

Electrochemical corrosion characteristics of RETiCo_{11} compounds

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Abstract

The corrosion behaviour of six RETiCo_{11} permanent magnet compounds (RE=Y, Pr, Nd, Sm, Gd or Dy) in sulphate solutions with pH=0–4 and in acetic acid salt spray were investigated. It was found that the tested RETiCo_{11} magnets were much more corrosion resistant than the alternative Nd–Fe–B and Sm–Co material. The kind of RE element in the magnet composition has practically no influence on the corrosion rates in the tested environments.

Keywords: Electrochemical corrosion; Permanent magnets

1. Introduction

Intermetallic compounds of rare earth (RE) elements and transition metals (TM) exhibit exceptionally advantageous permanent magnet properties and therefore they have found numerous applications over the last 20 years. Recent permanent magnet research has proceeded along with the improvement of the properties of Nd–Fe–B by alloying additions and by processing, the exploration of other alloy systems that feature tetragonal compounds of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ type and the systematic study of new magnetic compounds based on the ThMn_{12} structure [1,2]. The new permanent magnets based on the $\text{Sm}(\text{Fe}, \text{Ti})_{12}$ compound are considered to be competitive with the well known Nd–Fe–B-type magnets [2,3]. The intrinsic properties of RETM_{12} are comparable to those of $\text{RE}_2\text{Fe}_{14}\text{B}$ and can even be improved by Co substitution [3–5]. A systematic investigation of the magnetic properties of RETiCo_{11} compounds has been recently performed by Ohashi et al. [3]. It is worth noting that the new RETM_{12} -type compounds consist of ca. 17 wt.% of RE, i.e. half as much as commonly applied commercial magnets, e.g. Sm–Co and Nd–Fe–B. Thus it can be expected that the RETM_{12} -type permanent magnets will be more corrosion resistant. The corrosion behaviour of the RETM_{12} -type magnets, however, has not been tested yet.

As is known, the poor resistance to corrosion of the Sm–Co and Nd–Fe–B magnets in many environments results from the presence of relatively high amounts

of RE elements (30–35 wt.%) in their composition [6–9]. The RE elements are among the most electrochemically active metals, the standard potentials for RE^{3+}/RE systems being -2.6 to -2.0 V [10]. Especially sensitive to corrosion attack is the so called Nd-rich phase (Nd_4Fe) located between grains of the ferromagnetic phase ($\text{Nd}_2\text{Fe}_{14}\text{B}$) in Nd–Fe–B type magnets. The fast oxidation of the Nd-rich phase, especially in acidified, wet environments, shows sometimes drastic forms and leads to surface degradation and pulverization of the material [11,12]. In recent papers [6–9] we have shown that partial substitution of Fe by different TM elements allows the corrosion process of RE–Fe–B alloys to be inhibited 3–6-fold, but this is far too insufficient to protect the material against corrosion. The only promising method for distinct inhibition of corrosion of both Sm–Co- and Nd–Fe–B-type magnets seems to be to apply organic coatings [11–13].

Having in mind the increasing interest in new RETM_{12} permanent magnets, the purpose of this study was to evaluate the corrosion resistance of the RETiCo_{11} -type alloys and compare it with those of Sm–Co and Nd–Fe–B.

2. Experimental

Six RETiCo_{11} compounds (RE=Y, Pr, Nd, Sm, Gd or Dy) were used as test materials. The procedure for their preparation is described in Ref. [3]. For comparative purposes sintered samples of SmCo_5 and

$\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ (denoted in further parts of the paper as Sm–Co and Nd–Fe–B magnets) and specpure Co and Ti (99.99 wt.%) were applied.

The electrodes for corrosion tests had the form of rotating discs with an operating surface area of 0.2 cm^2 . As test solutions, argon-saturated sulphate solutions with a total concentration of sulphate ion of 0.5 mol l^{-1} and $\text{pH}=0.3\text{--}4.0$ were used. The desired pH values were obtained by suitable additions of $0.5 \text{ M H}_2\text{SO}_4$ to $0.5 \text{ M Na}_2\text{SO}_4$ solution. Some of the experiments were carried out in strong acid solution ($2.0 \text{ M H}_2\text{SO}_4$, $\text{pH} = -0.2$).

In order to avoid surface screening by hydrogen bubbles, the electrochemical corrosion tests were conducted at a fast stirring rate of the rotating discs, mainly 15 rps. All the experiments were performed in argon-saturated solutions at a temperature of $25 \pm 0.1 \text{ }^\circ\text{C}$. The following corrosion characteristics were investigated:

(i) potentiokinetic polarization curves at a scanning rate of 25 mV min^{-1} starting at a potential of -1.5 V (vs. saturated calomel electrode (SCE)) up to 2.5 V (SCE); most of the potentiokinetic tests were ended at a potential of 0.0 V (SCE);

(ii) gravimetric tests: spontaneous dissolution of the tested materials and periodical analysis of Co^{2+} ion content (AAS method) in 2.0 M sulphuric acid ($\text{pH} = -0.2$);

(iii) corrosion resistance tests (the Stern–Geary linear polarization method [14]) in a solution with $\text{pH} = -0.3$ and $+0.2$;

(iv) acetic acid salt-spray test (accelerated atmospheric corrosion test): exposure of the test samples in steam-saturated air containing 3 wt.% NaCl in $0.1 \text{ M CH}_3\text{COOH}$ solution at $40 \text{ }^\circ\text{C}$, according to ASTM B 287-62.

The electrochemical tests were conducted using an electrochemical automatic measuring system consisting of an EP-20 potentiostat (Elpan), scanner, logarithmic amplifier, data acquisition unit and a computer compatible with an IBM PC/AT.

3. Results and discussion

In Fig. 1 typical polarization curves of RETiCo_{11} with different potential scanning rates and in a wide potential range are presented. As can be seen, distinct differences between curves appear only in the range from -0.2 to $+1.3 \text{ V}$, i.e. in the range of formation of an oxide layer on the surface. Similarly as was found for Sm–Co and pure Co [15], the oxide layer did not exhibit protective properties with high anodic currents in this range of the order of $0.1\text{--}1 \text{ A cm}^{-2}$. The slower the potential scanning the thicker was the oxide layer and, consequently, the smaller the “passivation” current.

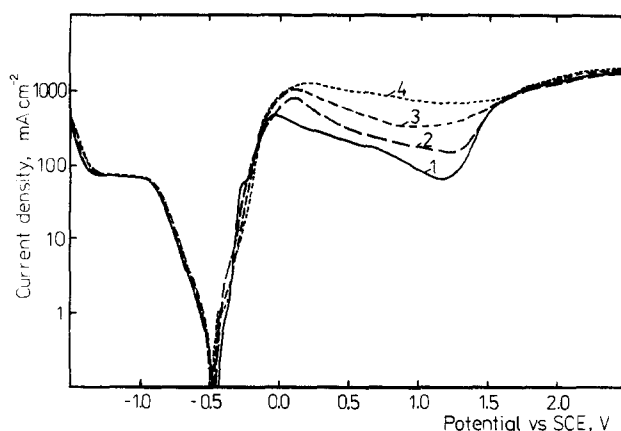


Fig. 1. Full potentiokinetic polarization curves for GdTiCo_{11} compound in 0.5 M sulphate solution with $\text{pH}=2.0$ at four different potential scanning rates: (1) 1, (2) 5, (3) 25 and (4) 100 mV s^{-1} ($25 \text{ }^\circ\text{C}$, Ar, 15 rps).

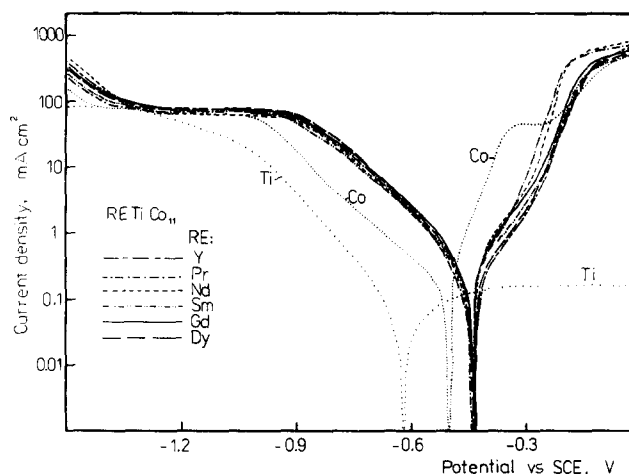


Fig. 2. Potentiokinetic polarization curves for six kinds of RETiCo_{11} compounds in 0.5 M sulphate solution with $\text{pH}=2.0$, and corresponding curves for specpure Co and Ti ($25 \text{ }^\circ\text{C}$, Ar, 25 mV s^{-1} , 15 rps).

In the active potential range the potential change rate practically does not affect the polarization curves.

Fig. 2 presents the polarization curves in the active state for all of the RETiCo_{11} -type magnets tested. For comparison, the curves for pure cobalt and titanium are also shown. Fig. 2 indicates that the kind of RE element has practically no influence on the polarization curve of RETiCo_{11} . The cathodic process of H^+ ion reduction occurs faster on RETiCo_{11} than on pure Co; however, the anodic process for the RETiCo_{11} magnet is distinctly inhibited. At potentials of -1.0 to -1.4 V the limiting current of H^+ ion is visible and its value ($60\text{--}70 \text{ mA cm}^{-2}$) does not depend on the kind of metal.

The effect of pH on the polarization curves is presented in Fig. 3. As can be seen, an increase in pH slightly inhibits the anodic dissolution process of the magnet. The corrosion process is controlled by the

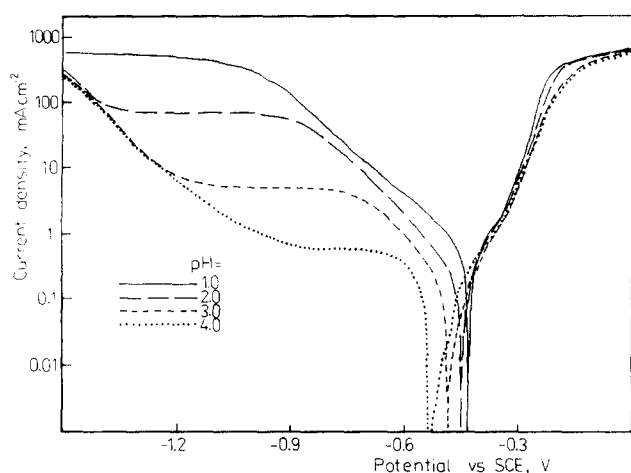


Fig. 3. Potentiokinetic polarization curves for PrTiCo₁₁ compound in 0.5 M sulphate solutions with different pH values (25 °C, Ar, 25 mV s⁻¹, 15 rps).

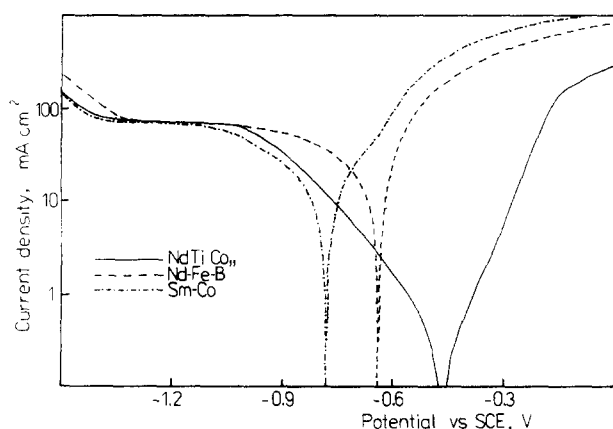


Fig. 4. Comparison of potentiokinetic polarization curves of NdTiCo₁₁ magnet with those for Nd-Fe-B- and Sm-Co-type magnets in sulphate solution of pH=2.0 (25 °C, Ar, 25 mV s⁻¹, 15 rps).

hydrogen ion reduction rate in the active range ($\text{pH} \leq 3$) or in the diffusional range ($\text{pH} = 4$). At sufficiently negative potentials cathodic currents increase over the limiting values owing to the reduction of water molecules [9].

In order to compare the corrosion behaviour of RETiCo₁₁ with Sm-Co and Nd-Fe-B type magnets, in Fig. 4 the polarization curves of these magnets are presented. It can be seen that for RETiCo₁₁-type magnets both cathodic and especially anodic electrode processes occur in the active state much more slowly than for the Sm-Co and Nd-Fe-B. Therefore, the RETiCo₁₁-type materials should be considerably more corrosion resistant in the acidified environments.

Extrapolation of linear segments of the cathodic curves to E_{corr} allows the corrosion rates of the magnets to be evaluated [16]. The corresponding values of i_{corr} and E_{corr} at pH 2 are presented in Table 1, which also includes the data for Sm-Co- and Nd-Fe-B type mag-

Table 1

Corrosion currents (i_{corr} , mA cm⁻²) and corrosion potentials (E_{corr} vs. SCE, V) determined by the method of extrapolation of the cathodic polarization curves to E_{corr} for the tested alloys in 0.5 M sulphate solution with pH=2.0 (25 °C, Ar, 15 rps)

Sample	i_{corr}	E_{corr}
YT ₁ Co ₁₁	0.24	-0.442
PrTiCo ₁₁	0.20	-0.445
NdTiCo ₁₁	0.26	-0.451
SmTiCo ₁₁	0.22	-0.446
GdTiCo ₁₁	0.23	-0.456
DyTiCo ₁₁	0.27	-0.443
Nd-Fe-B	9.24	-0.778
Sm-Co	6.94	-0.640
Pure Co	0.13	-0.504

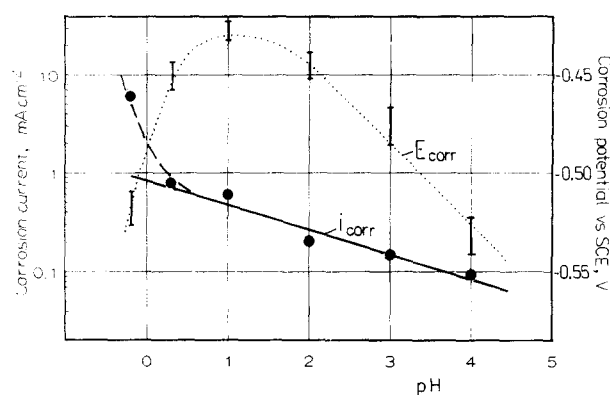


Fig. 5. Corrosion current and corrosion potential calculated from extrapolation of potentiokinetic polarization curves as functions of pH of 0.5 M sulphate solutions for PrTiCo₁₁ magnet (25 °C, Ar, 25 mV s⁻¹, 15 rps). The experimental point at pH = -0.2 corresponds to 2.0 M H₂SO₄.

nets. It can be seen that the corrosion currents of the RETiCo₁₁-type magnets practically do not depend on the kind of RE element and are in the range 0.20–0.27 mA cm⁻². These values are merely twice as great as that for pure cobalt ($i_{\text{corr, Co}} = 0.13$ mA cm⁻²). On the other hand, the corrosion process for the Sm-Co- and Nd-Fe-B-type magnets under the same conditions occurs 30–40 times faster.

As was shown in earlier papers [9,17,18], the corrosion process rate for Nd-Fe-B and Sm-Co magnets in the "low pH region", i.e. for pH=0–3, depended strongly on pH with $(\partial \log i_{\text{corr}} / \partial \text{pH})_{298 \text{ K}} = -0.5$ for both Nd-Fe-B- and Sm-Co-type magnets. In Fig. 5 the corrosion rate and corrosion potential of PrTiCo₁₁ magnets in 0.5 M sulphate solutions as a function of pH of the solution are presented. The slope of the rectilinear segment of the $\log i_{\text{corr}}$ -pH curve in the pH range of 0.3–4.0 is -0.28, which is nearly half that for Nd-Fe-B and Sm-Co magnets. Further increase in the acidity of the solution (2 M H₂SO₄, pH = -0.2) leads, however, to a strong increase in the corrosion rate for

the RETiCo_{11} magnets (corresponding tests were made for PrTiCo_{11} , GdTiCo_{11} and NdTiCo_{11} compounds). This strong increase in i_{corr} is most likely caused by a change of the corrosion mechanism and preferential dissolution of RE elements from the alloy, since for rare-earth elements the derivative $(\partial \log i_{\text{corr}}/\partial \text{pH})_{298\text{ K}}$ is of the order of -2 [18]. This supposition is also confirmed by the dependence of the corrosion potential on pH: at higher pH (2–4) the slope of the E_{corr} -pH curve is negative, similarly as found for many metals in acid solutions [19]. For more acid solutions, however, E_{corr} moves towards potentials typical for RE elements.

The tendency for preferential dissolution of RE elements from the alloy in strong acid solutions deserves more detailed consideration. It is especially important to know whether during the steady-state dissolution process of the RETiCo_{11} sample in strong acid solution the particular elements enter into the solution in the same proportion as they occur in the alloy. In Fig. 6 the dependence of the corrosion current, determined continuously by the Stern–Geary polarization resistance method and the rate of dissolution of Co from the alloy (periodic solution analysis using AAS), on the exposure time of the GdTiCo_{11} rotating disc in 2.0 M sulphuric acid (pH = -0.2) and in 0.5 M sulphate solution with pH = 2 are presented. As can be seen, at pH = -0.2 the corrosion current in the first period of etching (after 5–10 min of exposure) takes on a

minimum value (ca. 12 mA cm^{-2}) and after 40 min it settles down at $40\text{--}50 \text{ mA cm}^{-2}$. The simultaneously analytically measured (and expressed in current density units) rate of Co dissolution from the alloy (filled circles in Fig. 6(a)) is, for exposure times >40 min, about 70–80% smaller than i_{corr} of the alloy, which indicates uniform dissolution of the alloy (calculations show [20] that in case of uniform dissolution (lack of preferential dissolution) the contribution of cobalt dissolution current to the total corrosion current (current of dissolution of $\text{Co} \rightarrow \text{Co}^{2+}$, $\text{Ti} \rightarrow \text{Ti}^{3+}$ and $\text{Gd} \rightarrow \text{Gd}^{3+}$) is 78.5%). For the initial period of dissolution, however, the contribution of Co dissolution to the total corrosion current is 45–60% and therefore one can conclude that in this first period of etching RE elements are dissolved preferentially. The distinct increase in corrosion potential vs. etching time is certainly a result of surface enrichment with a more noble metal (Co). For a less acid solution (pH = 2, Fig. 6(b)), both corrosion current and corrosion potential of the GdTiCo_{11} compound do not change with the exposure time and the process occurs without preferential dissolution.

Similar shapes of the acid etching curves to those in Fig. 6(a) were observed for Nd–Fe–B-type magnets, for which the Nd-rich phase in the first period was selectively dissolved [6–8]. However, for Nd–Fe–B-type magnets this phenomenon took place even in weak acid solutions (pH < 3 [9,17]), whereas for the RETiCo_{11} alloys, as results from Fig. 5, it disappears at pH > 0.3 .

The electrochemical measurements testify to a much better corrosion behaviour of RETiCo_{11} magnets in

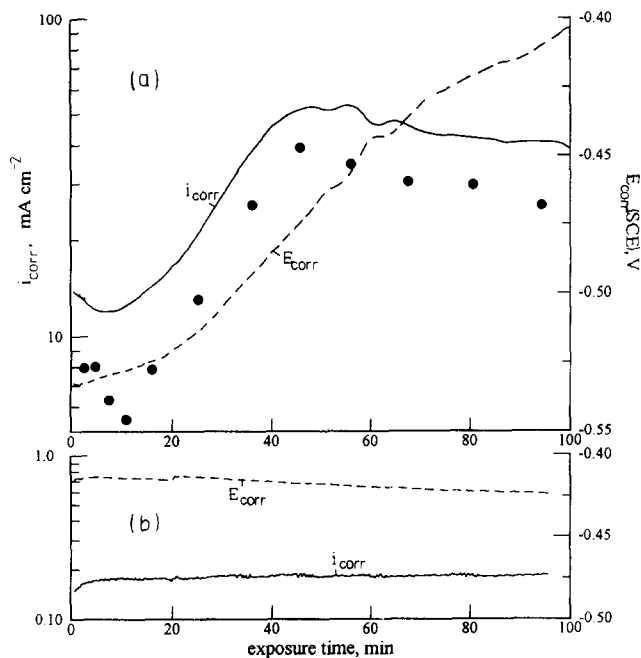


Fig. 6. Corrosion current (solid line) and corrosion potential (dashed line) determined by polarization resistance method and currents of cobalt etching from the GdTiCo_{11} alloy (full circles) found from solution analysis of Co^{2+} ions as a function of the etching time for (a) 2.0 M H_2SO_4 (pH = -0.2) and (b) 0.5 M sulphate solution with pH = 2.0 (25 °C, Ar, 15 rps).

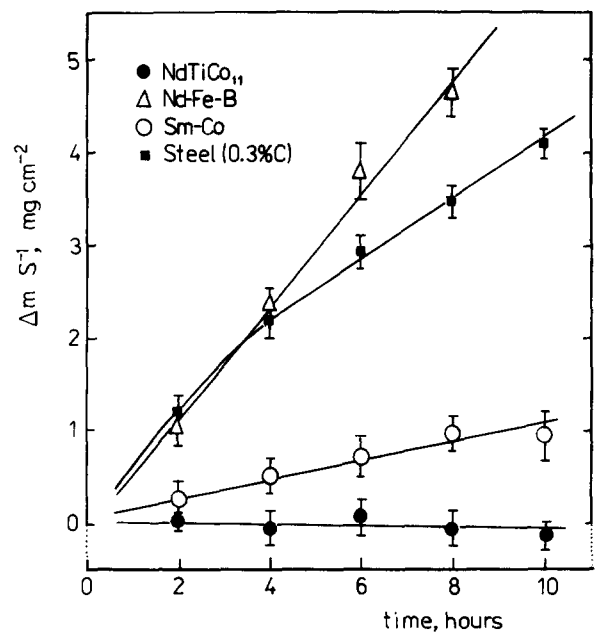


Fig. 7. Mass increments (per 1 cm^2) of the tested samples in acetic acid salt-spray as a function of exposure time (40 °C), with error bars.

sulphate solutions as compared with Nd–Fe–B- and Sm–Co-type magnets. For users corrosion resistance in atmospheric conditions is more important. Fig. 7 presents corresponding results of an accelerated atmospheric corrosion test in acetic acid salt-spray. The atmospheric corrosion behaviour of the RETiCo₁₁ magnets is compared with those for Nd–Fe–B- and Sm–Co-type magnets and also for medium-carbon steel. As can be seen from Fig. 7, the NdTiCo₁₁ magnet exhibits excellent immunity in the salt-spray environment (corresponding tests for PrTiCo₁₁ and GdTiCo₁₁ gave practically the same results). The corrosion rates of the tested samples in the salt-spray conditions, expressed in mg cm⁻² h⁻¹, are as follows: Nd–Fe–B, ~0.6; 0.3% carbon steel, 0.6–0.3; Sm–Co, 0.1; and RETiCo₁₁, <0.02, i.e. within the limits of experimental accuracy. This unusual resistance to atmospheric corrosion of the RETiCo₁₁ magnets can be ascribed to the presence of ca. 6 wt.% of titanium (easily passivated metal) in their composition and a limited content of RE elements as compared with Nd–Fe–B- and Sm–Co-type magnets.

4. Conclusions

In medium acidic (pH=2) sulphate solutions the RETiCo₁₁ alloys corrode at a rate 30–40 times slower than Sm–Co- and Nd–Fe–B-type magnets. An increase in the acidity of the solution increases the corrosion rate of the RETiCo₁₁ magnets to a much weaker degree than for Sm–Co- and Nd–Fe–B-type magnets. The RETiCo₁₁ magnets show great immunity to atmospheric corrosion. The kind of rare earth element in the RETiCo₁₁ composition does not affect the corrosion behaviour of the alloy.

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