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The effect of Cr, Co, W, Zr and Pb (M) substitution on the structure and corrosion resistance of nanocrystalline $Nd_{10}Fe_{84-x}M_xB_6$ magnets

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The effect of partial substitution of iron with Cr, Co, W, Zr or Pb in nanocrystalline $Nd_{10}Fe_{84-x}M_xB_6$ magnetic material on general corrosion in acidified sulphate environment is discussed in the paper. The materials were produced from spec pure powders of Nd, Fe, Fe–B and additive powders (Cr, Co, W, Zr or Pb) by mechanical alloying. The structural analysis was performed using a JEOL JEM 1200 TEM microscope and the stereological parameters of the microstructures were determined. The magnetic properties were measured with a pulse field hysteresigraph. The following substitutions are the most favourable in terms of the magnetic properties of nanocrystalline $Nd_{10}Fe_{84-x}M_xB_6$ magnets: cobalt (10 at. %), chromium (4 at. %), tungsten (15 at. %), lead (1.5 at. %) and zirconium (2 at. %). The samples for corrosion investigations were prepared from annealed powders by shock compaction. For electrochemical tests, electrodes made from the samples in the form of rotating discs were used. Resistance to general corrosion of the tested materials was evaluated by potentiokinetic polarisation tests. It was shown that the applied additions inhibit the corrosion process by up to 2–3 times. Chromium, cobalt and lead additives facilitate passivation of the alloys.

Key words: *corrosion; passivation; permanent magnets; nanocrystalline materials*

1. Introduction

Partial substitution, either of neodymium with other lanthanides or of iron with other transition metals, appeared to be an effective method of modifying magnetic properties of Nd–Fe–B-type magnets. A systematic classification of the elements that can substitute Fe in Nd–Fe–B magnets with more than 11.9 at. % of Nd was put forward by Fidler [1, 2]. The additives can be classified into those that dissolve in the $Nd_2Fe_{14}B$ ferromagnetic phase and those that occur in the form of inclusions. Among

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the latter group of elements, one can distinguish two types of additives: (i) additives forming new phases within the grain boundary area and dissolving in the Nd-rich eutectic thereby lowering the melting temperature and (ii) additives occurring in the form of inclusions enriched with Fe or B. Although Fidler's classification is valid for high-neodymium alloys, there is, however, strong evidence that this classification can also be used for nanostructured, low neodymium magnets [3, 4]. The magnetic properties of these materials can depend on: (i) intrinsic properties of the hard magnetic phase, (ii) grain size, (iii) interaction between the domain walls and the inclusions, (iv) change of the phase composition. Some of these factors and features strongly affect the corrosion resistance [5].

In modified sintered Nd–Fe–B-type magnets, iron is usually partially substituted by other transition metals. Their alloy contents may amount to 1–20 at. %. Small additions of chromium [6, 7] and large additions of cobalt [8] are considered to be the most favourable in enhancing the corrosion resistance of the sintered material.

The corrosion behaviour of a material is influenced both by its phase structure and by its grain size. In nanocrystalline materials, the order of magnitude of the grain size is in the 10–20 nm range, and the phase structure is different from that in sintered materials. In general, nanocrystalline materials exhibit higher corrosion resistance [9–11]. Alloy additives in nanomaterials may thus have an essentially different effect on corrosion processes than in the case of sintered materials. Within the present study, the effect of partial substitution of iron with such elements as Cr, Co, W, Zr and Pb on the corrosion behaviour of $Nd_{10}Fe_{84-x}M_xB_6$ nanocrystalline materials in acidified sulphate solutions was investigated.

2. Experimental

Nanocrystalline $Nd_{10}Fe_{84-x}M_xB_6$ materials (M = Cr, Co, W, Zr or Pb; the values of x were chosen in terms of optimum magnetic properties, Table 1) were tested. The materials were produced from spec pure powders of Nd, Fe, Fe-B and additive powders (Cr, Co, W, Zr or Pb) by mechanical alloying (MA). The mixture of the powders was milled in a high energy ball mill in a protective argon atmosphere for 90 h. The powders thus obtained, composed of an amorphous phase and Fe crystallites, were annealed in vacuum of 10^{-3} Pa at the temperature of 650 °C for 0.5 h. The magnetic properties were measured with a pulse field hysteresigraph, using the field of 4 T. The samples for investigations of corrosion were prepared from annealed powders by shock compaction. The details of the compacting systems are described in [12]. In our experiments, we used a two-stage process that included preliminary and final compaction carried out at detonation wave speeds of 3800 and 5240 m/s, respectively. The structural analysis was performed using a JEOL JEM 1200 TEM microscope and the stereological parameters of the microstructures were determined. For electrochemical tests, electrodes made from the above-mentioned samples in the form of rotating discs with an operating surface area of 0.1 cm^2 were used.

Table 1. Effect of the iron substitution in $Nd_{10}Fe_{84-x}M_xB_6$ (M = Cr, Co, W, Zr or Pb) nanocrystalline material on coercivity (H_c) and remanence (B_r)

Substitution	Coercivity H_c [kOe]	Remanence B_r [T]
–	2.90	0.83
1 at. % Cr	2.67	0.50
4 at. % Cr	3.65	0.61
7 at. % Cr	2.87	0.57
5 at. % Co	3.95	0.83
10 at. % Co	4.53	0.88
20 at. % Co	3.22	0.86
2 at. % W	3.48	0.74
15 at. % W	6.79	0.47
28 at. % W	10.78	0.22
2 at. % Zr	4.30	0.69
5 at. % Zr	4.17	0.98
0.5 at. % Pb	2.87	0.68
1.5 at. % Pb	2.11	0.70
3 at. % Pb	0.82	0.67

The resistance to general corrosion of the tested materials was evaluated by potentiokinetic polarisation tests. Polarisation measurements were carried out in deaerated (argon saturated) acidified sulphate solutions (pH = 3.0) at the temperature of 25 °C, at the disc rotation speed of 16 rps and at the potential scanning rate of 10 mV/s. A CHI 680 potentiostat (CH Instruments, Austin, Texas, USA) was used to record potentiokinetic polarisation curves. The values of electrode potentials were measured with respect to a saturated calomel electrode (SCE).

3. Results and discussion

The effect of the M = Cr, Co, W, Zr or Pb additives on the magnetic properties (coercivity and remanence) of nanocrystalline $Nd_{10}Fe_{84-x}M_xB_6$ magnets has been described in our earlier papers [3, 4, 13]. Co is the most frequently used substituent, which substitutes Fe in the $Nd_2Fe_{14}B$ phase. Zr, Cr, and W are substituents of type II, whereas Pb is a substituent of type I [1, 3, 4, 13]. The experiments with the Nd–Fe–Co–B magnets processed by mechanical alloying (MA) show that an addition of Co improves both the remanence and coercivity [13]. This improvement is due to the reduction of the grain size, which enhances magnetic exchange interactions. The TEM observations were performed with the $Nd_{10}Fe_{84}B_6$ and $Nd_{10}Fe_{64}Co_{20}B_6$ magnets (Figs. 1a, c). Although the microstructure was heterogeneous (larger and smaller grains), the substitution of 20 at. % Fe with Co results, in general, in the reduction of

the mean equivalent diameter from 18.9 nm in the Co-free magnets to 7.9 nm in the Co-enriched material [4]. The effect of tungsten content has been described in [3].

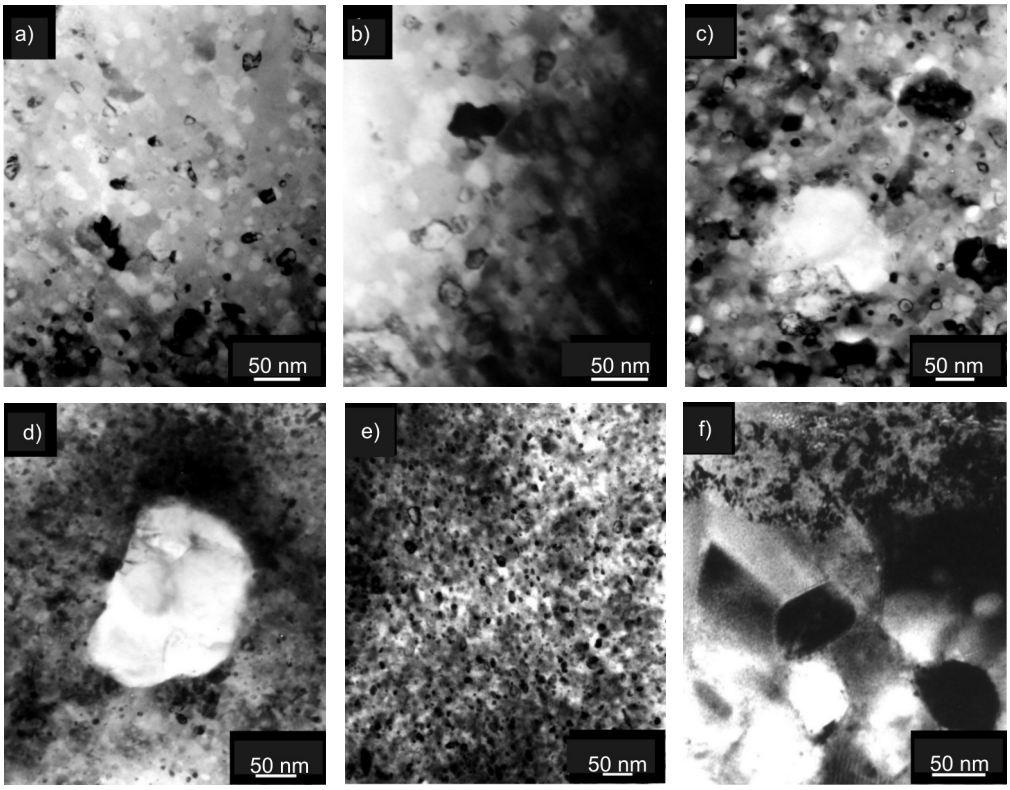

Fig. 1. TEM images of shock compacted samples with optimal magnetic properties: a) $Nd_{10}Fe_{84}B_6$, b) $Nd_{10}Fe_{80}Cr_4B_6$, c) $Nd_{10}Fe_{64}Co_{20}B_6$, d) $Nd_{10}Fe_{56}W_{28}B_6$, e) $Nd_{10}Fe_{79}Zr_5B_6$, f) $Nd_{10}Fe_{82}Pb_{1,5}B_6$

It was found that the addition of W leads to a substantial increase in the coercivity and a decrease in the remanence. An X-ray phase analysis showed that the material annealed at 650 °C contained practically pure W inclusions (magnets annealed at 850 °C contained the FeWB phase). The mean equivalent grain diameter in the magnets containing 28 at. % W was 10.2 nm and was smaller than that in the W free material which was 18.9 nm (compare Figs. 1a and d). An addition of Cr [4] results in the formation of Fe containing inclusions, and a decrease in the mean equivalent grain size diameter (in the $Nd_{10}Fe_{80}Cr_4B_6$ magnet, its measured value was 13.9 nm). However, the TEM studies also revealed the presence of large precipitates, testifying that Cr reacted with the basic alloying elements (Fig. 1b). A similar microstructure was observed in the microcrystalline magnets with a Zr content [4]. The Zr addition results in a strong reduction of the grain size and the effect is more distinct than that observed with Cr, Co and W. The mean equivalent diameter in the $Nd_{10}Fe_{79}Zr_5B_6$ magnets was as small as 7.2 nm. As with the magnets containing Cr, the magnets with Zr additive

contain large Zr-rich inclusions (above 50 nm in size, Fig. 1e). TEM observations of the material with Pb additive confirm that a new phase component has appeared (Fig. 1f). Fine grain areas occur together with a typical 80 nm grain structure. The microstructure evidently contains the Nd_5Pb_3 or Nd_2Pb phase, probably formed as a result of decomposition of the hard magnetic phase, and, thus, it also contains small Fe crystals [4]. The fine grain areas were about 100 nm wide. The addition of Pb increases the mean equivalent diameter (for the magnet with 1.5 at. % Pb it was evaluated to be 81.6 nm).

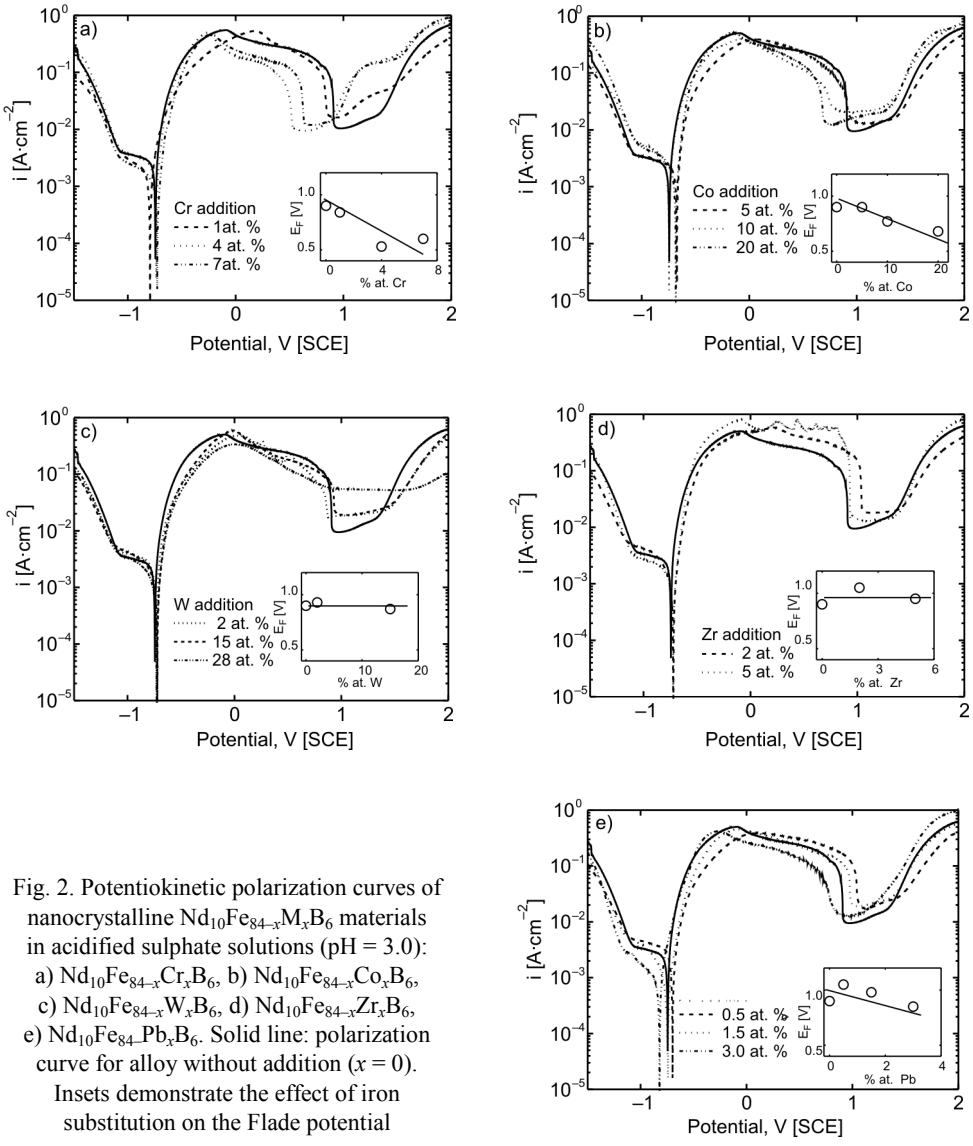

Fig. 2. Potentiokinetic polarization curves of nanocrystalline $Nd_{10}Fe_{84-x}M_xB_6$ materials in acidified sulphate solutions (pH = 3.0): a) $Nd_{10}Fe_{84-x}Cr_xB_6$, b) $Nd_{10}Fe_{84-x}Co_xB_6$, c) $Nd_{10}Fe_{84-x}W_xB_6$, d) $Nd_{10}Fe_{84-x}Zr_xB_6$, e) $Nd_{10}Fe_{84}Pb_xB_6$. Solid line: polarization curve for alloy without addition ($x = 0$). Insets demonstrate the effect of iron substitution on the Flade potential

In strongly acidic sulphate environments (pH = 0.3), where the corrosion behaviour of Nd–Fe–B-type sintered materials results from the electrochemical activity of rare earth metals, no major differences in the corrosion behaviour of Nd-(Fe,M)-B materials were established [6], therefore a less aggressive environment was chosen for corrosion tests within the present study. In medium acid solutions the mass loss of specimens is smaller, while the differences in the shape of the polarization curves are more distinct. The electrochemical tests were carried out in acidified sulphate solutions with pH = 3.0, due to, among others, a good repeatability of polarization curves and small changes in pH at the corroding surface during the experiment [6]. The sulphate solution of pH = 3.0 is, for the specimens tested, an environment, where the corrosion is controlled by diffusion (H^+ ion reduction current in the potential range from –1.2 to –0.8 V at the electrode rotation speed of 16 rps takes on the form of a limiting current with the density of 2–3 mA·cm^{-2}). In this environment, the materials tested exhibit a tendency to passivation, being dependent on the type and amount of the additive in the material. The most significant tendency to passivation is observed for the addition of chromium (Fig. 2). Figure 2a shows that the addition of 1 at. % of Cr does not considerably affect the shape of the curves. On the other hand, the additions of 4 and 7 at. % of Cr shift the Flade potential (the potential of transition into a passive state, E_F) of $Nd_{10}Fe_{84-x}Cr_xB_6$ material to a more negative value. This potential is 0.90 V for the specimen with no addition of Cr and 0.52 V (SCE) for the specimen containing 4 at. % Cr (compare the inset in Fig. 2a). Although Cr addition facilitates passivation, the width of the passive range for alloys containing 4 and 7 at. % Cr decreases due to the transpassive dissolution of Cr for $E > 1.0$ V ($2Cr + 7H_2O - 12e \rightarrow Cr_2O_7^{2-} + 14\ H^+$). The beneficial effect of Co is visible for the additions of 10 and 20 at. % (Fig. 2b). Although pure Co and RE-Co alloys do not passivate in either acid or neutral environments [14, 15], the increase in Co content facilitates the transition into the passive state of the nanocrystalline materials tested, similarly as it was in the case of sintered materials [8]. As can be seen from Fig. 2c, tungsten additions of up to 15 at. % have little effect on the corrosion behaviour of the Nd–(Fe,W)–B material. The additions up to 15 at. % W practically do not affect the value of E_F and only slightly increase (from 0.01 to 0.02 A·cm^{-2}) the value of the minimum current in the passive region. However, further increase in the tungsten content to 28 at. % unexpectedly decreases the material tendency to passivation: the transition into the passive state becomes poorly pronounced for this material, and the minimum current densities in the potential range from 1.0 to 1.5 V are comparatively high (0.05 A·cm^{-2}). The additions of 2–5 at. % of Zr slightly worsen the tendency to passivate the material (Fig. 2d) similarly as small additions of Pb (Fig. 2e). A greater amount of Pb in the alloy (3 at. % Pb) enhances the passivation process.

In Figure 3, the linear polarisations for potentials close to E_{cor} are presented. Based on the determined polarization resistances* $R_p = (\Delta E/\Delta i)_{E \rightarrow E_{cor}}$ it has been established

*According to Stearn and Geary [16,17], at potentials close to E_{cor} the dependence $E = f(i)$ is linear and the greater slope of $\Delta E/\Delta i$, the smaller is corrosion rate $i_{cor} = B(\Delta i/\Delta E)$, where B is a constant dependent on anodic and cathodic Tafel slopes.

that all additions investigated inhibit corrosion processes in the tested sulphate environment. The polarization resistance of the material without additions is 7.7 Ω·cm^2.

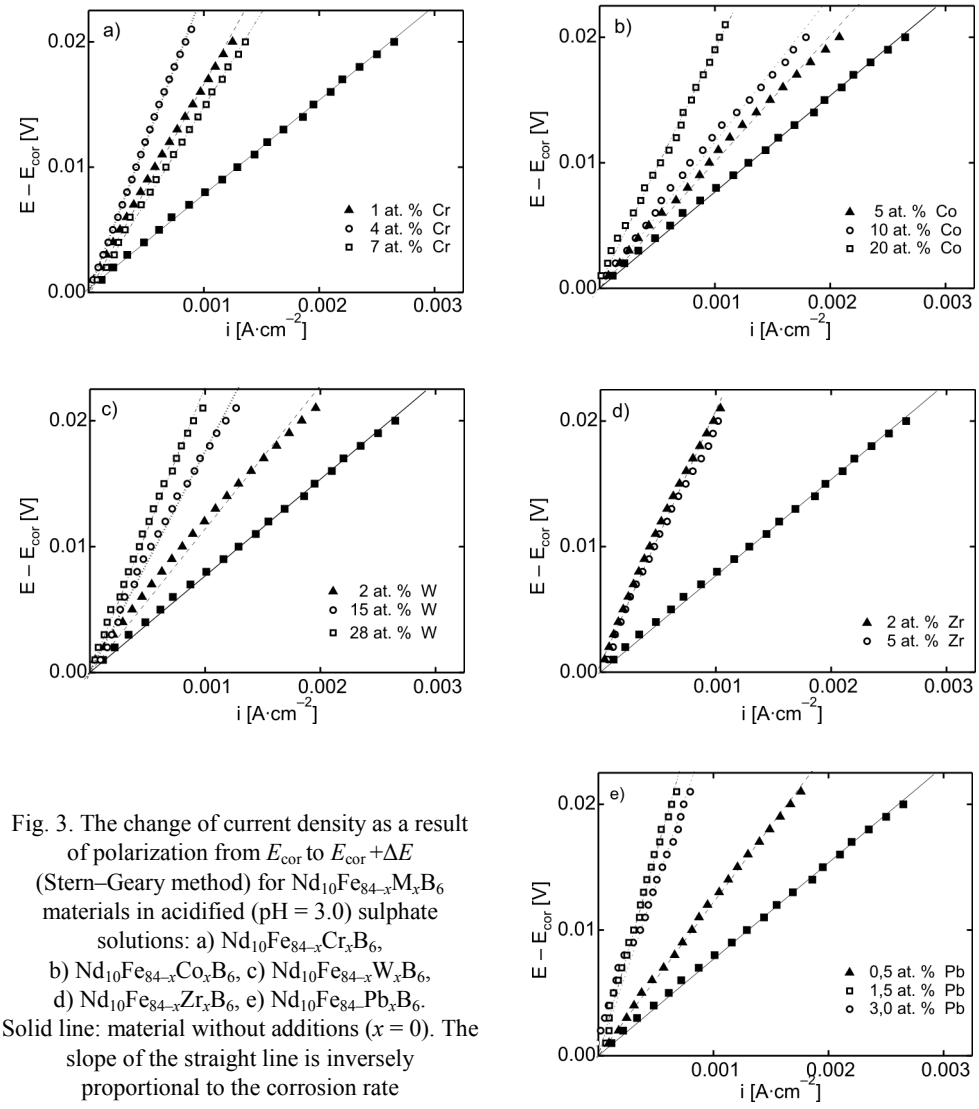

Fig. 3. The change of current density as a result of polarization from E_{cor} to $E_{cor}+\Delta E$ (Stern–Geary method) for $Nd_{10}Fe_{84-x}M_xB_6$ materials in acidified (pH = 3.0) sulphate solutions: a) $Nd_{10}Fe_{84-x}Cr_xB_6$, b) $Nd_{10}Fe_{84-x}Co_xB_6$, c) $Nd_{10}Fe_{84-x}W_xB_6$, d) $Nd_{10}Fe_{84-x}Zr_xB_6$, e) $Nd_{10}Fe_{84-}Pb_xB_6$. Solid line: material without additions (x = 0). The slope of the straight line is inversely proportional to the corrosion rate

A particularly clear corrosion inhibition effect is visible for 1.5 at. % of Pb (R_p = 27 Ω·cm^2), and for 4 at. % Cr (R_p = 24 Ω·cm^2). However, in the case of greater amounts of Co and W, the corrosion resistance is also very high and equal to 19-22 Ωcm^2. It should be noted, however, that such high contents of the above-mentioned alloying additives cannot be used in practical applications because the additives worsen the magnetic properties of the nanocrystalline material (see Table 1). If the considered additives are used in smaller quantities, the inhibition of corrosion is rather

negligible. The results obtained for nanocrystalline magnets are similar to those found for sintered Nd(Fe,M)B materials [18, 19]: the additives improve the corrosion behaviour of the magnets, however improvement is generally insufficient.

4. Conclusions

The following substitutions for iron are the most favourable in terms of the magnetic properties of nanocrystalline $Nd_{10}Fe_{84-x}M_xB_6$ magnets: cobalt (10 at. %), chromium (4 at. %), tungsten (15 at. %), lead (1.5 at. %) and zirconium (2 at. %).

The most pronounced tendency to passivation was observed for the magnets containing chromium (> 4 at. %), cobalt (>10 at. %) and lead (3 at. %). Tungsten has no effect on the tendency to passivate in the acidified sulphate environment, while zirconium slightly impairs the passivation ability of the material.

The metals substituting iron in the present study inhibit the corrosion process in an acidified medium by a factor of 2–3.

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