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Preparation of neodymium–iron alloys by electrolysis in a fused chloride bath

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The preparation of neodymium–iron alloys has been studied by fused salt electrolysis from a chloride bath using a consumable iron cathode. The effect of various process parameters such as concentration of neodymium chloride in the bath, temperature of electrolysis and cathode current density on current efficiency have been investigated. A maximum current efficiency of 38% and metal yield of 51% was obtained from a bath containing 25% $NdCl_3$ in KCl at 875 °C.

1. Introduction

The neodymium–iron–boron alloys ($Nd_2Fe_{14}B$) exhibit excellent permanent magnetic properties. These alloys have about 75% higher energy product ($BH_{max} = 45\,MGO_e$) than the samarium–cobalt alloys ($BH_{max} = 26\,MGO_e$) at significantly lower material cost [1, 2]. (B is remanence, H is coercivity and MGO_e is mega gauss oersted.)

Neodymium–iron master alloys required for preparing Nd–Fe–B alloys have been obtained by calciothermic reduction of a mixture of oxides [3] or fluorides [4] of neodymium and iron. They have also been prepared by reduction of Nd_2O_3 with sodium in the presence of calcium chloride [5]. As against the metallothermic route, electrolysis processes are inherently cheaper and offer the advantage of continuous operation and fewer steps. In neodymium metal extraction by electrolysis, the cell involving use of chloride electrolyte can be operated at much lower temperature compared to that of fluoride because the melting point of $NdCl_3$ (758 °C) is much lower than that of NdF_3 (1374 °C). To avoid formation of high surface area dendritic product, which results in increased contamination [6, 7], the cell has to be operated above the melting point of neodymium metal (1021 °C). However, at such a high temperature, there is considerable solubility of Nd metal in the molten bath and also substantial loss of $NdCl_3$ due to vaporisation. The liberated metal is also highly reactive. These problems can be circumvented by the use of a consumable iron cathode which results in *in situ* formation of a lower melting, less reactive and easy to handle Nd–Fe alloy. The phase diagram of the Nd–Fe system [8] shows the formation of a low melting eutectic alloy at 75 at % Nd–25 at % Fe (corresponding to 88.5 wt % Nd–11.5 wt % Fe) with a melting point of 640 °C. Such a eutectic alloy, which is obtained at low temperatures, can be diluted by melting with ferro-boron to obtain $Nd_2Fe_{14}B$ magnetic alloys containing $\sim$ 37.6 wt % Nd.

The present paper deals with the preparation of neodymium–iron alloys by electrolysis of fused $NdCl_3$–KCl bath using a consumable iron cathode. The effect of various process parameters such as concentration of $NdCl_3$ in the electrolyte, temperature of electrolysis, cathode current density and the excess charge passed on current efficiency and metal recovery were studied. Similar studies on the preparation of Ce, Ce–Co alloys [9], La [10] and misch metal [11] have been reported earlier from this laboratory

2. Experimental details

2.1. *Materials*

Neodymium oxide (Nd_2O_3) of 99% purity was obtained from Indian Rare Earths, Alwaye. Potassium chloride and hydrochloric acid were of LR grade and procured from local suppliers. High purity argon, IOLAR-2 grade, containing a maximum of 4 ppm each of oxygen and moisture, were supplied by Indian Oxygen Ltd, Bombay. The argon gas was further purified by passing it through a purification train containing towers of desiccants (silica gel and magnesium perchlorate) and copper turnings heated at 500 °C and titanium metal sponge maintained at 700 °C.

2.2. *Preparation of electrolyte*

Neodymium chloride ($NdCl_3$) was prepared by dissolving neodymium oxide in conc. hydrochloric acid followed by crystallisation of its hydrated form ($NdCl_3 \cdot 6H_2O$). The next step in electrolyte preparation was to obtain anhydrous chloride ($NdCl_3$) free from oxygen containing compounds such as NdOCl and Nd_2O_3. The dehydration of $NdCl_3 \cdot 6H_2O$ was carried out by slow heating to 300 °C in about 24 h under dynamic vacuum (better than 0.1 mbar). The escaping water vapour was collected by using liquid nitrogen traps. The product obtained was examined by X-ray diffraction (XRD) analysis and found to be $NdCl_3$.

The potassium chloride was also dried by heating in

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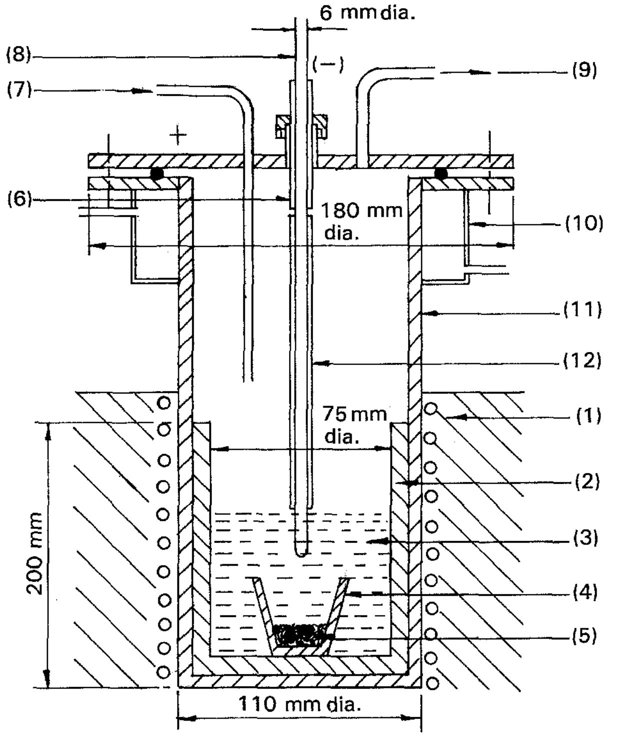

Fig. 1. Scheme of the electrolyte cell. (1) Furnace, (2) graphite crucible, (3) electrolyte, (4) alumina crucible, (5) Nd–Fe alloy, (6) Teflon insulation, (7) Ar gas inlet, (8) iron cathode, (9) Ar gas outlet, (10) cooling jacket, (11) Inconel retort, (12) alumina sheath. All dimensions in millimetres.

vacuum up to 250 °C for about 4 h. The anhydrous $NdCl_3$ and KCl were taken in the required proportion and mixed thoroughly in a moisture-free atmosphere.

2.3. *Electrolysis*

A schematic diagram of the electrolytic cell assembly is shown in Fig. 1. It consisted of a vacuum tight Inconel retort (of 100 mm diam.) fitted with a flange system having provisions for placing the cathode rod in the centre and gas inlet and outlet. About 800 g of electrolyte mixture was taken in a high density graphite crucible (75 mm ϕ i.d. × 90 mm ϕ o.d. × 200 mm height) which also served as the anode. An iron rod (6 mm diam.) was used as consumable cathode. The upper part of the iron rod had a close fitting Teflon sleeve for electrical insulation, while the lower part (except the portion dipping in molten electrolyte) was covered with a close fitting alumina tube to protect it from attack by liberated chlorine.

The electrolyte contained in the graphite crucible was placed in the retort and melted in purified argon gas atmosphere. After equilibrating the molten bath at the required temperature for about 0.5 h, the cathode rod was lowered into the melt and electrolysis was carried out for a specific time. The neodymium metal discharged at the cathode reacted with the cathode metal (Fe) to form a low melting Nd–Fe alloy. The molten alloy was collected in an alumina crucible positioned below the cathode. The alumina crucible, being nonconducting, helped to protect the Nd–Fe alloy from anodic attack as well as reaction with the graphite container. After electrolysis, the cell was cooled to room temperature under argon atmosphere. The alloy was recovered by dissolving the electrolyte in water. The alloy was then thoroughly washed, dried and weighed. The amount of alloy collected in an experiment was 50–70 g.

3. Results and discussion

The fused salt bath used in the present study consisted of $NdCl_3$–KCl where $NdCl_3$ acted as a functional electrolyte and KCl as a carrier electrolyte. Addition of KCl to $NdCl_3$ helped to increase the electrical conductivity and reduce the viscosity of the bath as well as vaporization losses of $NdCl_3$. The effect of variation of concentration of $NdCl_3$ in the electrolyte on the current efficiency (CE) was studied and the results are presented in Table 1. The CE was found to increase from 20 to 38% as the concentration of

Table 1. Influence of conc. of $NdCl_3$ in KCl–$NdCl_3$ bath, temperature of electrolysis and cathode current density on current efficiency

Excess charge passed over theoretical value = 35%

Serial	*Conc. of $NdCl_3$* /wt %	*Temp.* /°C	*Cathode current density (c.c.d.)* /A cm^{-2}	*CE* /%
1	15	875	5	20
2	22	875	5	25
3	25	875	5	38
4	30	875	5	17
5	25	800	5	0
6	25	850	5	20
7	25	875	5	38
8	25	900	5	33.3
9	25	875	0.74	0
10	25	875	1.70	19.0
11	25	875	4.28	28.8
12	25	875	5.00	38.0
13	25	875	7.35	20.5

CE = 3 × 26.8 × (wt. of Nd in alloy) × 100 ÷ 144 × (total charge passed).

$NdCl_3$ in the electrolyte was varied from 15 to 25 wt %. Further increase in concentration of $NdCl_3$ resulted in a decrease in CE. Such behaviour has also been observed in the electrodeposition of other rare earth metals and alloys [12]. At lower concentration of $NdCl_3$, the activity of $NdCl_3$ in the bath is reduced and the electrode potential for neodymium is shifted to a more active (negative) value, favouring deposition of potassium. The potential difference applied during electrolysis was 5 to 8 V. This voltage across the electrolyte cell includes the theoretical decomposition potential of $NdCl_3$, the *IR* drop due to resistance of the electrolyte, bus bars etc. and the overall potentials. Thus voltage applied is above the discharge potential of Nd^{3+} as well as K^+. Hence when the activity (concentration) of Nd^{3+} ions drops below a certain level, the chances of potassium deposition become high.

The KCl–$NdCl_3$ system forms a low melting eutectic at 16.5 mol % (40 wt %) $NdCl_3$ having a melting point of 615 °C [13] and the bath containing 25 wt % $NdCl_3$ has a liquidus temperature of about 700 °C. The effect of electrolyte temperature on CE was studied in the temperature range 800 to 900 °C. Table 1 also presents the results of these investigations. It is evident that no alloy was deposited at 800 °C. This is because the bath containing 25 wt % $NdCl_3$ (melting point $\sim$ 700 °C) has low conductivity up to 800 °C. The CE gradually improved from zero to 38% as the temperature increased from 800 to 875 °C. At still higher temperature (900 °C) there was a decrease in CE due to increased solubility of the metal in the melt. The solubility of Nd metal in $NdCl_3$ is 14 mol % at 640 °C and 30.5 mol % at 855 °C [14].

Investigations were also carried out to study the effect of variation of cathode current density (c.c.d.) on CE. The c.c.d. was varied from 0.74 A cm^{-2} to 7.35 A cm^{-2} and the results are also given in Table 1. It is clear that c.c.d. plays an important role in determining the CE. No metal deposit was obtained at a c.c.d. of less than 1 A cm^{-2}. The CE was found to improve from zero to 38% as the c.c.d. increased from 0.74 to 5 A cm^{-2}. At c.c.d. above 5 A cm^{-2}, there was a fall in CE which may be due to codeposition of potassium, as well as the inability of liberated Nd metal to alloy with the iron cathode at a sufficiently fast rate. Among the rare earth metals neodymium has the highest tendency to dissolve in chloride melts [14] to the extent of $\sim$ 31 mol % leading to the formation of Nd^{2+} ions via the reaction

$$Nd + 2\,Nd^{3+} = 3\,Nd^{2+} \qquad (1)$$

There is another problem: unless the Nd^{2+} species are immediately removed from the system, a cyclic reaction is set up which involves oxidation of Nd^{2+} at the anode

$$Nd^{2+} \longrightarrow Nd^{3+} + e^- \qquad (2)$$

Table 2. Influence of Excess Charge passed over theoretical requirement on metal recovery

Concentration of $NdCl_3$ in KCl–$NdCl_3$ bath: 25 wt %
Temperature of electrolysis: 875 °C
Cathode current density: 5 A cm^{-2}

Serial	*Excess charge* /%	*Metal recovery* /%
1	8.0	21.0
2	12.5	31.7
3	30.0	43.0
4	35.0	51.0
5	50.0	31.0

Excess charge = (Excess charge passed over theoretical requirement × 100) ÷ (Theoretical charge required for reduction of Nd^{3+} present in the bath)

Metal recovery = (Weight of Nd in the alloy) × 100 ÷ (Weight of Nd present in the bath as $NdCl_3$)

and reduction of Nd^{3+} at the cathode

$$Nd^{3+} + e^- \longrightarrow Nd^{2+} \qquad (3)$$

The result of Reactions 1 to 3 is a transfer of electricity without production of metal and, hence, loss of efficiency. These are the main reasons for the low current efficiency of the process. These limitations have also been pointed out by Christopher *et al.* [15].

Studies were also carried out on the influence of excess charge over theoretical requirement on the recovery of alloy. Table 2 indicates a maximum recovery of 51% when 35% excess charge was passed. Any further increase in excess charge resulted in a decrease in metal recovery. This may be because passage of excess charge involves greater electrolysis time and hence more loss of Nd metal due to dissolution in the melt.

Earlam [16] has hypothesized that at the temperature of electrolysis, the steel cathode will decarburize and lead to the formation of neodymium carbide on the surface, which passivates the cathode. In order to check if this passivation hypothesis is true or not and also to see if the carbon content of the cathode material had any influence on the ultimate carbon content of the Nd–Fe alloys, studies were carried out using iron cathodes having C-content in the range <0.01 to 0.17 wt %. No passivation of any of the cathodes used in the present study was observed. Further, the results in Table 3 show that Nd–Fe alloy invariably contains carbon in the range of 0.03 to 0.04 wt % irrespective of the carbon content of the iron cathode. Thus, the passivation hypothesis suggested by Earlam does not appear to be true. Further it is not necessary to use costly iron cathodes containing carbon <0.002%, as recommended by Earlam.

To sum up: a maximum current efficiency of 38% corresponding to a metal recovery of 51% was obtained when a bath containing 25 wt % $NdCl_3$ in KCl was electrolysed at 875 °C at a cathode current density of 5 A cm^{-2}, with 35% excess charge passed. The alloy obtained under optimum conditions was

Table 3. Results of carbon analysis of Nd–Fe alloys prepared by using different iron cathodes

Serial	*Cathode material*	*Carbon content/%*	
		Cathode	*Nd–Fe alloy*
1	Mild steel	0.17	0.04
2	Welding electrode	0.05	0.03
3	Armco iron	< 0.01	0.03

found to contain 82.3% Nd, 15.5% Fe and 0.03% carbon.

4. Conclusion

The process has demonstrated the feasibility of preparing Nd–Fe alloys by fused salt electrolysis of $NdCl_3$ using a consumable iron cathode. The reasons for low current efficiency are the partial loss of energy due to the cyclic oxidation/reduction reaction of neodymium ions (Nd^{2+}, Nd^{3+}) taking place at the anode and cathode, respectively, and the high solubility of neodymium metal in the electrolyte.

References

[1] W. E. Wallace, *in* 'Rare earths, resources, science, technology and applications' (edited by R. G. Bautista and Norton Jackson), The Minerals, Metals and Materials Society (1991) p. 409.

[2] K. S. V. L. Narasimhan, *ibid.*, p. 153.

[3] C. S. Hergert, *in* Proceedings of 8th International Workshop on *Rare Earth Magnets and their Applications* (edited by K. J. Stranat), Dayton Ohio, May (1985), p. 407.

[4] F. A. Schmidt, D. T. Peterson and J. T. Wheelock, *US Patent 4612047*, 16 Sept. (1986).

[5] Ram A. Sharma and Randell N. Seafurth, *Metall. Trans.* **20B** (Dec. 1989) 805.

[6] K. A. Gschneidner, *in* 'Science and technology of rare earth materials' (edited by E. C. Subba Rao and W. E. Wallace), Academic Press, New York (1980), p. 32.

[7] E. Morrice, J. E. Murphy and M. M. Wong, US Bureau of Mines Report Inv. 7308 (1969).

[8] W. G. Moffatt, 'Handbook of binary phase diagrams', GEC, New York (1978).

[9] Sohan Singh, A. L. Pappachan and H. S. Gadiyar, *J. Less Comm. Metals* **120** (1986) 307.

[10] Sohan Singh and A. L. Pappachan, *Bull. Electrochem.* **6** (1990) 97.

[11] Sohan Singh and J. Balachandra, *J. Electrochem. Soc. (India)* **22** (1973) 222.

[12] Y. Qiqin, L. Guankun, T. Yexiang, C. Qingsong and Z. Xianzhi, *Rare Metals* **10** (1991) 22.

[13] E. M. Levin, C. R. Robins and H. F. McMurdie (Eds), 'Phase diagrams of ceramists', The American Ceramic Society, Ohio (1964) p. 380.

[14] H. Bloom, 'The chemistry of molten salts', W. A. Benjmin Inc., New York (1967) p. 149.

[15] A. Christopher, Zing Ming-Zing Su, Senlin Du and Dinxiang Tang, *J. Electroanal. Chem. and Interf. Electrochem.* **263** (1989) 399.

[16] M. R. Earlam, *Metall. Trans.* **21B** (1990) 599.