calcium reduction of neodymium fluoroide is a good technique because, if the required procedure is followed, slag separation is easily accomplished (15). Although available for an industrial process, calcium (which has to be used in excess) is a costly reductant. Finally the calciothermic preparation is a batch process, while electrolysis of neodymium chloride is a continuous method. The molten alloy is produced at the bottom of the electrolytic cell whence it can be drained off (16). In addition, electrowinning offers great flexibility with respect to the amount of metal to be produced and potential low cost in the preparation of master iron-neodymium alloys to be used in obtaining the desired composition (30 – 37 wt % Nd, 1 – 7 % B, Fe) for permanent magnets.

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Table 1: Suppliers and purity level of the main reagents used.

| Products                        | Suppliers                        | Purity                                      |
|---------------------------------|----------------------------------|---------------------------------------------|
| Rare earth halides and oxides   | Rhone-Poulenc La Rochelle Plant  | Halides (*): 96 % Oxides (*): 99.0 or 99.9 % |
| Metallic Calcium                | China Nuclear Energy Industry Corporation | Ca grains ≥ 99.5 % main impurities Al: 0.01 % Mg: 0.02 % |
| Calcium chloride                | Rhone-Poulenc (Prolabo)          | CaCl₂, 2 H₂O RP (further dehydrated under reduced pressure). |
| Iron                            | Höganäs                          | Iron chips ≥ 99 % main impurities Si: 0.2 % C, P, S each < 0.01 % |
| Lithium halides                 | Parker                           | LiCl: 99.3 % LiF: 99.5 %                     |

(*) Ratio of neodymium/rare earth.

Table 2: Average analyses (wt %) of typical alloys resulting from either a calciothermic reduction or an electrolysis.

| Elements | Calciothermic reduction | Electrolysis production |
|----------|-------------------------|-------------------------|
| Nd       | 86.0                    | 88.2                    |
| Fe       | 13.0                    | 11.7                    |
| Ca       | 0.4                     | 0.002                   |
| Li       | -                       | 0.02                    |
| Mg       | 0.02                    | 0.01                    |
| Al       | 0.001                   | 0.20 (*)                |
| Si       | 0.05                    | 0.01                    |
| C        | 0.06                    | < 0.02                  |
| Mn       | 0.07                    | 0.03                    |
| Cr       | -                       | 0.02 (*)                |
| F        | ≤ 0.02                  | 0.04                    |
| Cl       | ≤ 0.01                  | 0.2                     |
| O₂       | 0.04                    | 0.08                    |
| N₂       | ≤ 0.01                  | 0.004                   |

(*) Crucible corrosion
Figure 1: Binary phase diagram Nd/Fe [after (13)].

Figure 2: Electrochemical cell
Figure 3: Nd/Fe electrowinning on consumable iron cathode. Effect of temperature on:

a) metal yield
b) neodymium content of resulting alloys
(NdCl₂ 25 wt % – LiCl – LiF; ccd 220 to 250 A dm⁻²; electrolysis time t = 1.5 t₀).

Figure 4: Nd/Fe electrowinning on horizontal iron cathodes – Relationships between metal yield RM, current efficiency RF, cumulative yield (RM x RF) and electrolysis time (given with respect to t₀).
(NdCl₂ 25 wt % – LiCl – LiF; T = 850°C; ccd = 220 to 250 A dm⁻²).

- - - - - : current efficiency
--- --- --- : cumulative yield.
Figure 5: Variation of metal yield as a function of melt composition. Replacement of LiCl by NaCl.

Figure 6: Variation of metal yield as a function of melt composition – complete replacement of LiCl by NaCl or KCl.
Figure 7: Variation of metal yield as a function of melt composition.

Figure 8: Evidence of a limiting NdCl₃ content in electrolytic melt.