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Classification

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Studies on sintered permanent magnets RE-Fe-M-Co-B (RE = Nd, Pr, Dy, Tb ; M = Si, Al, Cr)

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Résumé. — La microstructure, les propriétés magnétiques et le comportement à la corrosion des aimants frittés $\text{RE}_{16}\text{Fe}_{71-x}\text{M}_x\text{Co}_5\text{B}_8$ ont été étudiés. (RE désigne Nd, Pr, Dy, Tb et M désigne Si, Al, Cr). Il a été montré que la présence de composés RE-(Fe, Co, M) aux joints de grains est responsable de l'inhibition des corrosions acide et atmosphérique. Les propriétés magnétiques optimales déduites de cette étude sont $B_r = 1,26 \text{ T}$, $M H_c = 1\,730 \text{ kA/m}$ pour la composition $\text{Nd}_{14}\text{DyTbFe}_{70}\text{SiCo}_5\text{B}_8$.

Abstract. — The microstructure, magnetic properties and corrosion behaviour of $\text{RE}_{16}\text{Fe}_{71-x}\text{M}_x\text{Co}_5\text{B}_8$ (RE = Nd, Pr, Dy, Tb ; M = Si, Al, Cr) sintered magnets have been examined. It was established that the presence of Re-(Co, Fe, M) compound along the grain boundaries of these alloys was responsible for inhibition of the corrosion in acid solution and in atmospheric environment. The best magnetic properties obtained in these studies are $B_r = 1.26 \text{ T}$ and $M H_c = 1\,730 \text{ kA/m}$ for the $\text{Nd}_{14}\text{DyTbFe}_{70}\text{SiCo}_5\text{B}_8$ alloy.

1. Introduction.

In the last few years the discovery of high energy magnets based on tetragonal $\text{RE}_2\text{Fe}_{14}\text{B}$ (RE = rare earth element) compounds [1-5] has strongly stimulated the search for both RE-Fe high anisotropy phases synthesis and development for low cost processing. The improvement of properties of the $\text{RE}_2\text{Fe}_{14}\text{B}$ -type magnets is possible by substituting one or more other elements. The general tendency to application of alloy additions depends on selection of elements (i) increasing the coercive force with acceptable decrease in remanence, (ii) improving the thermal and time-dependent stability of magnetic properties, (iii) increasing the corrosion resistance of Nd-Fe-B magnets which may be of equal importance in permanent magnet applications [4-6].

The same tetragonal $\text{RE}_2\text{Fe}_{14}\text{B}$ phase is formed with various rare earth elements, but the best permanent magnetic properties may be reached for RE = Nd or Pr [1, 7]. A partial substitution of Dy or Tb for $\text{Nd}_2\text{Fe}_{14}\text{B}$ results in an increase of the hard magnetic properties but it decreases the saturation magnetization [1, 7]. A substitution of part of iron in

$\text{Nd}_2\text{Fe}_{14}\text{B}$ by Co has a beneficial effect on the Curie point, temperature coefficient and slight increase in magnetization (at low concentrations of Co) [8]. Moreover, the addition of this element ($\geq 5 \text{ wt\%}$) significantly improves the corrosion resistance of these magnets [9].

Quite a number of other investigations have dealt with the problem of changing the intrinsic properties of $\text{RE}_2\text{Fe}_{14}\text{B}$ compounds by substituting other elements than Co for one or more of the components of $\text{RE}_2\text{Fe}_{14}\text{B}$ compound. Substitution of Cr, Al and Si causes considerable increase of coercive force [10, 11]. On the other hand, Al and Cr produce quite a drastic lowering but Si causes an increase of the Curie point [12-14]. It should be also noticed that additions of Cr ($\leq 2 \text{ at\%}$), similarly as it has been observed for Co, improve the corrosion resistance of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets [15, 16].

Substitution of C for B in $\text{RE}_2\text{Fe}_{14}\text{B}$ results in the increase of anisotropy field. However, Curie point and saturation magnetization of Nd-containing compounds decrease then [17].

Having in mind the advantageous corrosive and magnetic properties of the Nd-(Fe, Co)-B magnets,

in this work we have taken up the task to improve further the properties of these alloys substituting iron by small quantities of Si, Al, Cr (totally ≤ 4 at%) at simultaneous addition of Dy and Tb and substitution of Nd by Pr. The research work undertaken in this study, in addition to their cognitive value may also be of importance for practical applications of the $\text{RE}_2\text{Fe}_{14}\text{B}$ -type magnets.

2. Experimental.

The sintered magnets

- A. $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- B. $\text{Nd}_{14}\text{DyTbFe}_{70}\text{SiCo}_5\text{B}_8$,
- C. $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{68}\text{SiAl}_2\text{Co}_5\text{B}_8$,
- D. $\text{Pr}_{13}\text{Dy}_3\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- E. $\text{Pr}_{14}\text{NdDyFe}_{68}\text{Al}_3\text{Co}_5\text{B}_8$,
- F. $\text{Pr}_{15}\text{DyFe}_{66}\text{Cr}_4\text{AlCo}_5\text{B}_8$,

were prepared with a powder metallurgical procedure. The alloys were melted in a vacuum induction furnace from 99.7 % or better for rare earths, 99.9 % for Fe. As a source for B, commercially available ferro-boron alloys were used. The ingots were crushed into 250 mesh powders and then ball milled to about $3\text{ }\mu\text{m}$ in alcohol. The powders were aligned in a magnetic field of 1 600 kA/m at a pressure of 200 MPa. The green compacts were sintered at 1 100 °C for two hours in an argon atmosphere and then cooled rapidly to room temperature and annealed at temperature 600 °C for one hour.

In order to minimize the influence of the method of preparation and heat treatment on the analyzed properties, all alloys were prepared in the same way.

Permanent magnet properties were measured by B-H tracer with a maximum magnetized field of 2 400 kA/m.

Metallography (optical and scanning microscopy) was employed to study microstructure of the magnets.

In order to characterize corrosion behaviour of the tested magnets the following corrosion tests were carried out :

1. Acid corrosion test — spontaneous dissolution of the tested samples in non-stirred, Ar-saturated 0.5 M H_2SO_4 solution at 25 °C.
2. Potentiokinetic polarization curves — Ar-saturated solution of 0.5 M Na_2SO_4 , 25 °C, disc rotation rate 13 rps, potential scanning rate 100 mV/min starting at $\varphi = -1.40\text{ V vs. saturated calomel electrode (SCE)}$ up to $\varphi = +2.30\text{ V vs. SCE}$.
3. Abnormal dissolution test — weight loss at strong cathodic polarization ($\varphi = -1.00\text{ V vs. SCE}$, Ar-saturated 0.5 M H_2SO_4 , 13 rps, 25 °C).

4. Accelerated test of atmospheric corrosion in « industrial » atmosphere — exposure of samples in steam-saturated air containing 3 mg SO_2/l , 40 °C ; according to DIN 50018 [18].

5. Acetic acid salt-spray test — exposure in steam-saturated air passed by the solution containing 3 % NaCl in 0.1 N CH_3COOH with the rate of 1.0 l/h at 40 °C ; according to ASTM B 287-62 [18].

Details of apparatus and test method are given in [19, 20].

3. Results and discussion.

3.1 MAGNETIC PROPERTIES AND MICROSTRUCTURE. — The demagnetization curves, magnetic properties and density of the studied magnets are shown in figure 1 and in table I. The band of demagnetization curves in figure 1 shows the magnetic values achieved with alloys of the above composition range. Remanences are 1.050-1.26 T, the coercive forces $B_r H_c \geq 735\text{ kA/m}$ and

Fig. 1. — Demagnetization curves of sintered permanent magnets :

- A) $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- B) $\text{Nd}_{14}\text{DyTbFe}_{70}\text{SiCo}_5\text{B}_8$,
- C) $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{68}\text{SiAl}_2\text{Co}_5\text{B}_8$,
- D) $\text{Pr}_{13}\text{Dy}_3\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- E) $\text{Pr}_{14}\text{NdDyFe}_{68}\text{Al}_3\text{Co}_5\text{B}_8$,
- F) $\text{Pr}_{15}\text{DyFe}_{66}\text{AlCr}_4\text{Co}_5\text{B}_8$.

Table I. — *Magnetic properties and density of sintered $\text{RE}_{16}\text{Fe}_{71-x}\text{M}_x\text{Co}_5\text{B}_8$ permanent magnets.*

No.	Compound	Magnetic properties			Density d (g/cm ³)
		B_r (T)	$B_r H_c$ (kA/m)	$M H_c$ (kA/m)	
A	$\text{Nd}_{14}\text{Dy}_2\text{Fe}_{71}\text{Co}_5\text{B}_8$	1.11	800	1 600	7.45
B	$\text{Nd}_{14}\text{DyTbFe}_{70}\text{Co}_5\text{SiB}_8$	1.26	780	1 730	7.40
C	$\text{Nd}_{14}\text{Dy}_2\text{Fe}_{68}\text{SiAl}_2\text{Co}_5\text{B}_8$	1.17	880	1 280	7.47
D	$\text{Pr}_{13}\text{Dy}_3\text{Fe}_{71}\text{Co}_5\text{B}_8$	1.15	815	1 440	7.43
E	$\text{Pr}_{14}\text{NdDyFe}_{68}\text{Al}_3\text{Co}_5\text{B}_8$	1.25	760	1 180	7.40
F	$\text{Pr}_{15}\text{DyFe}_{66}\text{AlCr}_4\text{Co}_5\text{B}_8$	1.07	735	1 345	7.39

$MH_c \geq 1\,160$ kA/m. As are expected the most favourable magnetic properties ($B_r = 1.26$ T, $MH_c = 1\,730$ kA/m) have been achieved for $Nd_{14}DyTbFe_{70}SiCo_5B_8$, since small additions of Dy and Tb form $RE_2Fe_{14}B$ phase with the highest anisotropies and greatly enhances the coercive force of the $RE_2Fe_{14}B$ base magnet [1]. Therefore, the additions of these elements efficiently counteract the decrease in the intrinsic coercive force and the deterioration of the squareness of the demagnetization curve. This latter phenomenon is caused by substitution of Fe by Co in the alloy. A partial substitution of Fe by Al and Cr decreases remanence (B_r) and maximum energy product ($(BH)_{max}$) and increases intrinsic coercive force (MH_c) [21-23]. It can also be seen from figure 1 and table I that magnetic properties of the $(PrRe)_{16}(FeM)_{71}Co_5B_8$ magnets are much lower than those of $(NdRE)_{16}(FeM)_{71}Co_5B_8$. This result is slightly astonishing because according to works of Sagawa *et al.* [1] and Croat *et al.* [2] $Pr_2Fe_{14}B$ compound produces almost the same properties as those of $Nd_2Fe_{14}B$ compound. On the other hand, Jiang *et al.* [24] found that the intrinsic coercive force of the $PrFeB$ magnets is about 50 % higher than that of the $NdFeB$ magnets, but B_r and $(BH)_{max}$ of $NdFeB$ magnets are slightly higher than those of $PrFeB$ magnets because of the higher magnetic moment of rare-earth ion (Nd) of the former. The values of coercive force which we have obtained for the sintered $(PrRE)_{16}(FeM)_{71}Co_5B_8$ magnets are lower than for the magnets of type $(NdRE)_{16}(FeM)_{71}Co_5B_8$. The microstructure of the alloys of the type $(PrRE)_{16}(FeM)_{71}Co_5B_8$ with $M = Cr$ and Al shows, in comparison with the alloy without additions, fine grains with high homogeneity

(Fig. 2b and d) which is a contributing factor to the increase of coercive force; a small mean grain size in the sintered magnets makes the magnetic isolation of individual grains larger and yields a large coercive force [25]. The experimental density values were found to be similar for all samples (see Tab. I), suggesting that the observed magnetic property variations may be due to differences in the phase distribution and not densification with the samples.

The high coercive force and high energy products of sintered Nd-Fe-B alloy were obtained for compositions with both Nd and B slightly more rich than the stoichiometric composition of Nd-Fe-B tetragonal phase ($Nd_2Fe_{14}B$). This alloy is composed mainly of three phases, namely, the hard magnetic tetragonal $Nd_2Fe_{14}B$ matrix, a grain boundary Nd-rich phase containing more than 80 at% Nd and paramagnetic B-rich phase, close to tetragonal $NdFe_4B_4$ phase [26-28].

The microstructure of the tested sintered magnets is characteristic for the sintered RE-Fe-B type magnets. Figure 2 shows, for comparison, an SEM composition micrographs of sintered alloys of $Nd_{14}DyTbFe_{70}SiCo_5B_8$ (B-alloy) and

(F-alloy). In the picture of microstructure equiaxial grains of the matrix 2 : 14 : 1 type phase are visible (Fig. 2a), divided by grain boundary or regions containing $Nd(Fe, Co)_2$ phase (bright precipitate). Moreover, a small amount of grains of the 1 : 4 : 4 type phase are apparent, in particular, in figure 2c (dark-grey precipitate). The Dy and Tb do not form additional phases, but they enter into the composition of identified phases. Co exists in the compo-

Fig. 2. — Back scattering electron image of sintered $Nd_{14}DyTbFe_{70}SiCo_5$ (a, c) and $Pr_{15}DyFe_{66}AlCr_4Co_5B_8$ (b, d) permanent magnets.

sition of both 2 : 14 : 1 and 1 : 4 : 4 phases. However, the latter phase contains greater amount of this element. The equal quantities of the Cr and Al elements enter into the composition of 2 : 14 : 1 and 1 : 4 : 4 phases. It is worth noting that the amount of the 1 : 4 : 4 phase in the alloy which contains Cr is much lower in comparison with the alloy not containing this element. Moreover, besides $\text{Nd}(\text{Fe}, \text{Co})_2$ phase, precipitate containing ~ 60 at% of Fe and ~ 40 at% of Cr are apparent on the grain boundaries. The Al addition does not change the phase composition of the studied alloys and this element enters into the 2 : 14 : 1, $\text{Nd}(\text{Fe}, \text{Co})_2$ and 1 : 4 : 4 phases in proportion 3 : 1 : 1, respectively.

Finally we should emphasize that, in the studied alloys with addition of 5 at % of Co, the RE-rich phase completely turns into RE-Co intermetallic compound. This fact is very important and advantageous because free RE metal at the grain boundaries owing to its great chemical reactivity easily corrodes, which quickly deteriorates magnetic properties of the material, and consequently, limits the application of the magnet.

3.2 CORROSION TESTS.

3.2.1 Acid corrosion test. — The kinetic curves of etching of the alloys tested in the 0.5 M H_2SO_4 solution, presented in figure 3, show similar courses. After initial period (4–6 min) in which etching of the Nd- and B-rich grain boundaries occurs, the corro-

Fig. 3. — Kinetic curves of etching of sintered $\text{RE}_{16}\text{Fe}_{71-x}\text{M}_x\text{Co}_5\text{B}_8$ magnets in 0.5 M H_2SO_4 solution (25 °C, no stirring) :

- A) $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- B) $\text{Nd}_{14}\text{DyTbFe}_{70}\text{SiCo}_5\text{B}_8$,
- C) $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{68}\text{SiAl}_2\text{Co}_5\text{B}_8$,
- D) $\text{Pr}_{13}\text{Dy}_3\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- E) $\text{Pr}_{14}\text{DyNdFe}_{68}\text{Al}_3\text{Co}_5\text{B}_8$,
- F) $\text{Pr}_{15}\text{DyFe}_{66}\text{AlCr}_4\text{Co}_5\text{B}_8$.

Filled circles — $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy.

sion rate reaches the values characteristic for individual alloys, $[\text{mg}/\text{cm}^2 \text{ h}]$: A-250, F-180, B-150, E-140, C-130, D-100. For comparison, the $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy (without additions) corrodes in the same solution with the rate of $360 \text{ mg}/\text{cm}^2 \text{ h}$ [16]. The determined rates of acid corrosion of the magnets tested are 200–500 times greater than those of carbon steel ($v_{\text{corr}} = 0.5 \text{ mg}/\text{cm}^2 \text{ h}$). The abnormally high values of acid corrosion rate of the alloys examined result from separation of grains of the basic 2 : 14 : 1 type phase from the surface of magnets, after previous selective etching of regions on the Nd- and B-rich grain boundaries.

3.2.2 Polarization curves. — In figure 4 the polarization curves of the magnets tested in Ar-saturated 0.5 M Na_2SO_4 solution are presented. From the course of the curves presented it results that within

Fig. 4. — Potentiokinetic polarization curves of sintered $\text{RE}_{16}\text{Fe}_{71-x}\text{M}_x\text{Co}_5\text{B}_8$ permanent magnets in 0.5 M Na_2SO_4 solution :

- A) $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- B) $\text{Nd}_{14}\text{DyTbFe}_{70}\text{SiCo}_5\text{B}_8$,
- C) $\text{Nd}_{14}\text{Dy}_2\text{Fe}_{68}\text{SiAl}_2\text{Co}_5\text{B}_8$,
- D) $\text{Pr}_{13}\text{Dy}_3\text{Fe}_{71}\text{Co}_5\text{B}_8$,
- E) $\text{Pr}_{14}\text{DyNdFe}_{68}\text{Al}_3\text{Co}_5\text{B}_8$,
- F) $\text{Pr}_{15}\text{DyFe}_{66}\text{AlCr}_4\text{Co}_5\text{B}_8$.

Solide line — $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy, dotted line—pure iron.

the cathodic range the rate of hydrogen depolarization process of the magnets with the tested additions is ca. 10 times lower than that of the magnet without these additions. This produces much lower absorption of hydrogen by the surface and lack of hydrogen (or hydrides) oxidation at more positive potentials (-1.0 – -0.8 V). The process of oxidation of hydrogen absorbed is distinct only in the case of the $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ magnet. For the tested alloys, within the range of active dissolution, the course of potentiokinetic polarization curves (except of alloy F) is practically identical and shows Tafel behaviour with the slope $b_a = 0.03$ – 0.04 V. Extrapolation of linear segments of anodic curves to φ_{corr} gives the value of corrosion current of the order of 0.1 mA/cm^2 ($\sim 0.1 \text{ mg/cm}^2 \text{ h}$). Similar values of v_{corr} were obtained by longlasting exposure of the tested magnets in some neutral Na_2SO_4 solutions ($\text{pH} = 6$ – 8). In similar conditions pure iron corrodes only 2–3 times slower. Furthermore, from the course of polarization curves it results also that within the active range the anodic process of the F-alloy (containing 4 at% Cr) is considerably inhibited as compared with the remaining alloys. The alloys tested, in contradistinction to pure iron, do not passivate practically in the neutral sulphate solution though the anodic current decreases distinctly at $\varphi > 0.8$ V. It should be, however, noticed that at $\varphi > 0.8$ V the anodic current densities are within the range of 10 mA/cm^2 . Therefore, one cannot tell about effective passivation of the alloys tested. Anyway, this tendency to passivation is the strongest for alloys A, B, C and F and the weakest for alloys E and D.

At potentials $\varphi \geq 1.5$ V, due to oxygen production, the anodic current raises again. For the alloys tested, this process does not occur according to the Tafel mechanism, as in the case of pure iron at $\varphi > 1.3$ V.

3.2.3 Abnormal dissolution. — The corrosion rates of the magnets tested in $0.5 \text{ M H}_2\text{SO}_4$ solution at external potential -1.0 V (SCE) are listed in table II. The cathodic current for the majority of alloys is close to 1 A/cm^2 for the potential applied and only for alloy A it is significantly lower whereas for alloy B, ca. 3 times greater. All the tested alloys at this cathodic potential corrode much slower (especially alloy D) as compared with $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy. In comparing the corrosion rate of magnets at strong cathodic polarization with rates of spontaneous dissolution (Fig. 4), it results that the values of these rates are similar only for alloys B and E. Then, for alloys C, D and F, corrosion at cathodic polarization performs 2–3 times faster than at the corrosion potential. The corrosion rate at cathodic polarization, as compared with spontaneous dissolution rate is slower only for alloy A.

The data given in table II do not allow one to draw

Table II. — Corrosion rate of sintered $\text{RE}_{16}\text{Fe}_{71-x}\text{M}_x\text{Co}_5\text{B}_8$ magnets at strong cathodic polarization (15 min, Ar — $0.5 \text{ M H}_2\text{SO}_4$, 13 rps, $\varphi = -1.0$ V vs. SCE).

No.	Compound	External cathodic current i (mA/cm^2)	Corrosion rate v_{corr} ($\text{mg/cm}^2 \text{ h}$)
A	$\text{Nd}_{14}\text{Dy}_2\text{Fe}_{71}\text{Co}_5\text{B}_8$	640	80
B	$\text{Nd}_{14}\text{DyTbFe}_{70}\text{SiCo}_5\text{B}_8$	2 800	160
C	$\text{Nd}_{14}\text{Dy}_2\text{Fe}_{68}\text{SiAl}_2\text{Co}_5\text{B}_8$	1 060	210
D	$\text{Pr}_{13}\text{Dy}_3\text{Fe}_{71}\text{Co}_5\text{B}_8$	820	290
E	$\text{Pr}_{14}\text{NdDyFe}_{68}\text{Al}_3\text{Co}_5\text{B}_8$	910	270
F	$\text{Pr}_{15}\text{DyFe}_{66}\text{AlCr}_4\text{Co}_5\text{B}_8$	1 010	150
—	$\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$	880	370

more quantitative conclusions regarding the effect of the alloy additions on the rate of abnormal dissolution. Rather generally distinct decrease of this type of corrosion as compared with the initial alloy should be connected with addition of 5 at% Co to the alloy. In fact, according to Ohashi *et al.* [9], the increase in Co content in the intergranular phase of the Nd-Fe-B-type magnets leads to inhibition of the rate of its selective dissolution. This can explain the greater immunity of the tested magnets during cathodic exposition as compared with $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy.

3.2.4 Atmospheric corrosion. — The results of accelerated tests of the kinetic of atmospheric corrosion of the magnets tested and, for comparative purposes, of carbon steel and $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ magnet are presented in figure 5. From the course of the curves obtained, it results that in « industrial » environment (Fig. 5a) only alloy D corrodes with the rate close to that of the initial alloy ($0.072 \text{ mg/cm}^2 \text{ h}$). The alloys A, B, C and E have shown corrosion rates within the range 0.040 – $0.050 \text{ mg/cm}^2 \text{ h}$, i.e. the values lower than that for carbon steel ($v_{\text{corr, steel}} = 0.058 \text{ mg/cm}^2 \text{ h}$). The lowest corrosion rate in the « industrial conditions » ($v_{\text{corr}} \sim 0.02 \text{ mg/cm}^2 \text{ h}$) has been shown by the alloy F that should be connected with the advantageous effect of Cr addition [16]. In more aggressive, from the corrosion point of view, environment of salt-spray (Fig. 5b) the magnets A, B, C and D corrode a little faster ($v_{\text{corr}} \sim 0.43 \text{ mg/cm}^2 \text{ h}$) as compared with $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy ($v_{\text{corr}} = 0.33 \text{ mg/cm}^2 \text{ h}$). The lowest corrosion rate ($v_{\text{corr}} \sim 0.17 \text{ mg/cm}^2 \text{ h}$) in these conditions exhibits magnet F, similarly as it has been observed in SO_2 -containing environment. For comparison, v_{corr} for carbon steel equals to $0.20 \text{ mg/cm}^2 \text{ h}$ in these conditions.

Finally, it should be added that the tests of atmospheric corrosion have generally shown low adherence of corrosion products to the surface of magnets tested (except for magnet F).

Fig. 5. — Kinetics of atmospheric corrosion of sintered RE₁₆Fe_{71-x}M_xCo₅B₈ permanent magnets and, for comparison, of carbon steel and sintered Nd₁₅Fe₇₇B₈ magnet in humid air atmosphere containing 3 mg SO₂/l (a) and in salt spray (b) :

- A) Nd₁₄Dy₂Fe₇₁Co₅B₈,
 B) Nd₁₄DyTbFe₇₀SiCo₅B₈,

- C) Nd₁₄Dy₂Fe₆₈SiAl₂Co₅B₈,
 D) Pr₁₃Dy₃Fe₇₁Co₅B₈,
 E) Pr₁₄DyNdFe₆₈Al₃Co₅B₈,
 F) Pr₁₅DyFe₆₆AlCr₄Co₅B₈.

Filled circles — Nd₁₅Fe₇₇B₈ alloy, filled squares carbon-steel.

4. Conclusions.

The investigations of the microstructure of the sintered permanent magnets RE₁₆Fe_{71-x}M_xCo₅B₈ (RE = Nd, Pr, Dy, Tb; M = Si, Al, Cr) reveal the individual large grains of the RE₂(Fe, M, Co)₁₄B phase, smaller grains of the phase RE(Fe, M, Co)₄B₄ being irregularly distributed between the grain matrix, and effectively isolated by pores and Nd-(Fe, Co, M) intermetallic compound. This type of structure seems to render an effective barrier of domain wall nucleation and limits good hard magnetic properties of the investigated alloys.

The existence of the RE-(Fe, Co, M) intermetallic

compound along the grain boundaries distinctly improves corrosion resistance of the magnets, which appears in decreasing of the acid and atmospheric corrosion rates in industrial environment. The abnormal dissolution process of these magnets is also restrained. Substitution of Fe by 4 at% of Cr in the Co-containing alloy causes considerable inhibition of the atmospheric corrosion rate which achieves the values much lower than for carbon steel. The improvement of the corrosion resistance of the RE₁₆Fe_{71-x}M_xCo₅B₈ magnets (as compared with magnets without Co and other alloying elements) gives new possibilities of application of these magnets in various environments.

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