PRODUCTION OF NEODYM AND ALLOE NEODYM – IRON DY ELECTROLYSIS OF OXIDE – FLUORIDE MELTS

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ABSTRACT
The given work is devoted to research of process of electrochemical reception of neodym and alloy of neodym – iron from oxide-fluoride systems. The mechanism of course of electrode reactions is offered. Voltampere curves from melts, which contain fluoric salts of lithium, potassium, sodium and oxide of neodym, are received. Values of an output on a current of neodym, optimum technological parameters: density of a current, temperature, structure of melts, are determined. Several constructions of equipment for electrolysis are considered. The experimental and industrial equipment for electrolysis is made. The hardware and technological scheme of the process is offered. The cost price of a kilo of metal neodym is calculated as 7-8 dollars.

Large quantities of less-common metals (LCM) are applied in different areas of science and technology every year. So fast growth of consumption is caused by many unique physical and chemical properties of these metals and their connection - optical, magnetic, electric, etc. The flow of scientific and technical researches on studying physical and chemical properties of LCM and materials on their basis, and also the application of these materials is increasing. It stimulates the further fast development of manufacture of LCM and new materials on their basis. The volume of manufacture and use of LCM to a great extent characterizes a level of development of science and technology in the country, especially in the newest branches.

**Figure 1.** Phase diagrams of alkaline metals fluorides and fluoride neodym

The most dynamically utilization of less-common materials for manufacture of unique high-energy constant magnets (HECM) on the basis of Sm-Co and Nd-Fe-B, has been recently developing [1]. Analysis of references has shown that now the one of the basic ways of reception of neodym is electrolytic reception of neodym from oxide-fluoride melts, practically superseded metallothermy. Applying the present technology, China became an undisputed leader in manufacture of less-common metals and their compounds: 85 % of rare landed production in the world made in China [2]. On the basis of known data, which are proceeding from diagrams of condition of salts...
which are a part of electrolit [4] (fig. 1), we selected the structure of melt: LiF - 76,8 %, NdF3 – 19,2 %, Nd2O3 - 4 %. This melt was put on electrolysis. At present the electrolit is tested, which has cheaper basic component than fluoric lithium salt NaF.

The theoretical pressure of expansion of oxide of neodym (Eexpansion) calculated on the reaction 1 at temperature of electrolysis, is a little bit different from results in work [5]. Value of pressure of expansion- 1,6 V, which was received by authors [5], is more then the one which is calculated by us, but in that work the formation of CO2 on reaction 1 was not considered.

Nd2O3 + 2C = Nd + CO + CO2

(1)

The mechanism of electrode processes, which are offered by us [3], differs from known earlier [6] by multi-stages and the discharge of ions of NdOF2 - on the cathode. Although the question about a character of electrode processes, which are proceeding at electrolysis of melts is difficult to solve unequivocally, but it is possible to assume an existence in melt the following ions: F-, NdF6 3-, NdOF2 -, NdOF3 2-, Nd 3+, NdO3 3- . The processes, which are proceeding in volume of electrolit and on electrodes, may be presented as follows:

3LiF + NdF3 = Li3NdF6         ( 2 )
2Li3NdF6 + 2Nd2O3 = 6LiNdOF2        ( 3 )
LiNdOF2 - ⇌ Li + + NdOF2 -         ( 4 )
3NdOF2 - = 3F- + 3/2O2 + Nd 3+ +2NdF3 + 6e
C+ O2 = CO2           ( 5 )
C+ O2 = 2CO
Nd 3+ + 3e = Nd
3NdOF2 - + 6e = 2 Nd + 6F- +NdO3 3-

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Figure 2. Apparatus scheme of electrolysis
1 – Initial reagent vessel. 2- Desiccator. 3 – Reagents Metering bunker. 4 – Drum mixer.
5 – Electrolyte metering bunker. 6 – Neodym oxide metering bunker. 7 – Electrolyzer.
8 - 11 – Apparatuses of anodic gases cleaning. 12 – Vacuum ladle. 13 – Metal ingot.

We developed the basic scheme of reception of neodym (fig.2) on the basis of reference and experimental data. Initial substances are exposed to drying at temperature of 300-350 °C for removal moisture, then the mix of the dried substances, which are corresponding on structure of
electrolit, is located in electrolysis. Salts turn into the molten condition at temperature of 720-
750 °C. The electrolit is transparent, easy fluid; at the bottom of equipment for electrolysis when
the moisture removes incomplete, sludge exudes. The pressure on equipment for electrolysis is made up 4-8 V. Allocation of gaseous substances
and a blue flame was observed at electrolysis, which is characteristic for burning of oxide of
carbon. Anode effect removed by addition of oxide of neodym, and hashing by a tungstic core. Polarizing curves, dependence of an output by current of neodym \( V_i \) from cathodic density of a
current \( i_k \) and the spectrogram of an alloy are shown on fig. 3-5.

![Figure 3. Volt-ampermetric curves](image)

**Figure 3.** Volt-ampermetric curves

![Figure 4. The dependence of current efficiency from current density](image)

**Figure 4.** The dependence of current efficiency from current density

![Figure 5. The roentgen fluorescent spectrum of neodym](image)

**Figure 5.** The roentgen fluorescent spectrum of neodym

It was not possible to receive greater output by a current, because a moisture and oxidation of
allocated metal by oxygen were not removed completely, as the inert atmosphere was not applied
by us. The received metal was analyzed by X-ray and fluorescence methods and went for
manufacturing of alloy of Nd₂-Fe₁₄-B. Electrolysis was realized with the purpose of reception of
metal neodym (in this case as the cathode was the core from tungsten) and alloy of Nd-Fe (the
cathode was a core from less carbon steel).
Neodym was precipitated on the cathode in the form of a liquid drop at reception of metal; there was crystallization in a process of take-out of an electrode from melt, and the ingot of neodym grew on a tungstic electrode. Low temperature eutectic mixture at 684 °C flew down in the mixture of metal at reception of an alloy of neodym with iron (fig. 6).

**Figure 6.** Phase diagram of Nd-Fe

We had been tested some kinds of equipment for electrolysis:

a) the case of equipment for electrolysis from ceramics, the anode is a graphite ring, the cylindrical cathode from less carbon steel in the center;

b) the case of equipment for electrolysis from less carbon steel as the cathode; anode and graphite core;

c) the case of equipment for electrolysis from graphite as the anode; the cathode is from less carbon steel, the mixture from a liquid alloy from ceramic.

d) the case of equipment for electrolysis from graphite is the anode; the cathode is from tungsten.

e) the case of equipment for electrolysis from graphite, the anode is also from graphite, the cathode is from tungsten.

Volume of electrolit in all equipments for electrolysis is 200-300 ml. Equipment for electrolysis from graphite is the most successful; it is rather cheap, heatproof and electroconductive. The ceramics in oxide-fluoride systems is unstable; steel cases are exposed to strong oxidation at a high temperature. We received ingots of neodym with weight of 150 grams with an output by a current of 80-82 % in laboratory equipments for electrolysis. On the basis of results of
experiment the equipment for electrolysis with volume of electrolit of 15 litres is calculated and made. We made a project of a site for reception of neodym on the basis of received technological parameters. This site has productivity of 10 tons per year. We determined financial and economic parameters. At the rate of refinancing of 25% the time of recovery of outlay will make 4, 9 years; the target price has made 314, 95 rubles/kg. It helps the manufacture to become competitive among the main manufacturers.

Literature

2. http://www.giredmet.ru/Obzory/7.05.03-2.html