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OBTAINING NEODYMIUM FROM MELTS BY ELECTROLYSIS

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The mechanism of electrode reactions at electrochemical obtaining neodymium and neodymium-iron alloy from fluoride oxide systems has been studied. Current-voltage dependences of electrochemical processes in melts containing fluorine salts of lithium, potassium, sodium and neodymium oxide were analyzed. Neodymium current yield values, optimal process variables: current density, temperature, melt composition were determined. Electrolyzers constructions were optimized, experimental-industrial electrolyzer was designed, process instrument flow diagram was developed.

Rare-earth metals are applied year by year in larger quantities in various fields of science and technology. Such rapid growth of consumption is stipulated by many unique physical and chemical properties of these metals and their compounds: optical, magnetic, electrical and others. Flow of scientific and technical researches on studying physical and chemical properties of REM and materials on their basis as well as on applying these materials increases that promotes further rapid development of manufacturing REM and new materials on their basis. Volume of production and use of REM characterizes to a considerable extent the degree of development of country science and technology especially new branches.

Use of rare-earth materials for manufacturing unique high-energy constant magnets on the basis of Sm-Co and Nd-Fe-B was developed more dynamically recently [1]. Literary analysis [2–5] showed that one of the main techniques of obtaining neodymium at the present time is electrolytic neodymium obtaining from oxide-fluoride melts which practically replaced metallothermy. Applying this technology China became the sole leader in manufacturing rare-earth metals and their compounds: 85 % of manufactured rare-earth production in the world falls on China [2].

The aim of the paper was to develop optimal process diagram of obtaining neodymium and neodymium-iron alloy.

On the basis of known data the composition of the melt [4], Fig. 1: LiF – 76,8 %, NdF_3 – 19,2 %, Nd_2O_3 – 4 % was selected in terms of salt state diagrams being a part of electrolyte composition. This composition underwent electrolysis. Besides, at present the electrolyte the main component of which is cheaper salt of sodium fluoride than lithium fluoride is tested $Nd_2O_3+2C=Nd+CO+CO_2$. At temperature of electrolysis the theoretical voltage of neodymium oxide decomposition was calculated by the reaction (1) slightly differing from that given in the paper [5]. The value of decomposition voltage – 1,6 V given by the authors [5] is larger than one which we calculated but formation of CO_2 by the reaction (1) is not taken into account.

The mechanism of electrode processes proposed by us [3] differs from those known before [6] in multistage and discharge on cathode of $NdOF_2^-$ anions. Though it is rather difficult to solve definitely the question about the character of electrode processes occurring at melt electrolyses it is possible to suppose the existence of the following ions: F^-, NdF_6^{-3}, $NdOF_2^-$, $NdOF_3^{-2}$, Nd^{+3}, NdO_3^{-3} in the melt. The processes occurring in the volume of electrolyte and on electrodes may be presented in the following way:

$$3LiF+NdF_3=Li_3NdF_6$$

$$2Li_3NdF_6+2Nd_2O_3=6LiNdOF_2$$

$$LiNdOF_2\leftrightarrows Li^++NdOF_2^-$$

$$3NdOF_2^-=3F^-+3/2O_2+Nd^{+3}+2NdF_3+3e$$

$$C+O_2=CO_2$$

$$2C+O_2=2CO$$

$$Nd^{+3}+3e=Nd$$

$$3NdOF_2^-+6e=2Nd+6F^-+NdO_3^{3-}$$

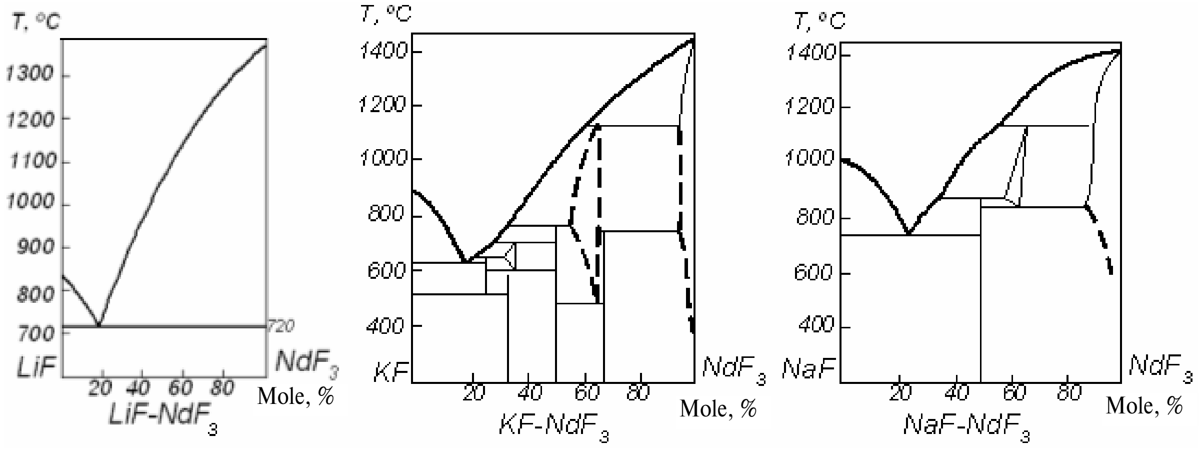

Fig. 1. *Phase diagram of alkali metal fluorides with fluoride neodymium [4]*

Thus, discharge of both simple neodymium ions and complex particles may occurs on electrodes that should result in considerable electrode polarization and voltage increase on electrolyzer. The given mechanism is tested at the present time.

On the basis of literary and experimental data the basic diagram for obtaining neodymium was developed (Fig. 2). The original substances (pure) are subjected to drying at temperature 300...350 °C during two hours for removing moisture then the mixture of dried substances correspon-

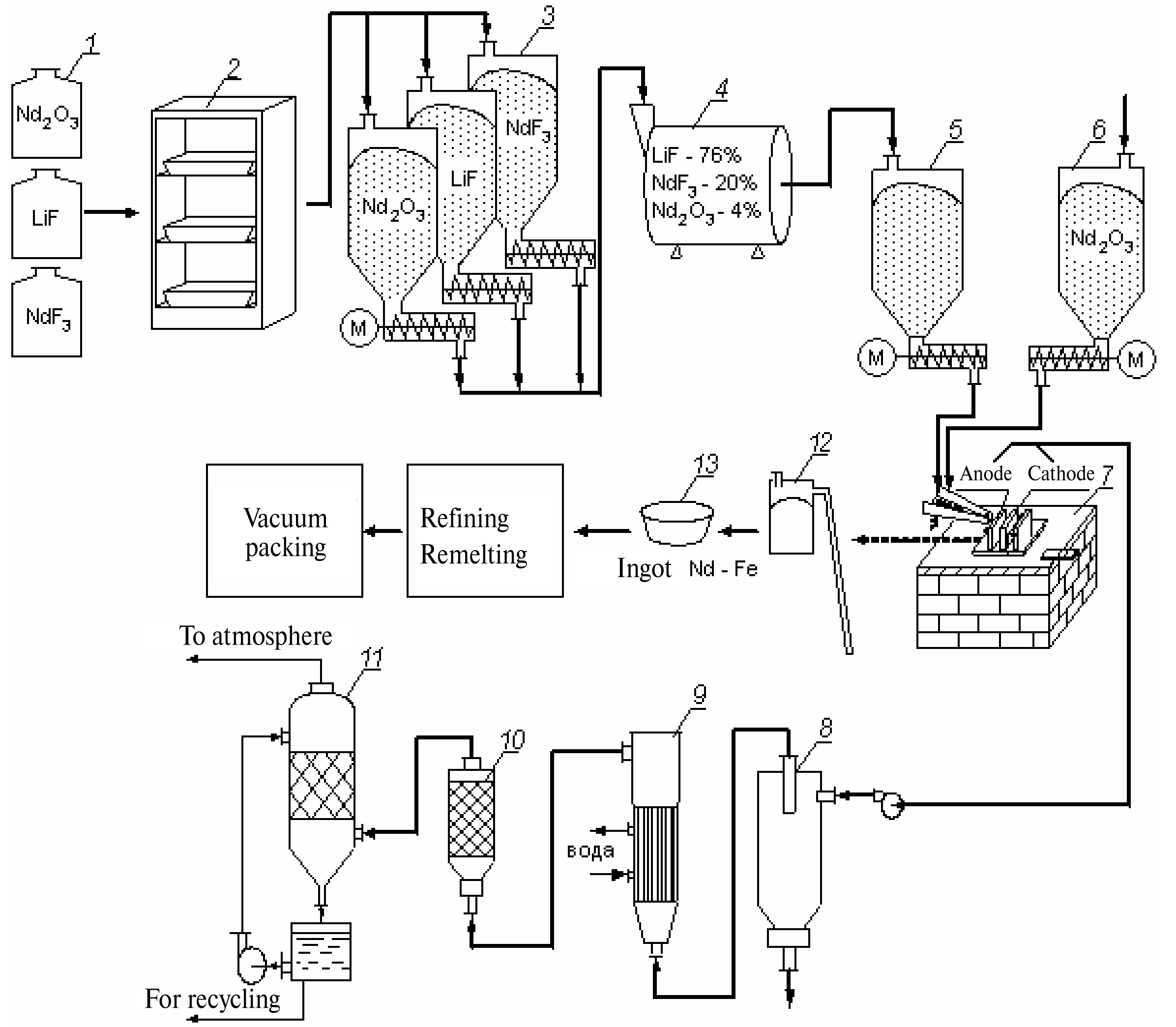

Fig. 2. *Instrument diagram of the process of neodymium electrolytic obtaining: 1) capacitors with original agents, 2) drying box, 3) agent metering hopper, 4) mixer, 5) electrolyte metering hopper, 6) neodymium oxide metering hopper, 7) electrolyzer, 8–11)devices for anode gas purificatio,12) vacuum-ladle, 13) metal ingot*

ding to electrolyte by composition is placed into electrolyzer. Salts transfer into molten state at temperature 720...750 °C. Electrolyte is transparent, very fluid; sludge settles on the bottom of electrolyzer at partial moisture removing. Voltage on electrodes amounted to 4...8 V. Extraction of gaseous substances and blue flame typical for carbon oxide burning was observed at electrolysis. Anode effect was removed by adding neodymium oxide and stirring with tungsten rod. Polarization graphs, dependence of current neodymium output on cathode current density and neodymium spectrogram are shown in Fig. 3–5.

Higher current output was not obtained due to incomplete moisture removing and oxidation of extracted metal with oxygen as inert atmosphere was not applied. The obtained metal was analyzed by X-ray fluorescence method and went for producing the melt Nd_2-Fe_{14}-B. Electrolysis was carried out for obtaining metal neodymium (in this case tungsten rod served as cathode) and melt Nd-Fe (cathode is a rod of low-carbon steel). Obtaining metal neodymium settled on cathode in the form of liquid drop; as electrode rose from the melt the crystallization occurred and neodymium ingot grew on tungsten electrode. Obtaining the alloy of neodymium with iron the low-temperature eutectic drained into metal collector at 684 °C (Fig. 4)

Time response of electrolysis process was also recorded (Fig. 8). At the beginning of electrolysis process (20...30 min) voltage and current steps are observed as the electrolyte run-in, electrode surface burning, volatile impurities extraction etc. occur then the process is stabilized about 2h (I=15...16 A; U=4...5 V) in this case extraction of gas (CO and CO_2) is observed. After this voltage increase and current decrease is observed however, after addition of a portion of neodymium oxide into the melt during 1...2 min it is stabilized again.

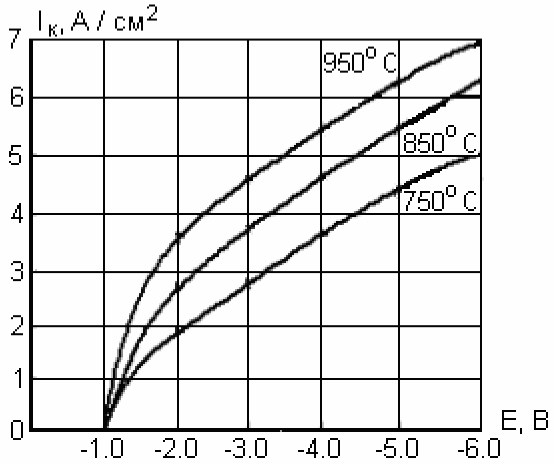

Fig. 3. *Dependence of cathodic current density on temperature*

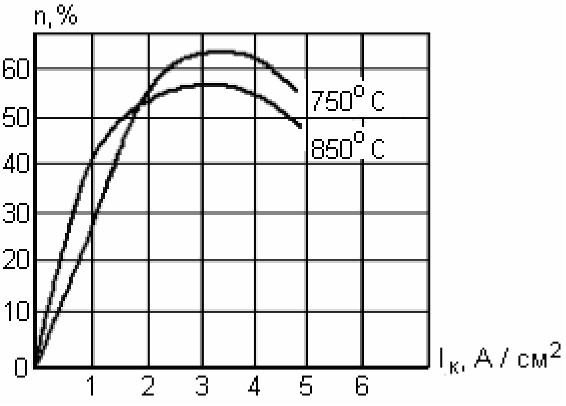

Fig. 4. *Dependence of neodymium current output on cathodic current density*

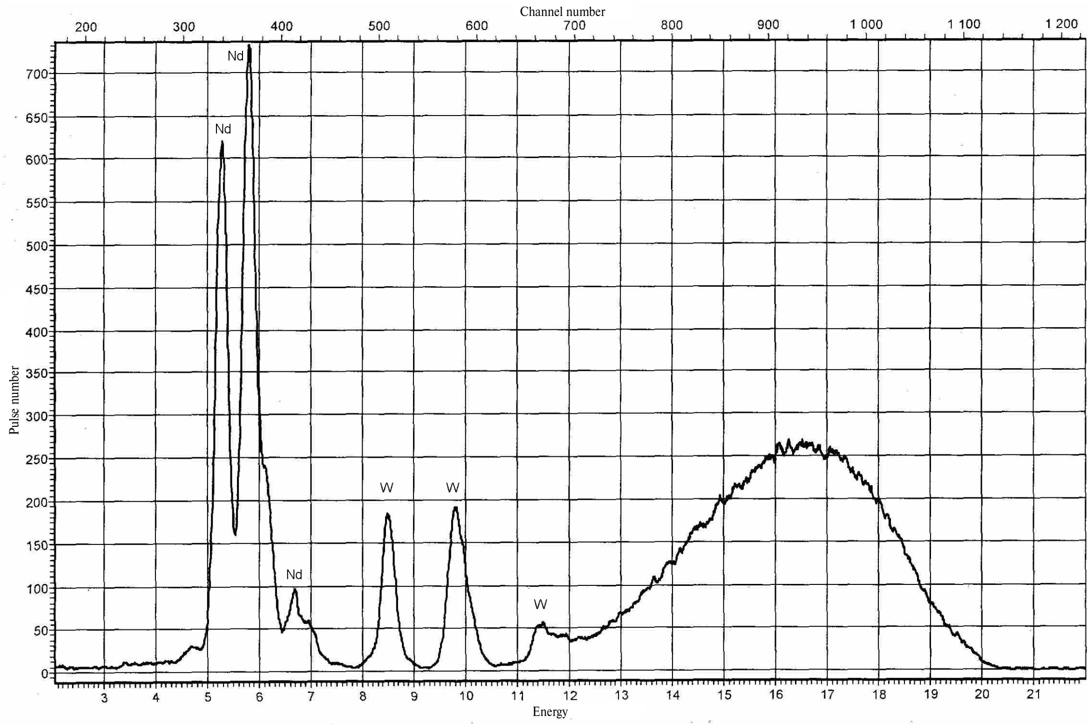

Fig. 5. *X-ray fluorescence neodymium spectrum on tungsten cathode*

The conclusion could be made from the above mentioned that the main raw-material at metal neodymium obtained by electrolysis is its oxide. The diagram of the experimental device is presented in Fig. 9.

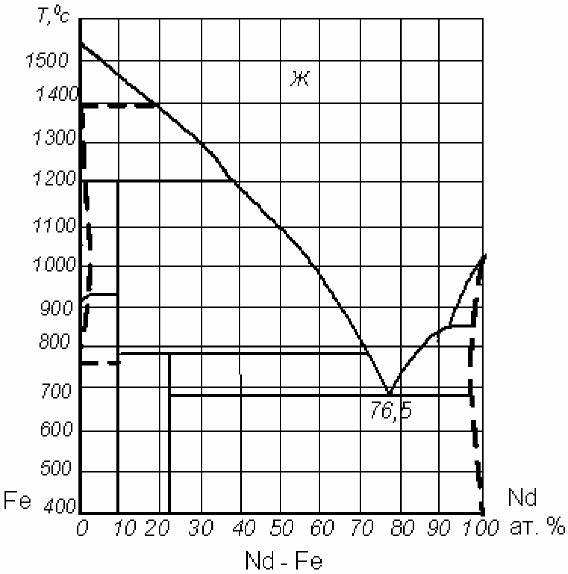

Fig. 6. *State diagram of neodymium-iron*

Several types of materials for electrolyzer body were tested:

- of ceramics, anode – graphite ring, cylindrical cathode of low-carbon steel is in centre;
- of low-carbon steel served as cathode; anode is a graphite rod;
- of graphite – anode; cathode is of low-carbon steel, liquid alloy collector is of ceramics.
- of graphite – anode; cathode is of tungsten.
- of graphite anode is also of graphite, cathode is of tungsten.

The volume of electrolyte in all electrolyzers is 200...300 ml.

Electrolyzers of graphite should be considered as the most successful: they are relatively cheap, heat-resistant, electricity-conductive. Ceramics in oxide-fluoride systems is not stable; steel bodies undergo strong oxidation at high temperature. Neodymium ingots with mass 150...200 g with current output 80...82 % were obtained in laboratory electrolyzers. Electrolyzer with electrolyte volume of 15l was calculated and made on the basis of the experiment results.

In terms of the obtained technological indices the project of neodymium obtaining area with the capacity of 10 t/year was made and financial-economic indices were determined: at refinancing rate of 25 % the payback period amounts to 4,9 years; guide price amounted to 314,95 r/kg that allows the manufacturer to be competitive relative to the main manufacturers.

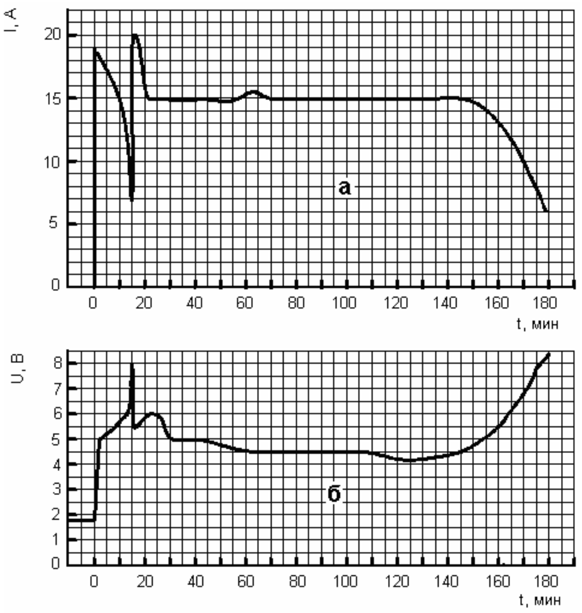

Fig. 7. *Dependence on time: a) current б) voltage*

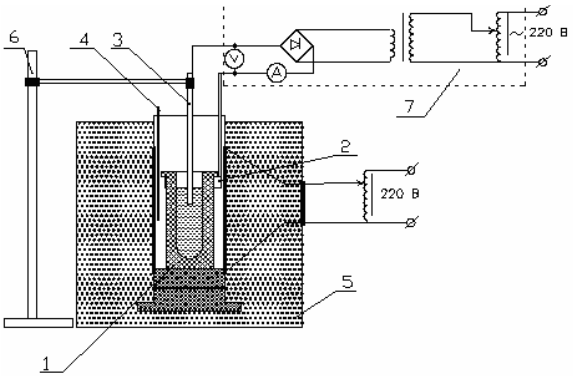

Fig. 8. *The diagram of experimental device: 1) crucible, 2) current contact jaw, 3) cathode, 4) chromel-alumel thermocouple, 5) muffle furnace, 6) tripod, 7) constant-current source*

Electrolyte volume in all electrolyzers is 200...300 ml.

The result of studying the process of neodymium and neodymium-iron alloy electrochemical obtaining from oxide-fluoride systems is:

- development of mechanism of electrode reaction behavior;
- obtaining current-voltage dependences of electrolysis process from melts containing fluoride salts of lithium, potassium, sodium and neodymium oxide;
- defining neodymium current output value;
- defining optimal process variables: current density, temperature, melt composition;
- optimization of electrolyzer construction;
- production of experimental-industrial electrolyzer;
- development of instrument-technological diagram of the process.

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PHASE REVERSAL ORGAIZATION IN GALLIUM-EXCHANGE SYSTEMS

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Phase reversal stages at alkalis separation by chemical exchange method in LiGa-NaOH and LiGa-KOH systems have been studied. Pilot laboratory plants for intermittent and continuous obtaining lithium gallium in metal melts were developed and tested. The possibility of realization of alkalis multiple separation process by gallium-exchange method in packed column was shown.

Introduction

One of perspective substance segregation and purification techniques is chemical exchange method as it does not require energy consumptions for direct segregation process. The gas-liquid system is the most manufacturable of all systems for element segregation by this method. However, many elements of Periodical system, in particular, a number of alkalis have no gaseous compounds [1]. These elements may be segregated by the chemical exchange method using liquid-liquid system. Water solution of alkaline element salt is one liquid as a rule and amalgam is used as the second one. Amalgam-exchange segregation method has a significant disadvantage as it uses high-toxic mercury in large quantities. We proposed to change high-toxic amalgams used in processes of exchange segregation and purification of alkali metals for environmentally safe compounds of gallium with alkalis – gallamas [2].

Segregating alkalis (Li, Na, K) by gallam-exchange method the exchange reaction

$$\mathrm{LiGa+MeOH \leftrightarrow LiOH+MeGa},$$

occurs in gallama system lithium-water solution of sodium hydroxide (potassium), where Me is sodium or potassium.

Simultaneously with the given exchange reaction the intermetallic compound (gallama) is decomposed by the reaction

$$\mathrm{MeGa+H_2O \rightarrow MeOH+Ga+1/2H_2}, \qquad (*)$$

in this case alkali transfers into solution. If decay rate of gallama is higher or equal to the rate of elemental exchange in the given system then it is impossible to separate alkalis in it. Therefore, the kinetics of the given processes in the systems LiGa-NaOH and LiGa-KOH in temperature range 40...80 °C were studied [3]. It was stated that the rate of exchange process exceeds the rate of gallama decomposition process approximately in 40...70 times in the studied temperature range. So, it is arguable that manifold multiplication of single separation effect is possible in these systems.

For implementation of multiple separation process of alkalis by gallama-exchange method in packed columns the questions of organizing counterflow and reversal of exchanging phases are required to be considered. The possibility of organizing phase counterflow and conditions necessary for this are showed in the paper [4]. The given article is devoted to the study of organization of exchanging phase reversal in the systems Li-Ga-NaOH and LiGa-KOH.

The process of phase reversal includes two stages of metal conversion: 1) from gallama phase into hydroxide solution – gallama decomposition; 2) from hydroxide solution into gallama – gallama obtaining.

First of all, as it was said above, the kinetics of alkali gallama decomposition process was studied. It was stated that gallama is well decayed with water by the reaction (*), and the rate of its decomposition is about two times higher than the rate of amalgam decomposition in similar conditions. Besides, it is possible to increase the rate of the given process behavior with the help of catalysts (for example, graphite). Thus, the first stage of phase reversal is easily implemented.