REFERENCES

Received on 07.12.2006

OBTAINING NEODYMIUM FROM MELTS BY ELECTROLYSIS
V.A. Grebnev, V.P. Dmitrienko
Tomsk Polytechnic University
E-mail: dvpts@mail.ru

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 %, NdF₃ – 19.2 %, Nd₂O₃ – 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 Nd₂O₃+2C=Nd+CO+CO₂. 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 CO₂ 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 NdOF₂⁻ 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⁻, NdF₆⁻³, NdOF₂⁻, NdOF₂⁻², Nd⁺³, NdO₃⁻³ in the melt. The processes occurring in the volume of electrolyte and on electrodes may be presented in the following way:

3LiF+NdF₃=Li₃NdF₆
2Li₃NdF₆+2Nd₂O₃=6LiNdOF₂
LiNdOF₂=Li⁺+NdOF₂⁻
3NdOF₂⁻=3F⁻+3/2O₂+Nd⁺³+2NdF₃+3e⁻
C+O₂=CO₂
2C+O₂=2CO
Nd⁺³+3e⁻=Nd
3NdOF₂⁻+6e⁻=2Nd+6F⁻+NdO₃⁻³
Thus, discharge of both simple neodymium ions and complex particles may occur 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 °С during two hours for removing moisture then the mixture of dried substances correspon—
Sleeping to electrolyte by composition is placed into electro-
lyzer. 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 re-
moving. Voltage on electrodes amounted to 4...8 V. Extrac-
tion of gaseous substances and blue flame typical for car-
bon oxide burning was observed at electrolysis. Anode ef-
effect was removed by adding neodymium oxide and stirring
with tungsten rod. Polarization graphs, dependence of cur-
rent neodymium output on cathode current density and
neodymium spectrogram are shown in Fig. 3–5.

Higher current output was not obtained due to in-
complete 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 NdFeB. Elec-
lysis was carried out for obtaining metal neody-
nium (in this case tungsten rod served as cathode) and
melt NdFe (cathode is a rod of low-carbon steel). Ob-
taining 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 recor-
ded (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, volati-
ble 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 CO₂) is observed. After this
voltage increase and current decrease is observed howe-
ever, after addition of a portion of neodymium oxide in-
to 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.

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.

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.
REFERENCES
2. http://www.giredmet.ru/Obsory/7.05.03н2.html

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

LiGa+MeОН ↔ LiОН+MeGa,

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

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

MeGa+H2O → MeOH+Ga+1/2H2, (*)

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 realization of alkalis multiple separation process by gallium-exchange method in packed column was shown.

UDC 669.871.5

PHASE REVERSAL ORGAIZATION IN GALLIUM-EXCHANGE SYSTEMS

D.G.Vidyaev
Tomsk Polytechnic University
E-mail: vidyaev@phtd.tpu.edu.ru

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.