

## HYDROGEN STABILITY OF $\text{SmCo}_5$ PERMANENT MAGNET

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The kinetic parameters of the destructive hydrogenation process of  $\text{SmCo}_5$  type permanent magnet: activation energy and reaction order with respect to gaseous hydrogen are calculated. No hydride phases in the permanent magnet structure resulting from hydrogenation at the hydrogen pressure of ca. 0.3 MPa in the temperature range of 273–373 K are found. The effect of hydrogen pressure and temperature of the environment on the permanent magnet exploitation period are determined.

**Key words:** magnetic intermetallics, kinetics of hydrogen absorption, destructive hydrogenation

### STABILITA VODÍKA V PERMANENTNOM MAGNETE $\text{SmCo}_5$

Vypočítali sme kinetické parametre deštrukčného hydrogenizačného procesu permanentného magnetu typu  $\text{SmCo}_5$ : aktivačnú energiu a poriadok reakcie s uvažovaním plynného vodíka. V štruktúre permanentného magnetu sme nepozorovali žiadne hydridné fázy, ktoré by vyplývali z hydrogenizácie pri tlaku vodíka 0,3 MPa v teplotnom intervale 273–373 K. Stanovili sme vplyv tlaku vodíka a teploty prostredia na životnosť permanentného magnetu.

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## 1. Introduction

Hard magnetic alloys based on  $\text{SmCo}_5$  type compounds are industrially produced and commonly applied, especially in energetic and instrument-making industry, which use great part of high-energy permanent magnets production [1, 2]. This is explained by a favourable combination of the high magnetic energy product, demagnetization resistance, satisfactory thermal stability and adaptability to manufacture [3, 4]. For further development of rare earth (RE) based permanent magnets a detailed knowledge of their operational characteristics including resistance to the influence of various factors of the surrounding environment, especially corrosion characteristics, is necessary [5–7]. Assuming that  $\text{H}_2$  gas can be one of the corrosion products and taking into account that hydrogen can be absorbed by  $\text{SmCo}_5$ , the studies of hydrogen interaction with Sm-Co type magnets seem to be still actual. It is connected with both the permanent magnet production technology (e.g. application of hydrogen dispersion of alloys [8, 9]) and ensuring their operational stability (e.g. resistance to influence of exterior hydrogenation by working environments). Also the search for new fields of applications is of great importance.

The present work has been performed with purpose to determine the level of hydrogen stability of sintered  $\text{SmCo}_5$  permanent magnets by means of accelerated tests, to study the effect of hydrogen on the magnetic and mechanical properties of the permanent magnets and to establish the criteria of hydrogenation level and the activation energy of this process. In addition, the effect of hydrogen on the properties of sintered  $\text{SmCo}_5$  permanent magnets in specific conditions of exploitation and storage durability of instruments was studied.

## 2. Experimental details

The object of tests were industrially produced sintered  $\text{SmCo}_5$  permanent magnets. Composition and magnetic properties of the tested permanent magnets are given in Table 1. The microstructure of as-sintered  $\text{SmCo}_5$  permanent magnet

Table 1. Chemical composition and magnetic properties of sintered  $\text{SmCo}_5$  permanent magnet

Chemical composition		Magnetic properties				
		Remanence	Induction coercivity	Magnetization coercivity	Energy product	Temperature coefficient of induction
Sm [wt.%]	Co [wt.%]	$B_r$ [T]	$B H_c$ [kA/m]	$1 H_c$ [kA/m]	$(BH)_{\max}$ [kJ/m <sup>3</sup> ]	$\alpha_B$ [%/K]
37.1	62.9	0.82	-630	1820	160	-0.026

was very similar to that reported for sintered  $\text{SmCo}_5$  permanent magnets by other authors [3, 8]. The characteristic feature of the present structure was the variation in grain size: beside fine grains of 7–12  $\mu\text{m}$  in diameter there were also large grains of diameter 20–25  $\mu\text{m}$ , while grain boundaries were surrounded by fine precipitates  $\leq 1 \mu\text{m}$ . From X-ray analysis these precipitates were identified as samarium compounds with light elements, mainly O but also C and N. Phases present in the structure of the permanent magnet include, beside the main  $\text{SmCo}_5$  phase, also the  $\text{Sm}_2\text{CO}_{17}$  phase of various size. This type of structure seems to provide an effective barrier for domain wall nucleation as it may be seen from magnetic properties presented in Table 1.

The sintered  $\text{SmCo}_5$  permanent magnets in form of cylinders with diameter of 70 mm and height of 6 mm were subjected to exposure to gaseous hydrogen in steel containers. Hoods of the containers had the special valves for air pumping and hydrogen admission and also controlling manometer for fixing the working pressure. During the tests the containers were placed in thermostat and held during necessary time at given temperature. The parameters of hydrogen exposure were as follows: pressure  $p_{\text{H}_2}$  [MPa] – 0.027, 0.080 and 0.304; temperature  $T$  [K] – 273, 323, 353, and 373. The reproducibility of the time period up to shape dropping of hydrogen pressure (the incubation period) was generally better than  $\pm 10\%$ .

A simulation of exploitation condition was carried out at temperature 378 K for 18 days (432 hours). The tested samples were sealed in glass ampoules filled up with hydrogen gas at pressure of 0.1 MPa. Heating of the ampoules with samples was carried out at a thermostat with  $\pm 0.5$  K temperature control accuracy (the  $\text{H}_2$  pressure increased to ca. 0.13 MPa) after heating.

Phase and crystal structure of the as-received and hydrogenated permanent magnets were investigated using X-ray diffraction method. The flux change of the permanent magnet before and after hydrogenation were measured by an open circuit method with a Helmholtz coil and an integral digital fluxmeter with accuracy up to 1%.

### 3. Results and discussion

During testing it was found that permanent magnets which were exposed to the hydrogen-gas atmosphere were damaged. At all regimes of the exposure the tested samples showed the presence of the incubation period for which the constructive intactness and magnetic flux of permanent magnets were unchanged. The incubation period varied from 40 days to several hours depending on the regimes of testing (hydrogen gas pressure and temperature). At the end of the incubation period a relatively quick complete damage (cracking into pieces) of the magnet was observed.

Because the sample during the hydrogenation test was in a closed area the visual observation of its surface was inaccessible. Hence, it was impossible to

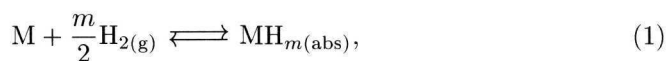
determine the moment of the beginning of sample damage. However, it was found in testing that the permanent magnet damage was always directly followed by the sharp drop of the hydrogen gas pressure. This moment of pressure fall was taken as a criterion for the beginning of damage.

Primarily, according to the methodology of the present work, the other controlling parameters giving the information about the level of material hydrogenation such as magnetic flux were supposed to be changed. However, this mechanism was not confirmed experimentally. Magnetic flux has not been practically changed during hydrogenation\* up to complete damage of the product. The analysis of magnetic properties of the material after its self-cracking showed their distinct worsening. In particular, the strong decrease of coercivity took place.

Taking into account that the damage of sintered  $\text{SmCo}_5$  permanent magnets shows intermittent character, it can be assumed that such damage serves as a criterion of the achievement of certain level of hydrogenation which corresponds to the defined quantities of the absorbed hydrogen.

It is necessary to note that permanent magnets of a few common product batches damaged practically simultaneously at given regimes of tests, which confirms that the shape of the sample does not affect the incubation time. In separate cases the time for damage of various batches of the permanent magnet was essentially different. This phenomenon may be explained by difference in structural characteristics and heterogeneity of the material when it is used for large-size sintered bars.

The hydrogenation process (absorption of hydrogen) of the permanent magnet (M) can be given by the following general equation



where  $m$  is stoichiometric index.

The symbol "abs" denotes absorbed hydrogen and refers to creation both solid solution and hydride phases. Preliminary tests showed that the duration of the incubation period for permanent magnets in hydrogen exposure decreased with increasing temperature. Thus the duration of the incubation period ( $\tau$ ) can be assumed to be a degree of the rate of the destructive hydrogenation process. In order to find relations between observed incubation periods, hydrogen partial pressure and temperature, it is reasonable to assume that the duration of the incubation period is inversely proportional to the destructive hydrogenation rate. This assumption is justified in view of relation between initial reaction rate and time necessary for its occurring (e.g. half-time –  $\tau_{1/2}$ ), well known from chemical

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\* In a few cases, after hydrogenation of the sample but before its total cracking, 4–5% decrease of the magnetic flux was found.

kinetics. So we can write the following expression for the rate of the destructive hydrogenation process

$$\nu_{\text{H}} = \frac{A}{\tau}, \quad (2)$$

where  $\nu_{\text{H}}$  is the formal hydrogenation rate,  $\tau$  is the incubation period,  $A$  is a coefficient of proportionality.

The rate of reaction (1) can be described by common kinetic equation

$$\nu_{\text{H}} = k_{\text{H}} p_{\text{H}_2}^n, \quad (3)$$

where  $p_{\text{H}_2}$  is the hydrogen pressure over the sample,  $n$  is the order of reaction with respect to hydrogen,  $k_{\text{H}}$  is the rate constant.

The dependence of  $\nu_{\text{H}}$  on temperature ( $T$ ) obeys the Arrhenius law

$$k_{\text{H}} = k_0 \exp\left(-\frac{E_{\text{a}}}{RT}\right), \quad (4)$$

where  $k_0$  is the frequency factor, constant for a given reaction,  $E_{\text{a}}$  is the activation energy of the hydrogenation reaction,  $R$  is gas constant equal to 8.314 J/K·mol.

Assuming the constant pressure of hydrogen ( $p_{\text{H}_2} = \text{const}$ ) and independence of constant  $A$  on temperature, we obtain the following expressions for the hydrogenation rate for two chosen temperatures  $T_1$  and  $T_2$  ( $T_1 < T_2$ )

$$\ln \frac{A}{\tau_1} = \ln k - \frac{E_{\text{a}}}{RT_1}, \quad (5a)$$

$$\ln \frac{A}{\tau_2} = \ln k - \frac{E_{\text{a}}}{RT_2}, \quad (5b)$$

where  $k$  is a new constant, equal to  $k_0 p_{\text{H}_2}^n$ .

And, finally

$$E_{\text{a}} = \frac{T_1 T_2}{T_2 - T_1} R \ln \frac{\tau_1}{\tau_2}. \quad (6)$$

Equation (6) is similar to the one presented by Kolachev [10]. The results of incubation period ( $\tau$ ) for different temperatures at constant  $p_{\text{H}_2}$  and activation energy values, calculated on the basis of the Eq. (6), are summarized in Table 2. From data in Table 2 it can be derived that the average value of the activation energy of hydrogenation process at  $p_{\text{H}_2} = 0.304$  MPa is  $81 \pm 2$  kJ/mol. Similar values of  $E_{\text{a}}$  were found also for the two other partial pressures of hydrogen.

Table 2. Hydrogenation process parameters and calculated activation energy values of sintered  $\text{SmCo}_5$  permanent magnet at hydrogen pressure of 0.304 MPa

$T$ [K]	$\tau$ [h]	$E_a$ [kJ/mol]
273	$\gg 10^4$	–
323	1050	–
353	77	82.6
373	18	79.6

In order to determine the hydrogenation reaction order with respect to  $\text{H}_2$  we measured incubation periods for different hydrogen pressure (at  $T = \text{const}$ ). After transformation of Eqs. (2) and (3) we obtain

$$\log \tau = b - n \log p_{\text{H}_2}, \quad (7)$$

where  $b$  is new constant equal to  $\log(A/p_{\text{H}_2})$ .

The dependence of incubation period for damage of  $\text{SmCo}_5$  permanent magnets versus hydrogen pressure at 373 K is shown in Fig. 1. The obtained dependence of  $\log \tau$  vs.  $\log p_{\text{H}_2}$  is rectilinear with the slope equal to  $-1.08 \pm 0.25$  which justifies the reaction order with respect to hydrogen equal to 1.

The capability of many alloys and metals to self-pulverization as a result of the interaction with gaseous hydrogen was repeatedly mentioned in literature. Regarding to RE–Co alloys such self-pulverization is ascribed as a rule to significant increase of the crystal lattice volume. The last was conditioned by its transformation from hexagonal structure to orthorhombic one at anisotropy expansion in basic plane ( $\alpha \rightarrow \beta$ ) transition [13]. According to data in ref. [14] the formation enthalpy of hydride phase of  $\text{SmCo}_5$  alloys at  $\alpha \rightarrow \beta$  transition exhibits the value equal to approximately  $\Delta H^\circ = -32.6$  kJ/mol. It is easy to calculate that the equilibrium pressure of this transition is equal to 0.33 MPa at 293 K and 0.124, 1.1, 3.2, and 6.5 MPa at the applied temperatures of 273, 323, and 373 K, respectively.

Consequently, in the given tests the parameters of hydrogen exposure are thermodynamically insufficient for creation of the order hydrogen-capacious hydride  $\beta$ -phase. X-ray analysis of the  $\text{SmCo}_5$  permanent magnets confirmed that after hydrogenation the hydride phase did not occur in the sample\*. As seen, hydrogen absorbed in solid solution state itself is able to damage the  $\text{SmCo}_5$  sintered material.

\* More precisely speaking, the hydride phase was not revealed within the limits of X-ray analysis accuracy, because a threshold volume fraction of the hydride phase should be of the order of several percent to be detected by X-ray.

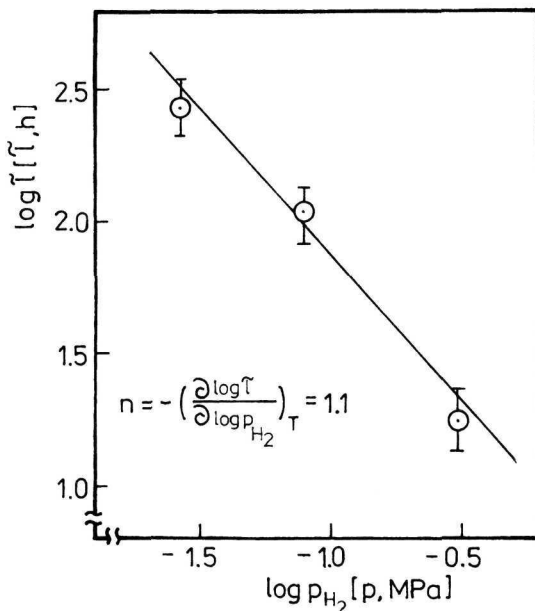


Fig. 1. Plot of incubation period for damage of sintered  $\text{SmCo}_5$  permanent magnet vs. hydrogen pressure at  $T = 373$  K.

The determination of kinetic parameters of hydrogenation process, namely the activation energy ( $E_a$ ) and the order of reaction with respect to hydrogen ( $n$ ) allows to estimate approximately the time-limits of permanent magnets keeping quality in exploitation conditions. As the value of the incubation period  $\tau_1$  (found from the experiment performed at  $p_1$  and  $T_1$ ) is known, it could be possible to predict the duration of the permanent magnets storage  $\tau_x$  at real environmental hydrogen pressure and temperature ( $p_x, T_x$ ). Starting from equations (2-4) we obtain

$$\frac{A}{\tau_x} = k_0 p_x^n \exp\left(-\frac{E_a}{RT_x}\right), \quad (8a)$$

$$\frac{A}{\tau_1} = k_0 p_1^n \exp\left(-\frac{E_a}{RT_1}\right), \quad (8b)$$

hence

$$\tau_x = \tau_1 \left(\frac{p_1}{p_x}\right)^n \exp\left(\frac{E_a(T_i - T_x)}{RT_i T_x}\right). \quad (9)$$

A similar phenomenological approach was presented in ref. [12]. Putting into Eq. (9) the constants ( $R = 8.31 \text{ J/mol}\cdot\text{K}$ ) and calculated kinetic parameters ( $E_a = 81 \text{ kJ/mol}$ ,  $n = 1$ ), we receive

$$\tau_x = \tau_i \frac{p_i}{p_x} 10^{\frac{4230(T_i - T_x)}{T_i T_x}}. \quad (10)$$

It follows from Eq. (10) that the increase of temperature by 10 K decreases three times the period in which  $\text{SmCo}_5$  permanent magnets preserve their quality. On the other hand, decrease of hydrogen pressure by an order of magnitude leads to ten-fold increase of the storage time. The presence of hydrogen in  $\text{SmCo}_5$  permanent magnets at exploitation conditions is caused mainly by corrosion of the material even at weak-acid environments [5, 6]. As it is known, rare earth elements belong to the group of most reactive metals (their standard potentials  $E_{\text{RE}^{3+}/\text{RE}}^0$  is  $-3 - -2.5 \text{ V}$ ). They form hydrogen in contact with water. The destruction of  $\text{SmCo}_5$  permanent magnets is especially strong at presence of cathodic polarization and is distinctly proportional to the hydrogen evolution rate [5].

In Fig. 2 the parameters of the crystal lattice of  $\text{SmCo}_5$  permanent magnet as a function of their exposure time at hydrogen environment (hydrogen-gas pressure

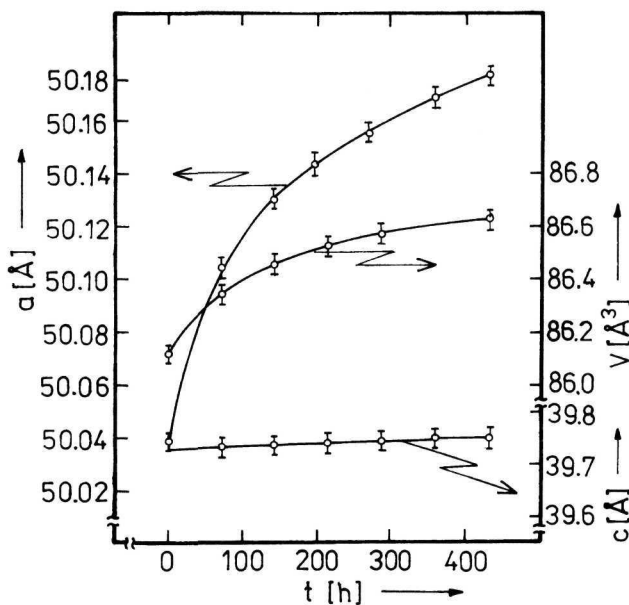


Fig. 2. Lattice parameters  $a$  and  $c$  and volume of elementary cell  $V$  as functions of exposure time in hydrogen atmosphere at 0.1 MPa pressure and  $T = 378 \text{ K}$ .



of 0.1 MPa and temperature 378 K) are given. As seen, the crystal lattice of  $\text{SmCo}_5$  phase undergoes the significant changes in the hydrogen atmosphere: increase of  $a$  and  $c$  lattice parameters leads to increase of elementary cell volume by ca. 0.6 percent after 400 hours of hydrogenation.

#### 4. Conclusion

1. The activation energy of the destructive hydrogenation process for  $\text{SmCo}_5$  permanent magnets in hydrogen-gas environment is 81 kJ/mol.

2. The destructive hydrogenation reaction for  $\text{SmCo}_5$  permanent magnet is of the first order with respect to hydrogen.

3. The period of keeping quality for  $\text{SmCo}_5$  permanent magnets decreases proportionally to the partial hydrogen pressure of surrounding environment. Increasing of temperature by 10 K decreases this period by about three times.

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