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Mihaela Raluca Ciumag, Mathieu Gibilaro, Laurent Massot, Richard Laucournet, Pierre Chamelot. Neodymium electrowinning into copper-neodymium alloys by mixed oxide reduction in molten fluoride media. *Journal of Fluorine Chemistry*, 2016, 184, pp.1-7. 10.1016/j.jfluchem.2016.02.001 . hal-01890092

HAL Id: hal-01890092

<https://hal.science/hal-01890092>

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Ciumag, Mihaela Raluca  and Gibilaro, Mathieu  and Massot, Laurent  and Laucournet, Richard and Chamelot, Pierre  *Neodymium electrowinning into copper-neodymium alloys by mixed oxide reduction in molten fluoride media.* (2016) *Journal of Fluorine Chemistry*, 184. 1-7. ISSN 0022-1139

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Neodymium electrowinning into copper-neodymium alloys by mixed oxide reduction in molten fluoride media

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ABSTRACT

The possibility of neodymium electrowinning from neodymium oxide using a reducing agent (RA) produced in-situ by solvent reduction was investigated in molten LiF–CaF₂–Li₂O between 900 °C and 1040 °C. Nd₂O₃ galvanostatic electrolyses were performed and reaction products were analyzed by SEM, XRD and electron-probe microscopy. Metallic neodymium was not directly obtained, due to several limitations for Nd₂O₃ reduction: low electrical conductivity, unfavourable Pilling–Bedworth coefficient and formation of a dense insulating CaO layer on the sample surface.

Consequently, the reduction of a pellet made of a neodymium oxide-metallic oxide mixture was carried out as an alternative pathway. Nd₂O₃–CuO reduction led to metallic neodymium production in the form of liquid Cu–Nd alloys. A reaction mechanism was proposed based on these experimental results:

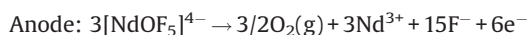
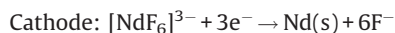
1. Introduction

Needs of metallic neodymium and its alloys are lately increasing, particularly in the fields of magnetism, energy and high technology, as in permanent magnets, lamp phosphors and rechargeable NiMH batteries [1]. Neodymium is industrially produced by both calciothermic reduction of NdF₃, requiring several purification steps, and by molten salt electrolysis, which enables continuous operation and is more suitable for mass metal production.

Metallic neodymium electrodeposition can take place in fused chloride salts [2–13], but this process has several drawbacks, such as the evolution of chlorine gas at the anode and low faradic yield. Thus, neodymium metal is currently produced by electrowinning from neodymium oxide in a molten fluoride media containing high amounts of NdF₃ (up to 87 mass %) [14].

Several authors suggested different reduction mechanisms of Nd₂O₃ in NdF₃-based molten salt [16–19], but no agreement has been found yet. Stefanidaki et al. [15,16] detailed neodymium

production in LiF–Nd₂O₃ and LiF–NdF₃–Nd₂O₃ systems. In LiF–Nd₂O₃ no characteristic signal for neodymium oxide reduction into metal was observed and metallic neodymium deposition did not occur in this molten mixture. In LiF–NdF₃–Nd₂O₃, fluoride and oxyfluoride complexes such as [NdF₆]^{3–} and [NdOF₅]^{4–} were proposed to be formed, and metallic neodymium was observed. The following electron transfer mechanism was suggested:

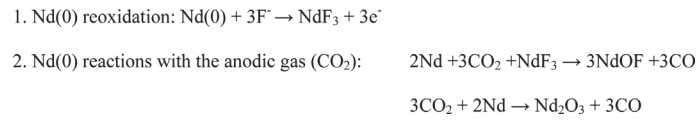


The authors concluded that electrowinning of metallic neodymium can be performed by controlled cell-voltage electrolysis in LiF–NdF₃–Nd₂O₃.

Thudum et al. [17] proposed a different reduction pathway for Nd₂O₃ in LiF–CaF₂–NdF₃, suggesting both [NdFO₅]^{4–} and [NdF₆]^{3–} complexes were reduced to metallic neodymium, depending on the OF/F molar ratio: for low ratios, [NdF₆]^{3–} was reduced, whereas above a critical value, [NdFO₅]^{4–} was reduced.

Dysinger and Murphy [18] tested Nd₂O₃ reduction in LiF–CaF₂–NdF₃ on tungsten cathode, for temperatures from 1030 °C to

1060 °C, and highlighted several side reactions occurring at the anode:



The authors concluded metallic neodymium electrowinning from LiF–CaF₂–NdF₃–Nd₂O₃ was only possible at high current density (1 A cm⁻²) and high temperature ($T > 1021$ °C = Nd fusion temperature).

Fe–Nd alloys were obtained by Morrice et al. [19], by Nd₂O₃ electrolysis on reactive iron cathode at 990 °C in LiF–NdF₃ (89 mass %). Later, Nd₂O₃ electrolysis in fused fluorides for Fe–Nd fabrication was patented by Pechiney [20]. Alloys were obtained by long duration (> 25 h) Nd₂O₃ electrolyzes on reactive iron cathode, performed in LiF–NdF₃–BaF₂–B₂O₃, between 750° and 1000 °C, and at constant cell voltage.

Nowadays, neodymium is industrially produced by Nd₂O₃ reduction in NdF₃-based mixtures (NdF₃ > 70 mass % [21]) using Mo, W or Fe as cathodic materials [22]. Nevertheless, several drawbacks can be pointed out for this process:

- The solubility of Nd₂O₃ is only 5 mass % (at 1100 °C) [23], which makes the oxide feeding into the electrolyte difficult to control and can lead to formation of sludge at the cell bottom [24].
- The overall cost of the industrial process is high due to the price of NdF₃ (~ 1000 euros/kg).

The aim of this work is to investigate a lower cost production process for neodymium electrowinning from Nd₂O₃ in molten fluoride media, in absence of NdF₃ (LiF–CaF₂ eutectics containing Li₂O 2 mass %), by a new approach: the neodymium oxide is used as solid pellets at the cathode, similarly to the FFC–Cambridge [25] and OS processes [26], and no more as the feed material (current industrial process). The two main advantages of this approach are: firstly, Nd₂O₃ solubility limitation, encountered for the conventional electrolytic system, is eliminated. Secondly, the overall price of the process is reduced, due to the lower cost of LiF–CaF₂–Li₂O: 1 kg of LiF–CaF₂–Li₂O mixture costs 200 euros (~ 60 mass % LiF at 100 euros/kg, ~40 mass % CaF₂ at 60 euros/kg and 2 mass % Li₂O at 4800 euros/kg); while 1 kg of LiF–NdF₃ mixture costs ~750 euros (~30 mass % LiF at 100 euros/kg, and 70 mass % NdF₃, at 1000 euros/kg).

With this new approach, Nd₂O₃ electroreduction was studied by linear voltammetry and galvanostatic electrolyses at different operating parameters: temperatures from 900 °C to 1040 °C and imposed currents from 0.15 to 0.8 A. Elemental analyses of compositions and microstructures (SEM, XRD and electron-probe microanalyser) were performed, and the limiting factors for Nd₂O₃ reduction into Nd in molten fluorides, in absence of NdF₃, were elucidated for the first time.

Nd₂O₃ electroreduction in presence of an electrical conducting metallic oxide was also investigated. Indeed, this strategy was already shown to be suitable for preparing Nd–Co alloys by electrochemical reduction of Nd₂O₃–Co₃O₄ mixtures in molten chloride media [27]. Other rare earths alloys with heavy metals, such as La–Ni [28], Ce–Co [29], Ce–Ni [30], Tb–Fe [31] and Tb–Ni [32], were also obtained by electrochemical reduction of rare earth oxides and metallic oxides mixtures.

In this study, the electrochemical behaviour of Nd₂O₃–CuO was investigated at different temperatures by linear voltammetry and

constant current electrolyses. Analysis of microstructures showed formation of Cu–Nd alloys and allowed proposing a reduction pathway. For high purity metallic Nd recovery, a further separation of Cu and Nd can be easily realised with electrorefining, by exploiting the electrochemical potentials of the two constituents.

2. Results and discussion

2.1. Preliminary discussion and solvent selection

Rare earth oxides can be electrochemically reduced by two different pathways, depending on their electrical conductivity:

1. Highly conductive oxides are subject to direct electrochemical reduction by FFC–Cambridge process [25], where the oxide is reduced into metal on the cathode surface.
2. Oxides presenting low electrical conductivity are subject to indirect reduction by OS process [26]. In this case, a reducing agent (produced by solvent reduction) reacts with the rare earth oxide to form a metallic phase.

Nd₂O₃ has a very low electrical conductivity ($\sigma_{650^\circ, 0.2\text{barO}_2} = 1,45 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ [33]) therefore it is expected to be reduced following the indirect OS process, as illustrated in the equation:



where RA is the reducing agent and RA_xO is the oxidized form of the reducing agent.

The reducing agent (RA) could be an alkaline (K, Na, Li) or alkaline-earth metal (Ca) obtained by cathodic reduction of fluoride solvents (KF, NaF, LiF, CaF₂). The Gibbs energy of the reaction ($\Delta_r G^\circ$) between neodymium oxide and the reducing agent indicates whether the neodymium oxide is reduced into metallic neodymium or not: if $\Delta_r G^\circ$ is negative, the reduction of neodymium oxide by the alkaline or alkaline-earth is thermodynamically achievable. As presented in Table 1, neodymium oxide can be reduced into metallic neodymium by Ca only.

Nevertheless, because of CaF₂ too high fusion temperature (1418 °C), a lower working temperature was chosen: LiF–CaF₂ eutectics ($T_{\text{fusion}} = 767$ °C). Because the reduction potentials of Li⁺ and Ca²⁺ are close ($E_{\text{Li}^+/\text{Li}} = -5.31$ V vs F₂/F⁻ and $E_{\text{Ca}^{2+}/\text{Ca}} = -5.33$ V vs F₂/F⁻), their simultaneous reduction at the cathode surface was already observed [34].

Table 1
Standard free energy data for Nd₂O₃ reduction with different alkali and alkaline-earth metals, following equation (1) at 900 °C.

RA	K	Na	Li	Ca
$\Delta_r G^\circ$ at 900 °C (kJ mol ⁻¹)	863.3	713.7	154.1	-57.2

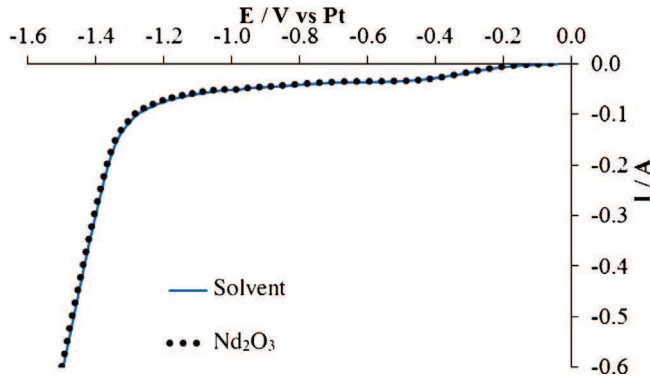


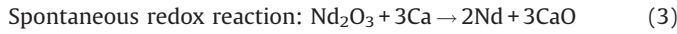
Fig. 1. Linear sweep voltammograms on Mo grid in LiF-CaF₂-Li₂O (2 mass % Li₂O) at 10 mV s⁻¹ and 900 °C. Continuous line: solvent, dotted line: Nd₂O₃ pellet.

2.2. Electrochemical characterization in LiF-CaF₂ by linear sweep voltammetry

To provide O²⁻ ions in the molten fluoride media and ensure the anodic reaction, Li₂O was used. Gibilaro et al. [35] showed in LiF-CaF₂-Li₂O mixture, Li₂O had to be maintained at a concentration higher than 1 mass % to prevent the Au anode oxidation and to ensure the oxidation of O²⁻ into gaseous O₂ [36].

In this work, Nd₂O₃ reduction mechanism was studied in LiF-CaF₂-Li₂O (2 mass %). The linear voltammogram obtained at 10 mV s⁻¹ and 900 °C, is presented in Fig. 1, compared with the solvent.

The two curves display no significant difference, meaning that no specific Nd₂O₃ electrochemical reaction occurs. Therefore, its reduction is indirect and the proposed reaction pathway is the following:



The Ca reducing agent [34] produced on the Mo cathode reduces the neodymium oxide into metallic neodymium, and the resulted O²⁻ ions are oxidized into gaseous O₂ on the gold anode.

2.3. Galvanostatic electrolyses of neodymium oxide

2.3.1. Neodymium oxide reduction

To investigate Nd₂O₃ reduction, experiments were carried out in constant current mode. Because stable reference electrodes in

fluoride salts are not available yet (no accurate control of cathodic potential), the constant potential mode was not used during electrolyses.

Several reduction tests were performed in LiF-CaF₂-Li₂O (2 mass %) at 900 °C. The theoretical charge Q_{th} needed for the reduction of one neodymium oxide pellet is calculated as follows:

$$Q_{th} = \frac{m\text{Nd}_2\text{O}_3}{M\text{Nd}_2\text{O}_3} nF \quad (5)$$

where Q_{th} is the theoretical charge calculated (C), $m\text{Nd}_2\text{O}_3$ is the oxide pellet weight (g), $M\text{Nd}_2\text{O}_3$ is the oxide molecular weight (336.48 g.mol⁻¹), n is the number of electrons exchanged per mole of Nd₂O₃, F is the Faraday constant (96,480 C mol⁻¹).

The pellet cross-section after electrolysis at $I = -0.4\text{ A}$ and $t = 1320\text{ s}$ (500% Q_{th}), observed by SEM, shows three different zones (Fig. 2). Quantitative electron-probe microanalysis allowed identifying the composition of these zones, as follows:

– The internal zone (1) is mainly NdOF, formed by spontaneous decomplexation of Nd₂O₃:



This phenomenon was also observed by Nourry [37] when adding O²⁻ ions in LiF-CaF₂-NdF₃.

– Zone 2 is formed by recrystallized fluoride salts (LiF and CaF₂).
 – A dense layer mainly composed of low electrical conducting CaO, formed by O²⁻ and Ca²⁺ co-precipitation, is observed overall the surface of the neodymium oxide pellet (zone 3). The CaO layer acts as a barrier, limiting the diffusion of O²⁻ from the pellet towards the molten salt, preventing the Nd₂O₃ reduction to take place. This phenomenon explains the absence of metallic Nd at the end of electrolysis.

2.3.2. Temperature influence

To increase CaO solubility in LiF-CaF₂ (from 0.5 mol % at 730 °C to 2.9 mol % at 1 000 °C, [38]) and to attempt to remove the layer on the sample surface, experiments were performed at higher temperature, where liquid metallic neodymium could be formed. Fig. 3 illustrates the cross-section of Nd₂O₃ sample after electrolysis at 1040 °C and -0.4 A (500% Q_{th}).

As expected, no CaO layer was formed on the sample surface, but X-ray diffractometry (Fig. 4) did not highlight either the presence of metallic Nd.

When comparing Fig. 2 (900 °C) and Fig. 3 (1040 °C), it can be pointed out that the pellet structure and composition changed: Nd₂O₃ chemical decomplexation at 900 °C led to NdOF, while at 1 040 °C Nd₂O₃ clusters appeared, enhancing significantly the

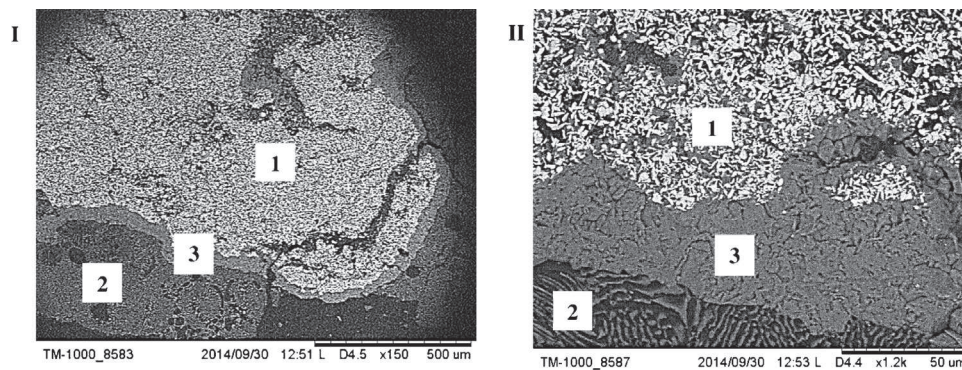


Fig. 2. (I and II) Micrographs of Nd₂O₃ pellet cross-section after electrolysis ($I = -0.4\text{ A}$ and $t = 1320\text{ s}$) at 900 °C in LiF-CaF₂-Li₂O (2 mass % Li₂O).

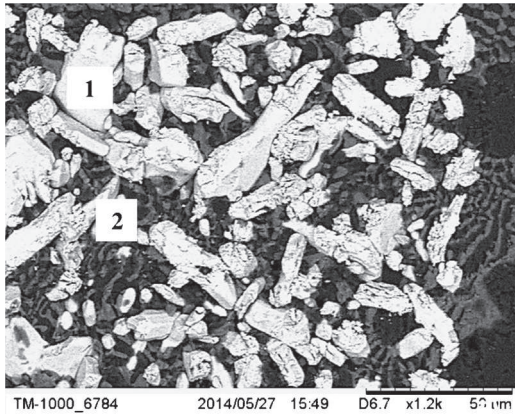


Fig. 3. Micrograph of Nd_2O_3 pellet cross-section after electrolysis ($I = -0.4 \text{ A}$, $500\% Q_{th}$) at 1040°C in $\text{LiF-CaF}_2\text{-Li}_2\text{O}$ (2 mass %).

porosity. This phenomena was also confirmed by the X-ray diffractogram (Fig. 4) where Nd_2O_3 , LiF and CaF_2 are present, but no NdOF was detected.

To investigate the temperature effect, a Nd_2O_3 pellet was exposed at 1040°C in the molten salt bath without polarisation, and SEM analysis showed similar structures to those presented in Fig. 3. Batsanov et al. [39] had already observed a similar behaviour of neodymium oxide powder (grain size $1\text{-}10 \mu\text{m}$) under high pressure and temperature, where $100\text{-}1000 \mu\text{m}$ crystalline aggregates were created.

The influence of the applied cathodic current (from 0.15 A to 0.8 A) and neodymium oxide pellets fabrication (pressure applied for sinterizing the oxide powder from 2 to 4 t cm^{-2}) was also studied, but metallic neodymium was still not obtained.

To resume, Nd_2O_3 electrochemical reduction did not lead to metallic neodymium, whatever the operating parameters. Moreover, several limiting phenomena were highlighted:

1 Related to Nd_2O_3 physicochemical characteristics:

- low electrical conductivity ($\sigma_{650^\circ\text{C}, 0.2\text{barO}_2} = 1,45 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$) [33];
- unfavourable Pilling-Bedworth coefficient ($V_{\text{Nd}}/V_{\text{Nd}_2\text{O}_3} = 0.89$). Pilling-Bedworth rule considerations [40], as illustrated by Li et al. [41] and Gibilaro et al. [42], indicate that during oxide reduction, if the molar volume of the formed metal V_m is smaller than the molar volume of the oxide V_o , the metal obtained is porous enough to allow the molten salt electrolyte accessing the underlying oxide. For neodymium, the metal to oxide molar volume ratio is $V_{\text{Nd}}/V_{\text{Nd}_2\text{O}_3} = 0.89$, meaning that volume constriction is not enough during Nd_2O_3 conversion into metal: the metallic neodymium formed would thus act as a diffusion barrier.

2 Related to solvent:

- neodymium oxide can only be reduced by Ca metal, limiting the selection to CaF_2 -based solvents;
- in CaF_2 -based solvent, at 900°C , the precipitation of a dense insoluble CaO layer on the sample surface is observed, preventing Nd_2O_3 reduction.

2.4. Reduction of neodymium oxide in presence of copper oxide

To obtain metallic Nd , the addition of an electrical conducting oxide in the neodymium oxide pellet was tested. CuO was chosen for its good electrical conductivity ($\sigma_{127^\circ\text{C}} = 10^{-1} \Omega^{-1} \text{ cm}^{-1}$ [43]) and its favourable Pilling-Bedworth coefficient $V_{\text{Cu}}/V_{\text{CuO}} = 0.56$

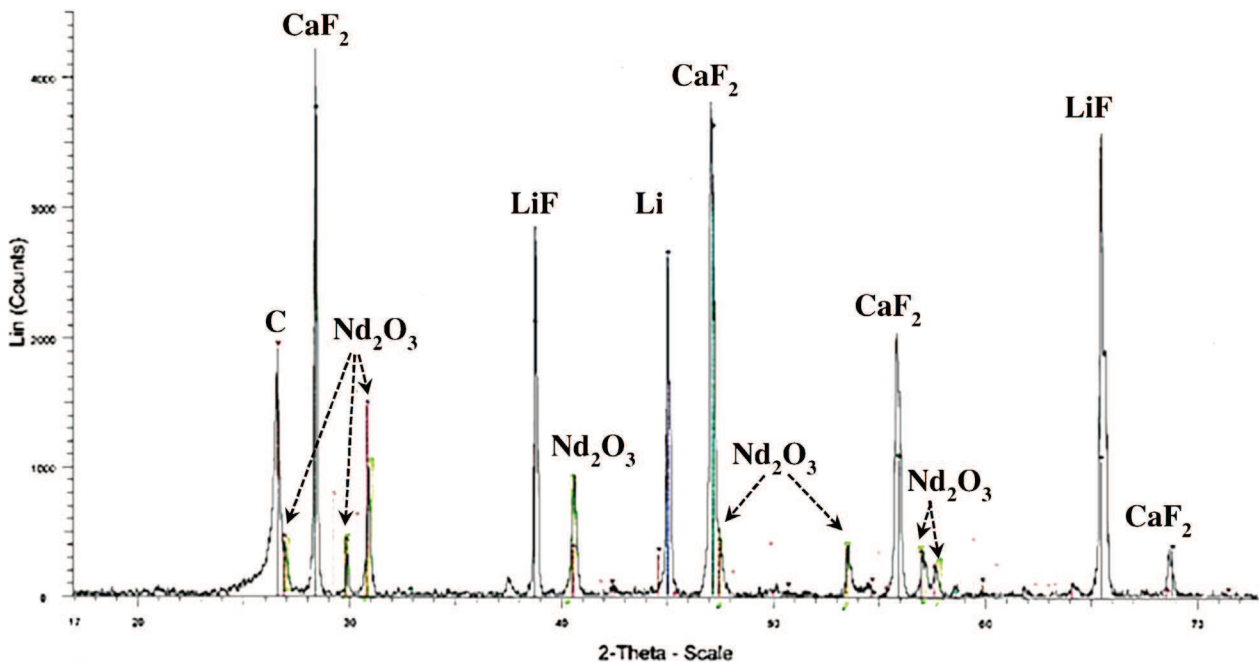


Fig. 4. X-ray diffractogram of Nd_2O_3 pellet after electrolysis ($I = -0.4 \text{ A}$, $500\% Q_{th}$) at 1040°C in $\text{LiF-CaF}_2\text{-Li}_2\text{O}$ (2 mass %).

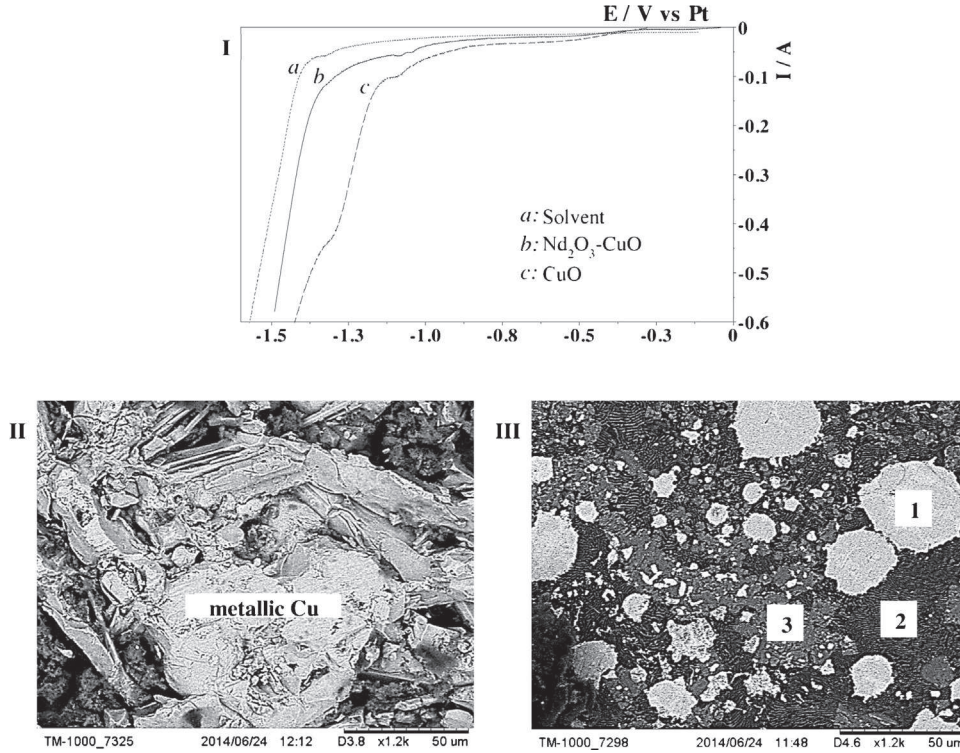


Fig. 5. I Linear sweep voltammograms in LiF–CaF₂–Li₂O (2 mass %) at 10 mV s⁻¹ and 900 °C. Dotted line: solvent, continuous line: Nd₂O₃–CuO, interrupted line: CuO. II, III Micrographs of pellets cross-sections after electrolyses ($I = -0.15$ A, 500% Q_{th}) at 900 °C in LiF–CaF₂–Li₂O (2 mass %). II. CuO; III. Nd₂O₃–CuO: 65 atomic % Nd – 35 atomic % Cu.

[36], enhancing pellet porosity. CuO is therefore expected to undergo direct electrochemical reduction into metallic Cu, and to confirm it, CuO reduction in LiF–CaF₂–Li₂O (2 mass %) was first studied. The linear voltammogram obtained at 10 mV s⁻¹ (voltammogram c in Fig. 5, I) displays a reduction signal at -1.3 V vs Pt, assigned to the direct electrochemical reduction of CuO into metallic Cu, following the equation:



Moreover, the electrolysis of a CuO pellet at -0.15 A and 900 °C confirmed this result: 100 μm to 1000 μm metallic Cu clusters (micrograph in Fig. 5, II) were obtained.

The current efficiency was also calculated, following the equation:

$$\eta = \frac{m_{\text{experimental}}}{m_{\text{theoretical}}}$$

where $m_{\text{experimental}}$ is the mass of the metallic deposit obtained by electrolysis (g) and $m_{\text{theoretical}}$ is the theoretical mass of metallic deposit expected to be obtained by electrolysis (g), calculated as following:

$$m_{\text{theoretical}} = \frac{I \cdot t}{n} \cdot F \cdot M_{\text{metal}}$$

where I is the intensity of the imposed current (A), t is electrolysis duration (s), n is the number of exchanged electrons per mole of metallic oxide ($n=2$ for CuO→Cu reduction), F is the Farady constant (96 480 C mol⁻¹), and M_{metal} is the atomic mass of the metal (for Cu, $M=63,54$ g mol⁻¹).

The calculated current efficiency for CuO reduction into metallic Cu was very close to 100%.

Nd₂O₃ reduction in presence of CuO was further investigated. Cu–Nd phase diagram [44] presents several liquid and solid alloys, and composition of Nd₂O₃–CuO pellets was chosen to be in the zone where liquid alloys are formed: 65 atomic % Nd and 35 atomic % Cu. The linear voltammogram of Nd₂O₃–CuO at 10 mV s⁻¹ in LiF–

CaF₂–Li₂O (2 mass %) (voltammogram b in Fig. 5, I) shows also a reduction signal starting from -1.4 V vs Pt, due to the direct electrochemical reduction of CuO. Additional cathodic signals, between -1.0 and -1.3 V vs Pt, were assigned to impurities present in the solvent (compared to voltammogram a in Fig. 5, I) and in the 99% purity CuO (comparison with voltammogram c in Fig. 5, I). After electrolysis at -0.15 A (500% Q_{th}) and 900 °C, the sample presented several zones (Fig. 5, III):

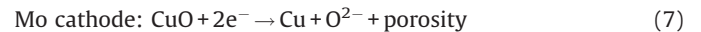
- Zone 1, composed of NdCu₄, NdCu₅ and NdCu₆ droplets (size < 50 μm);
- Zone 2, composed of recrystallized LiF and CaF₂;
- Zone 3, composed of NdOF and CaO, but no compact layer is observed on sample surface.

These results confirm Nd₂O₃ reduction is possible when CuO is simultaneously present, leading to formation of Cu–Nd alloys, and a multi-step reduction mechanism was proposed, as follows:

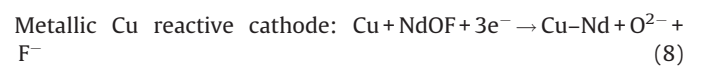
1st step: Chemical decomplexation of Nd₂O₃ into NdOF:



2nd step: CuO direct reduction at the cathode, leading to metallic Cu, behaving as reactive cathode:



3rd step: NdOF reduction on the surface of metallic Cu, leading to Cu–Nd alloys:



The third step of this mechanism was confirmed by electrolyses of Nd₂O₃–Cu metallic powder mixture, which also led to the formation of Cu–Nd alloys. Nourry et al. presented also similar results, showing that Nd³⁺ reduction on copper cathode led to formation of Cu–Nd alloys [37,45,46].

Several authors proved the reduction of rare earth oxides in presence of metallic oxides to be suitable for obtaining rare earth alloys in molten chlorides. Moreover, they also proposed reduction mechanisms where the metallic oxide (Co_3O_4 , NiO , Co_3O_4 , Fe_2O_3) was first reduced on the cathode, followed by the reduction of rare earth oxide and formation of alloys [27–32].

The current efficiencies for Nd_2O_3 reduction in presence of CuO or metallic Cu powder could not be estimated, due to the lack of homogeneity of the sample and the small size of Cu-Nd alloys droplets ($<50\ \mu\text{m}$ diameter, Fig. 5, III), which could not be fully recovered to be weighted.

Nevertheless, when $\text{Nd}_2\text{O}_3\text{-CuO}$ electrolyses were performed at higher temperature (1040°C), coalescing of Cu-Nd droplets occurred (size $\sim 500\ \mu\text{m}$ to $2\ \text{mm}$), facilitating their recovery at the end of electrolysis. In this case, the global current efficiency could be estimated using the equation (8) and its value was $\sim 70\%$. The remaining 30% current fraction could be related to solvent reduction (Ca^+ and Li^+) and uncomplete recovery and separation of Cu-Nd alloys from the salt.

The reduction of neodymium oxide in presence of copper oxide presents several advantages:

- CuO direct reduction led to creation of porosity in the pellet, enabling the penetration of molten salt in the bulk of the sample and thus enhancing the interaction between the solvent, the metallic Cu obtained by reduction and the neodymium oxide;
- Under polarization, the metallic copper obtained by CuO direct reduction behaves as reactive cathodic material, leading to formation of Cu-Nd alloys.

To recover high purity metallic Nd , Cu and Nd separation can be easily accomplished by the electrorefining process, due to the large differences of their electrochemical potentials: in LiF-CaF_2 at 840°C , $E_{\text{Cu}^{2+}/\text{Cu}} = 2.83\ \text{V}/\text{Li}^+/\text{Li}$ and $E_{\text{Nd}^{3+}/\text{Nd}} = 0.35\ \text{V}/\text{Li}^+/\text{Li}$ [37]. Thus, Nd from Cu-Nd alloys can be selectively oxidized into Nd(III) , which will be further deposited as high purity metallic Nd on the cathode. Meanwhile, pure metallic Cu remaining at the anode can be recycled and reused for Nd_2O_3 reduction.

3. Conclusions

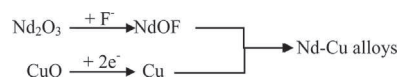
In molten fluoride media, the reduction of Nd_2O_3 was shown to be indirect, similar to the OS process. Nevertheless, reduction of neodymium oxide into metallic neodymium did not occur when using an inert cathodic material (Mo), regardless of the operating parameters (temperature, current, fabrication of the oxide pellet). The limiting factors were related to the:

1. Physical characteristics of Nd_2O_3 : low conductivity and unfavourable Pilling-Bedworth coefficient.
2. Solvent: Indirect reduction of Nd_2O_3 in molten salts is thermodynamically achievable ($\Delta_r G^\circ < 0$) for Ca -based solvents only, when metallic Ca is obtained. However, a dense insoluble CaO layer was formed overall the sample surface, acting as diffusion barrier for O^{2-} , preventing the reduction of the oxide pellet.

Moreover, Nd_2O_3 behavior was influenced by temperature: at 900°C , the oxide was decomposed into insoluble chemically stable NdOF , while at 1040°C it led to formation of crystalline aggregates. Thus, electrowinning of metallic neodymium from neodymium oxide cannot be performed in molten fluoride media in absence of NdF_3 .

Addition of a conductive metallic oxide to the neodymium oxide was further investigated. When $\text{Nd}_2\text{O}_3\text{-CuO}$ and $\text{Nd}_2\text{O}_3\text{-Cu}$ pellets were electrolyzed, metallic neodymium was recovered as

alloyed Cu-Nd droplets, and at higher temperature ($T > 1040^\circ\text{C}$) a better coalescence was observed. The following reduction mechanism was proposed:



The Cu , initially present in mixture with Nd_2O_3 or produced by CuO direct electroreduction, acts as a depolarizing reactive cathode for Nd^{3+} (NdOF) reduction, leading to Cu-Nd alloys. This strategy is the only one viable for obtaining metallic Nd from neodymium oxide in molten fluorides without NdF_3 . Furthermore, high purity metallic Nd can be recovered by a simple electrorefining process, while the metallic Cu can be recycled and reused for Nd_2O_3 reduction.

4. Experimental

The cell design consisted in a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel. The inner part of the cell wall was protected against fluoride vapours by a graphite liner. Experiments were performed under inert argon atmosphere. The molten salt (200 g) was composed of LiF-CaF_2 eutectic, dehydrated by heating under vacuum from room temperature up to melting point (767°C). Li_2O powder (Cerac 99.5%) was used to provide O^{2-} ions in the bath, to ensure the anodic reaction ($2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$). Nd_2O_3 (Aldrich 99.9%), CuO (Merck 99%) and Cu metallic powder (Goodfellow 99.8%) were used in the form of pellets sintered by applying a pressure of $3.2\ \text{t cm}^{-2}$ to several milligrams (from 100 to 300 mg) of powder, at 25°C . The pellets, attached with a molybdenum grid connected to the current lead by a molybdenum wire, were used as working electrodes. The auxiliary electrode was a gold wire or plate, with a large surface area ($S = 3\ \text{cm}^2$), and all potentials were referred to a platinum wire (0.5 mm diameter), acting as a quasi-reference electrode $\text{Pt}/\text{PtO}_x/\text{O}^{2-}$.

The electrochemical experiments were performed with an Autolab PGSTAT 30 potentiostat-galvanostat. After resin embedding and polishing, the cathode bulk was examined with a scanning electron microscope SEM (LEO 435 VP) equipped with an EDS probe (Oxford INCA 200). XRD characterisations were performed with an Equinox 1000 diffractometer. Quantitative analysis were performed with a Cameca SXFive electron probe microanalyser. Nevertheless, neither SEM-EDS nor electron-probe microanalysis do not provide data on Li . Meanwhile, SEM-EDS do not provide data analysis on light elements such as fluoride and oxygen.

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