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Fluoride technology of obtaining REM magnetic alloys and master alloys

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Abstract. Rare earth permanent magnets (REPM) based on neodymium-Fe-boron system are the most promising, since they have the highest magnetic and satisfactory mechanical characteristics. The paper covers physical-chemical principles and shows the results of experimental studies of the process of obtaining REM alloys and master alloys using fundamentally new fluoride technology based on ladle calciothermal REM fluorides and Fe reduction.

1. Introduction

Magnetic materials are alloys of, at least, one rare earth element with one 3d - transition metal [1].

Fluoride technology is one of the methods of obtaining magnetic materials to produce REPM. It includes the following stages: fluorination of raw materials with fluorine or another fluorinating agent, calciothermal reduction of fluorides with obtaining compact alloy ingots and (or) REM-Fe master alloys and magnets manufacturing based on metal powder industry method using the mechanical or hydride grinding and recycling [2, 3]. The main advantages of this technology are shown in [4].

2. Physical and chemical principles of the reduction process

2.1. Thermodynamics of the process

The thermodynamics of the process of metals fluorides reduction was discussed in the paper [5].

The obtaining Nd-Fe master alloys and Nd-Fe-B alloys can be represented by the equations:

$$NdF_3 + nFeF_3 + 1.5(1 + n)Ca = \mathbf{NdFe_n} + 1.5(1 + n)CaF_2, \qquad (1)$$

$$NdF_3 + nFeF_3 + mFe + gB + 1.5(1 + n)Ca = \mathbf{NdFe_{(n+m)}B_g} + 1.5(1 + n)CaF_2, \qquad (2)$$

where n, m, g – stoichiometric coefficients.

Table 1 shows the thermodynamic parameters (ΔH, q, T_a) for the process of REM fluorides combined reduction reaction 1.

Table 1 shows that part of the alloys and master alloys components could be added to the reaction charge in order to reduce thermicity of the process in the form of a powder or facings. The same effect is achieved by the addition of inert components, e.g. CaF_2, to the charge.

Table 1. The values of enthalpy, thermicity and adiabatic temperature of the reaction of obtaining $NdFe_n$ depending on the master alloy composition

Parameters	Composition of master alloy $NdFe_n$, % Wt. with neodymium content							
	100	90	80	70	60	50	40	30
$-\Delta H°_{298}$, kJ/mol	170	410	650	1050	1530	2250	3130	4970
q, J/g	650	1310	1780	2320	2750	3160	3530	3820
T_a, K	1400	1860	2335	2700	3000	3300	3600	3900

Note. The thermodynamic calculations do not take into account the heat of Fe and neodymium mixing.

2.2. Kinetics of the process

The main kinetic characteristics of metallothermic reactions are: the activation energy E_a, the rate constant K_c, and the rate of the W process. Activation energy of the process of obtaining magnetic alloys and master alloys, described by equations 1 and 2, was determined by the equation [6]:

$$T_a - T_M = R(T_M - 273)^2/E_a, \quad (3)$$

where T_a – adiabatic temperature of the process;

$T_м$ – maximum process temperature. It was determined empirically by direct measurement using a tungsten-rhenium thermocouples VR-1 and low-inertia locking device (loop oscillograph).

The data obtained are presented in Table 2.

Table 2. The maximum temperature and the activation energy of calciothermal process of obtaining alloys and master alloys of different composition

Parameter	Master alloy composition containing Nd, %Wt. (reaction 1)				Amount of Fe in the form of metal powder, % Wt. (reaction 2)		
	100	90	80	70	55	60	65
T_a, K	1400	1860	2335	2700	2520	2380	2240
$T_м$, K	–	1700	2100	2400	2260	2140	2020
E_a, kJ/mol	–	126,2	120,8	115,3	105,8	118,0	125,4

Table 2 shows that the activation energy of the process of coreduction of REM fluorides and transition metals with the formation of alloys and master alloys depends on their composition and is within 105.8-126.2 kJ/mol.

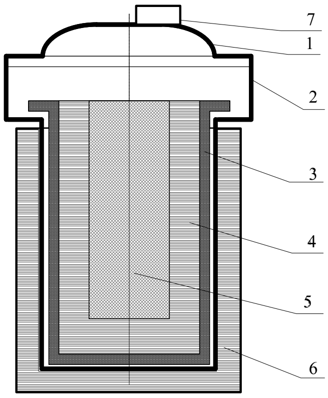
3. Experimental study

3.1 Installation description and the research methods

Study of the process of ladle calciothermal reduction of metal fluorides was carried out on the reduction reactor shown in Figure 1. It is made as a cylindrical unit (2) whith cover (1). Outside, the reactor is equipped with a cooling jacket (6). Its inner part is equipped with steel pad (3) with CaF_2 lining (4) and the prepared charge (5). The reaction in the reactor starts with electric-squib ignition.

The methodology of the study was as follows. Necessary amounts of trifluorides metals, Fe, FeB metal powders and Ca facing were weighed separately, laminated, stirred in a rotating drum mixer for 10-20 minutes and, then, were charged into the crucible. Ignition device, consisting of a metal spiral, was assembled on the surface of the charge. All the items were placed in a reactor and sealed. Initiation of the reduction melting reaction was carried out with a spiral, heated by the transformer.

For conducting calciothermal reduction the following materials were used: metal fluorides with a conversion coefficient of the native oxides into fluorides for: Nd_2O_3 – 94-96 % ($\alpha_{ТФН}$), for Fe_2O_3 – 92-94 % ($\alpha_{ТФЖ}$); Fe metal powder of the PZHV-1, 2 (GOST 9849) brands; FBO-20 with a particle size of not more than 0.25 mm; Metallic Calcium (TC 95824) in the form of facing.



1 – reactor cover; 2 – reactor housing; 3 – steel pad; 4 – CaF_2 lining;
5 – charge; 6 – cooling jacket; 7 – emergency pressure relief valve

Figure 1. General view of the reduction reactor

3.2 Studies of the influence of various factors on the yield of the metal into the ingot
The influence of overreductant, reducing melting scale, alloy and master alloy composition, the degree of metals oxides fluorination, the wall thickness of the lining of the crucible to the reduction degree of fluorides, metal yield into an ingot and its quality were studied. The data are shown in Figures 2 and 3.

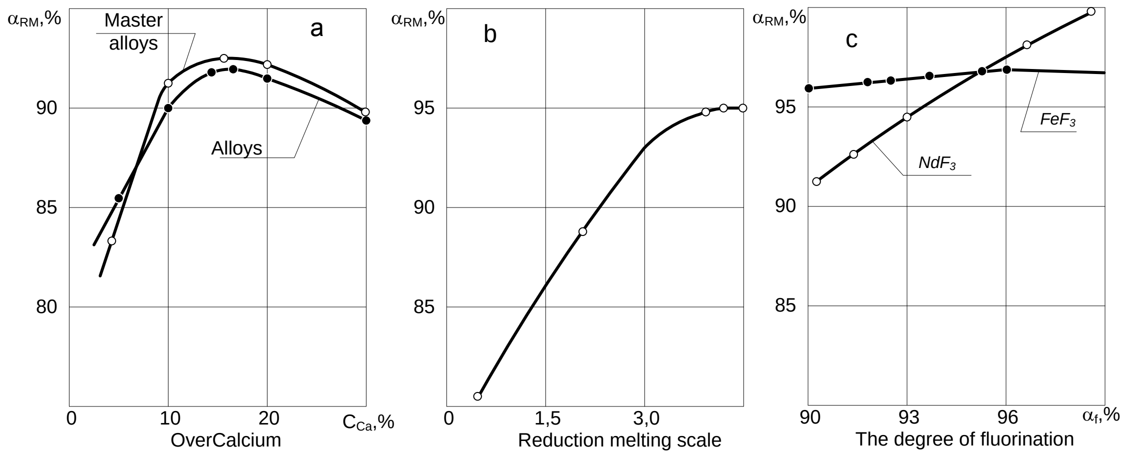


Figure 2. Dependence of the metal yield into the ingot on overcalcium (a), reduction melting scale (b), the oxides fluorination degree(c)

The data in Figures 2 and 3 show that the alloys and master alloys (metals) yield into the ingot and the reduction degree of REM fluorides and Fe are influenced by many factors.

Reduction melting scale. With increasing the scale up to 4 kg for the amount of metal, the yield of the metal into the ingot increases. This is due to decrease of heat loss from the reduction melting products, and, respectively, increase of the system duration of the stay in a molten state.

OverCalcium. With increasing of overCalcium up to 10%, metal yield into the ingot increases, and, then, with overreductant from 10 to 20%, practically does not depend on its quantity, and it starts decreasing with an excess of more than 20%.

The fluorination degree. Fluorination degrees of neodymium and Fe oxides have different effects on the metal yield into the ingot. The oxide content in Fe fluoride in up to 10% does not have serious effect on the metal yield into the ingot, but the same change of the content of neodymium oxide in fluoride reduces its yield up to 91-92%.

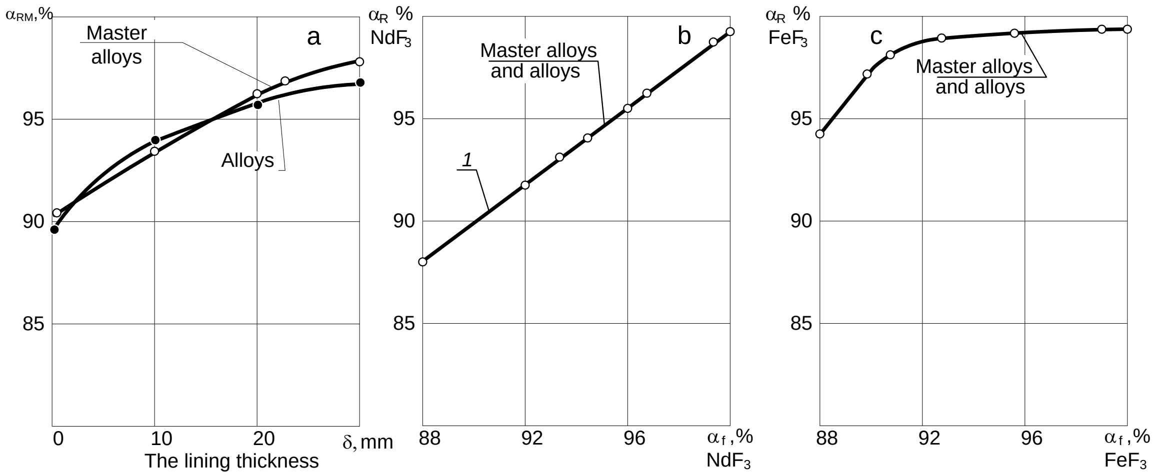


Figure 3. Dependence of Nd, Fe yield, as well as alloys and master alloys into ingot on the thickness of the lining layer (a), the fluorination degree of neodymium (b) and Fe (c)

3.3 The study of the alloys and master alloys quality

To assess the quality of materials 2 alloys and master alloys ingots were subjected to chemical (emission spectrometer with inductively-coupled plasma ICAP 6200 DUO), X-ray diffraction (X-ray diffractometer ARL'XTRA) and electron microscopy (scanning electron microscope Vega 3 SBH (TESCAN)) analysis, the results of which are shown in Table 3 and in Figures 4-7.

Table 3. Alloys and Master alloys chemical composition

N RM	$\alpha_{вп}$, %	M_{ingot}, kg	Calculated alloy composition, % (Wt.)		The results of chemical analysis, % (мWt.)				Yield into ingot, α, %	
			$C_{(Nd+Pr)}$	C_{Fe}	C_{Nd+Pr}	C_{Fe}	C_{B}	$C_{\Sigma(Nd, Pr, Dy, Tb, Fe, B)}$	FeF_3	$P3F_3$
1	97.8	4.89	32	67	31.1	67.5	1.1	99.7	98.5	95.0
2	98.4	4.92	36	63	34.8	63.6	1.1	99.5	99.4	95.2
3	98.0	4.90	40	60	39.7	59.9	-	99.6	99.5	95.0
4	97.8	4.89	40	60	39.8	60.0	-	99.8	99.5	97.0

Note: 1, 2 - Alloys chemical composition; 3, 4 - Master alloys chemical composition

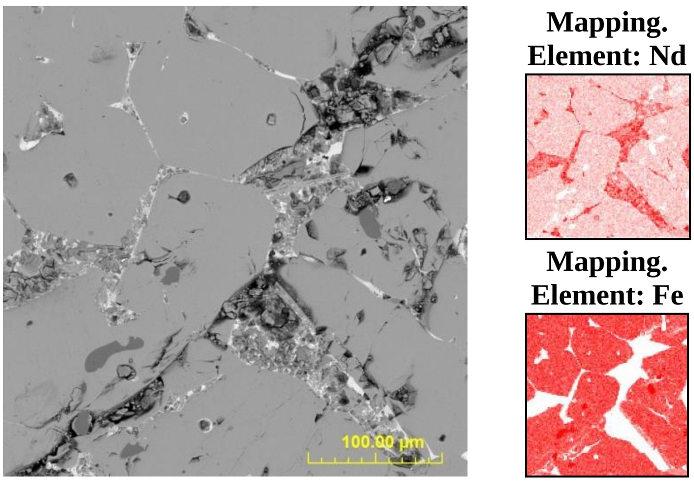


Figure 4. The results of electron microscopy analysis of alloy sample

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The theoretical weight of alloys and master alloys at the initial charge is 5 kg.

Data analysis in Table 3 shows that the total content of REM, Fe and boron is greater than 99.5% for alloys and 99.6% for master alloys (REM and Fe), the degree of fluorides reduction is 98.5% (Fe) and 95 % (REE).

Figure 4 shows that the phase composition of the alloy is nonhomogeneous. Conducted mapping finds out that the grain slice consists essentially of Fe and neodymium. Dark spots on the image of grains slices are the phases, enriched with Fe. The grains boundaries and the grains pores are saturated with neodymium, containing a minor amount of oxygen.

Figure 5 shows that the surface of the sample is inhomogeneous The surface of the edges has the defects with the size up to 1 micron.

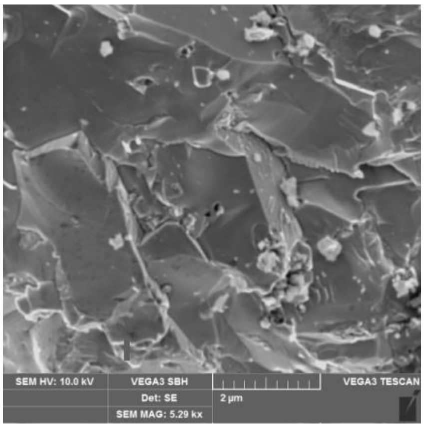

Figure 5. The results of electron microscopy analysis of master alloy

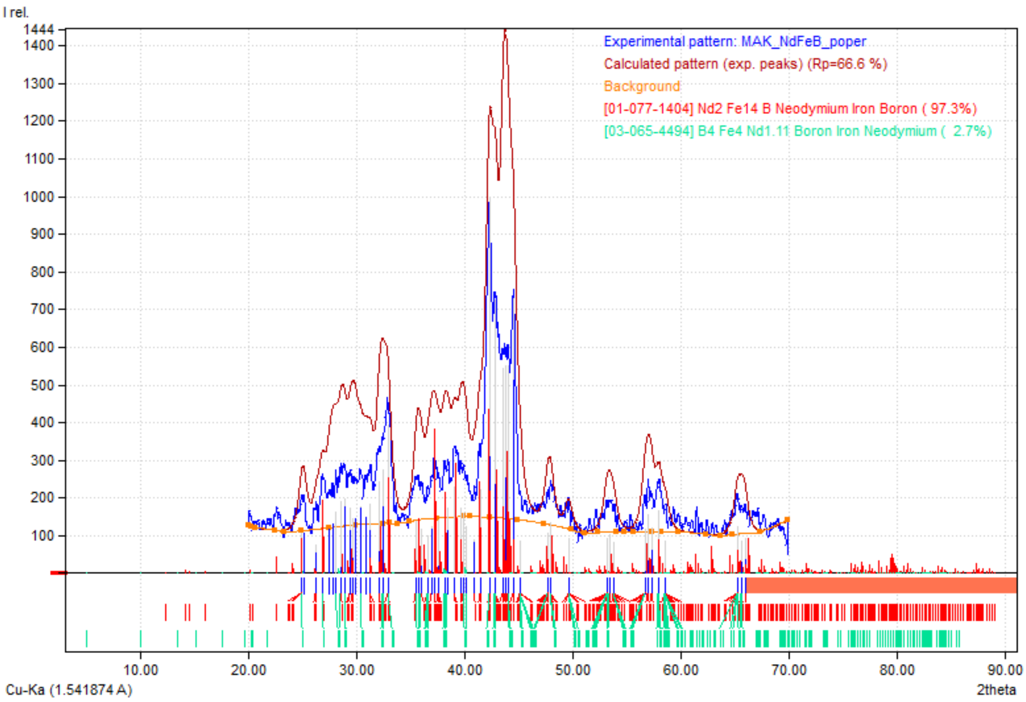

Figure 6. The results of X-ray diffraction analysis of alloy sample

Figure 6 shows that the content of the main magnetic phase $Fe_2Nd_{14}B$ in the sample is 97.3%, the rest is $Nd_{1,11}Fe_4B_4$ phase.

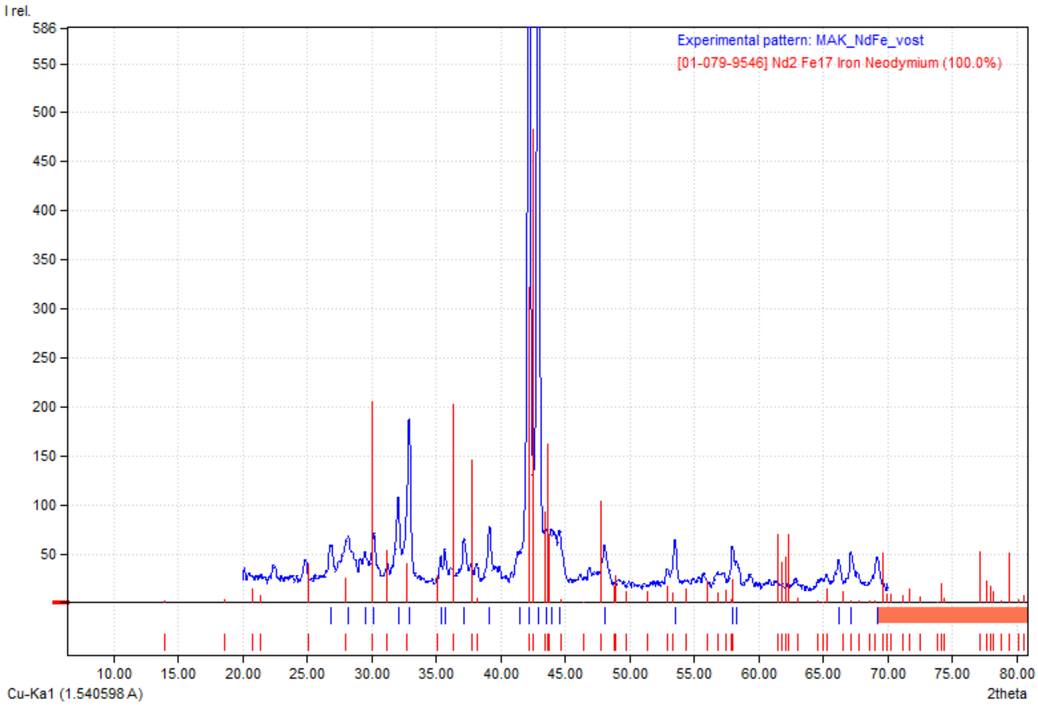

Figure 7. The results of X-ray diffraction analysis of master alloy sample

Figure 7 shows that the main Nd_2Fe_{17} phase content in the sample is 100%.

4. Conclusion

1 The thermodynamics of the REM and Fe fluorides reduction process is considered. It is shown that the alloys based on Nd-Fe-B system and Nd-Fe master alloys could be obtained with ladle calciothermal metal fluorides reduction.

2 The kinetics of the process of the complex reduction of REM fluorides and Fe is studied and the activation energy of the process is determined, which is in the range of (105,8-126,2) kJ / mol.

3 Experimental studies of the process of obtaining alloys and master alloys by ladle complex reduction of RE fluorides and Fe are carried out.

4 The quality of the alloys and master alloys obtained is proved with chemical, X-ray diffraction and electron microscopic analysis.

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