HYDROGEN DIFFUSION AND STRAIN DISTRIBUTION IN AMORPHOUS Fe-BASED RIBBONS

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ABSTRACT

The paper deals with the study of strain distribution in hydrogenated FeB ribbons prepared by rapid quenching from the melt. Hydrogen atoms introduced during the process of hydrogenation induce internal stresses in the sample. This causes bending of a one side hydrogenated non-fixed ribbon. The ribbon bending reflects hydrogen concentration. When the ribbon is dehydrogenated the ribbon shape is fully restored for the studied $Fe_{85}B_{15}$ sample. A simple theoretical model is proposed to describe dependence of ribbon bending on the hydrogen concentration during process of hydrogenation as well as in the process of spontaneous dehydrogenation. A proposed theoretical model is in a good agreement with experimental results. Its fitting to experimental data provides important information on the local enlargement of the space around introduced hydrogen atoms.

Keywords: *hydrogenation, concentration, magnetoelastic anisotropy, amorphous ferromagnetic ribbons*

1. INTRODUCTION

Amorphous ferromagnetic materials prepared by rapid quenching from the melt [1] are very promising materials for technical applications and for this reason they are quite often the subject of basic research. The results reported in this paper follow on the study of hydrogenation of amorphous ferromagnetic ribbons as the method for non-destructive investigation of their mechanical-magnetic properties and their possible modification [2,3,4,5] which has been published recently [6]. In the latter paper a theoretical model for hydrogenation and spontaneous dehydrogenation of ferromagnetic ribbons was proposed. Hydrogen atoms introduced into studied amorphous FeB materials increase internal stress in their structure. The rate of hydrogen diffusion in these materials is not fast enough to produce homogeneous hydrogen distribution in the ribbon cross section [6] and consequently also the stress distribution in the ribbon cross section is not homogeneous. The ribbon bending reflecting this non-homogeneity in the case of one side hydrogenation process (see Fig. 1) can provide information on the induced stress which depends on the hydrogen concentration. This information is of great importance for the studied Fe-based materials which possess large magnetostriction. In the present paper a simple theoretical model is proposed to describe dependence of ribbon bending on the hydrogen concentration during the process of hydrogenation as well as in the process of spontaneous dehydrogenation. Proposed theoretical model is in good agreement with experimental results. Fitting model equation to experimental data makes it possible to obtain important information of local enlargement of the space close to the introduced hydrogen atom, which can change local magnetic characteristics. The theoretical results obtained are the base for further study of such important magnetic characteristics of studied materials as e.g. magnetoelastic anisotropy constant.
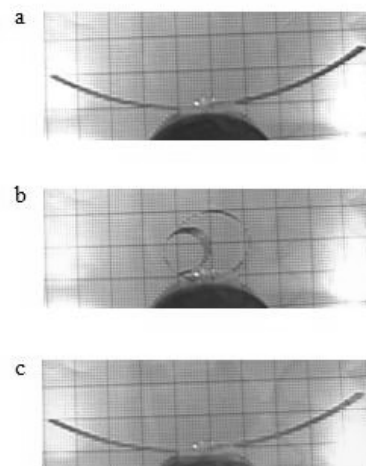

Fig. 1 Bending of hydrogenated sample: (a) - before hydrogenation, (b) - strong hydrogenated, (c) - after dehydrogenation

2. MODEL

We consider a model situation in which the length and width of the ribbon are much larger than its thickness *L*, and the material of a ribbon has no affinity to hydrogen. The aim of the following considerations is to study the influence of one side hydrogenation on the bending of a thin amorphous ferromagnetic ribbon and also on strain distribution.
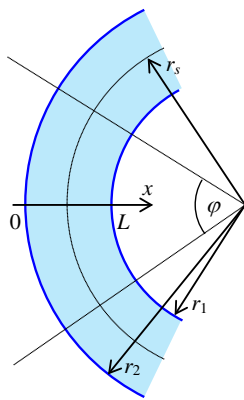
In the ribbon hydrogenated from one side (from the left side in Fig. 2) the hydrogen located in the matrix causes local volume increase which results in an observable isotropic elongation (perpendicular to the *x*-axis, see Fig. 2) of each elementary layer from which the ribbon can be considered to consist of. An elongation in the direction perpendicular to the plane of the sample (in the *x*-axis direction) is negligible small for thin ribbon and

its influence on the bending of hydrogenated sample in the simple model presented here is neglected. In the case of one-side hydrogenation (in the x-axis direction) sample bending is observed as can be seen in Fig. 1.
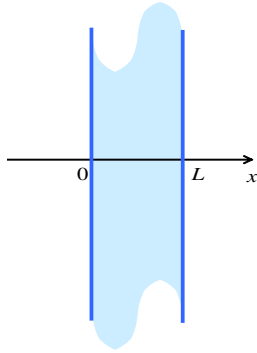
Fig. 2 Sample with a thickness L

Due to the isotropic enlargement of the surface of one side of hydrogenated sample the ribbon bends and its surface becomes spherical which reflects successively decreasing hydrogen concentration inside the sample with the distance from the hydrogenated surface [6]. Curvature radius as a function of hydrogen concentration can be obtained from the experiment and can give important information on material constants of a deformed ribbon. Side view of the bent ribbon hydrogenated from the left side (surface $x = 0$) is schematically depicted in Fig. 3.

Fig. 3 Side view of the ribbon hydrogenated from the surface $x = 0$, where r_1 and r_2 are minimum and maximum radii, respectively and r_s is a mean curvature radius

Theoretical dependence of a mean curvature radius r_s on hydrogen concentration can be obtained in the following way.

The length of middle circular arc l_s with radius r_s of a deformed (hydrogenated) sample is

$$l_s = l_0 + \Delta l \,, \tag{1}$$

where l_0 is the length of the ribbon before hydrogenation and Δl is an elongation of its middle part in hydrogenated sample. The length of an arbitrary arc l_r with radius r is

$$l_r = r\varphi \,, \tag{2}$$

where φ is its central angle. Difference in arc lengths l_s and l_r is (see Fig. 3)

$$l_r - l_s = (r - r_s)\varphi = \Delta r\varphi = \left(\frac{L}{2} - x\right)\varphi \,. \tag{3}$$

Using Eqs. (3,1) the length of l_r is

$$l_r = l_s + \Delta r\varphi = l_0 + \Delta l + \left(\frac{L}{2} - x\right)\varphi \,. \tag{4}$$

The strain ε (relative elongation) for the arc with radius r can be obtained from Eq. 4)

$$\varepsilon = \frac{l_r - l_0}{l_0} = \varepsilon_0 + \varepsilon_r \,, \tag{5}$$

where

$$\varepsilon_0 = \frac{\Delta l}{l_0}, \varepsilon_r = \frac{(L/2 - x)\phi}{l_0} \,. \tag{6}$$

The ribbon bending is caused by the presence of hydrogen inside its structure, therefore the strain has to depend on hydrogen concentration[1]. In the presented model we assume that hydrogen concentration ϕ is not very high, so Young's modulus E can be considered as constant. Under this assumption strain ε can be expressed in the form

$$\varepsilon = K\phi + \frac{\sigma}{E} \,, \tag{7}$$

where σ is internal stress, coefficient K characterizes a volume which is occupied by hydrogen inside the material– volume expansion due to the presence of hydrogen atoms in the matrix per one hydrogen atom. In the presented model, for not very high concentration, it can also be considered to be constant.

The mean value[2] of hydrogen concentration $\langle\phi\rangle$ in the sample as well as curvature of the ribbon can be obtained experimentally. Therefore, to confront experimental results with theoretical model, the dependence of the middle radius of curvature of the ribbon on the hydrogen concentration $\langle\phi\rangle$ should be found.

The bent sample is in equilibrium state therefore mean value of internal stress is equal to zero

$$\langle\sigma\rangle = 0 \,. \tag{8}$$

Also the mean value of ε_r, as follows from Eq. (6), equals to zero,

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[1]An influence of gravitational field is negligibly small and will not be taken into account.

[2]All quantities depend only on variable x (see Figs. 1 and 3) or r for the bent sample (see Fig. 3), therefore the mean value of quantity f over the sample volume is

$$\langle f \rangle = \frac{1}{L}\int_0^L f(x)\mathrm{d}x \,.$$

$$\langle \varepsilon_r \rangle = 0 . \tag{9}$$

Using Eqs. (5,7,8,9) we obtain

$$\varepsilon_0 = K \langle \phi \rangle . \tag{10}$$

Finally, using Eqs. (5,7,10), the internal stress σ can be expressed as

$$\frac{\sigma}{E} = K \left(\langle \phi \rangle - \phi \right) + \varepsilon_r . \tag{11}$$

In the equilibrium the energy associated with the deformation ($\sim \frac{1}{2} \sigma^2 / E$) is minimal as well as its mean value

$$\frac{\langle \sigma^2 \rangle}{2E} = \frac{E}{2} \left\langle \left(K \left(\langle \phi \rangle - \phi \right) + \varepsilon_r \right)^2 \right\rangle . \tag{12}$$

Using Eqs. (9,12) the last equation can be rewritten in the form

$$\frac{\langle \sigma^2 \rangle}{2E} = \frac{E}{2} \left[K^2 \left\langle \left(\langle \phi \rangle - \phi \right)^2 \right\rangle + \langle \varepsilon_r^2 \rangle - 2K \langle \varepsilon_r \phi \rangle \right] . \tag{13}$$

The expression for mean values[2] in the last two terms in Eq. (13) can be found using Eqs. (1,2,6)

$$\langle \varepsilon_r^2 \rangle = \frac{1}{12} \frac{l_s^2}{l_0^2 r_s^2} L^2 , \tag{14}$$

$$\langle \varepsilon_r \phi \rangle = - \frac{l_s}{l_0 r_s} \left(\langle \phi x \rangle - \frac{L}{2} \langle \phi \rangle \right) . \tag{15}$$

Finally, using Eqs. (14,15), Eq. (13) can be rewritten in the form

$$\frac{\langle \sigma^2 \rangle}{2E} = \frac{E}{2} \cdot u , \tag{16}$$

where

$$u = K^2 \left\langle \left(\langle \phi \rangle - \phi \right)^2 \right\rangle + \frac{1}{12} \frac{l_s^2}{l_0^2 r_s^2} L^2 + 2K \frac{l_s}{l_0 r_s} \left(\langle \phi x \rangle - \frac{L}{2} \langle \phi \rangle \right)$$

As was mentioned above, in the equilibrium the value of deformation energy is minimal and mean radius of curvature r_s, can be found as a solution of equation

$$\frac{\mathrm{d}}{\mathrm{d} r_s} u = 0 . \tag{17}$$

For our model, the hydrogen concentration ϕ will be assumed to be independent on the degree of ribbon bending. Solution of Eq. (17) gives the following expression for the mean radius of curvature r_s

$$r_s = \frac{l_s}{l_0} \frac{L^2}{12K} \frac{1}{\frac{L}{2} \langle \phi \rangle - \langle \phi x \rangle} . \tag{18}$$

Using Eqs. (1,6,10), the fraction l_s / l_0 can be expressed via $\langle \phi \rangle$

$$\frac{l_s}{l_0} = 1 + K \langle \phi \rangle . \tag{19}$$

Finally, the middle radius of curvature for hydrogenated bent ribbon is

$$r_s = \frac{L^2}{12K} \frac{1 + K \langle \phi \rangle}{\frac{L}{2} \langle \phi \rangle - \langle \phi x \rangle} \approx \frac{L^2}{12K} \frac{1}{\frac{L}{2} \langle \phi \rangle - \langle \phi x \rangle} , \tag{20}$$

since $K \langle \phi \rangle \ll 1$.

A more appropriate parameter for analytic description of the curvature of a hydrogenated sample is the mean curvature C_s of a sample

$$C_s = \frac{1}{r_s} \approx \frac{12K}{L^2} \left(\frac{L}{2} \langle \phi \rangle - \langle \phi x \rangle \right) . \tag{21}$$

In the following section expression for the curvature as a function of time will be obtained for the processes of hydrogenation and dehydrogenation, respectively.

2.1. Sample curvature during hydrogenation

Hydrogen diffusion, i.e. concentration of hydrogen inside the sample as function of time was recently studied in [6]. For the process of one side hydrogenation the concentration can be expressed as [6]

$$\phi(x,t) = \phi_0 - \phi_0 \frac{x}{L} - \frac{2\phi_0}{\pi} \sum_{n=1}^{\infty} \frac{\sin\left(\frac{n\pi}{L} x \right)}{n} \mathrm{e}^{- \frac{n^2 \pi^2 D}{L^2} t} . \tag{22}$$

Using Eq. (22) average values in Eq. (21) can be calculated and the curvature of sample during the process of hydrogenation is expressed by the function

$$C_s = \frac{K \phi_0}{L} \left(1 - \frac{6}{\pi^2} \sum_{l=1}^{\infty} \frac{\mathrm{e}^{- \frac{(2l)^2 \pi^2 D}{L^2} t}}{l^2} \right) . \tag{23}$$

2.2. Sample curvature during hydrogenation

For the process of subsequent dehydrogenation from both sides of the ribbon the concentration can be expressed as [6]

$$\phi(x,t) = \frac{2\phi_0}{\pi} \sum_{n=1}^{\infty} \frac{\sin\left(\frac{n\pi}{L} x \right)}{n} \left(1 - \mathrm{e}^{- \frac{n^2 \pi^2 D}{L^2} t_0} \right) \mathrm{e}^{- \frac{n^2 \pi^2 D}{L^2} t} , \tag{24}$$

where t_0 is the time of hydrogenation. And again, using Eq. (24) average values in Eq. (21) can be obtained and the curvature of sample during the process of dehydrogenation is expressed by function

$$C_s = \frac{K\phi_0}{L}\frac{6}{\pi^2}\sum_{l=1}^{\infty}\left(1 - e^{-\frac{(2l)^2\pi^2 D}{L^2}t_0}\right)\frac{e^{-\frac{(2l)^2\pi^2 D}{L^2}t}}{l^2} \quad . \qquad (25)$$

3. RESULTS AND DISCUSSION

The studied $Fe_{85}B_{15}$ amorphous ribbon was prepared by rapid quenching from the melt in KFKI MTA in Budapest. This alloy does not exhibit any affinity to hydrogen. The length of sample used in experiments was 104 mm, the width $w = 11.8$ mm, thickness $L = 0.029$ mm. Atomic hydrogen was introduced into the sample electrolytically from air side of the ribbon [6]. The duration of hydrogenation was $t_0 = 2$ hours.

The ribbon bending during the process of spontaneous dehydrogenation was recorded every 15 minutes (see Figs. 1,4).
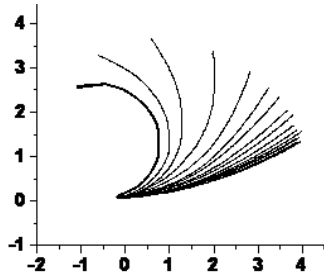
Fig. 4 Records of ribbon shape processed graphically which were used for the calculation of mean curvature as a function of time [7]. The curves from the left to the right were recorded every 15 minutes. The scale on both axes is centimetre.

Using these records experimental dependence of the sample curvature as function of the time (concentration) was obtained [7]. Experimentally obtained values and corresponding fitted curve (Eq. (26)) are shown in Fig. 5
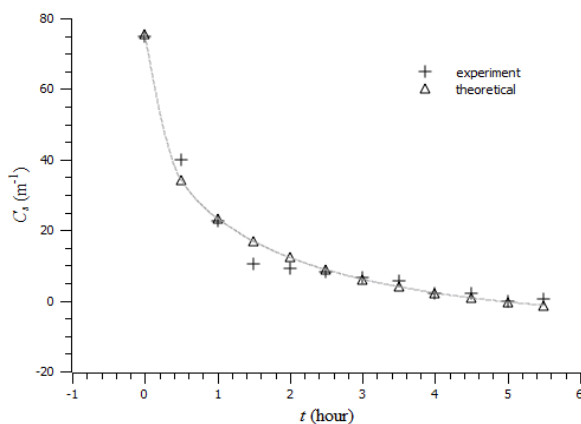
Fig. 5 Mean curvature C_s of $Fe_{85}B_{15}$ amorphous ribbon during process of dehydrogenation.

The known values [6] of concentration $\phi_0 = 2160$ ppm and diffusion coefficient $D = 2.3 \cdot 10^{-15}$ m^{2}s^{-1} were used in the fitting procedure. As a result of this procedure the parameter K introduced in Eq. 7 was obtained:

$K\phi_0 = 0.0033 \rightarrow K \approx 0.016$ (nm)^3. This parameter gives information about an increase of the volume caused by the presence of hydrogen atom. The value obtained approximately corresponds in all three dimensions to the so called Van der Waals radius for hydrogen (120 pm).

4. CONCLUSION

The proposed simple theoretical model for curvature of the one side hydrogenated thin ribbon from material without an affinity to hydrogen is in a good agreement with experimental results. Its fitting to experimental data provides important information on the local space enlargement around introduced hydrogen atom, which can change local magnetic characteristics.
Proposed method also provides information on the distribution of internal stresses depending on the distribution of hydrogen concentration in the sample. Since the studied materials exhibit high magnetostriction, the obtained theoretical results can be the base for further study of such important magnetic characteristics of the studied materials as e.g. magnetoelastic anisotropy constant [8].

REFERENCES

[1] SALIMON, A. I. – ASHBY, M. F. – BRECHET, Y. – GREER, A. L.: *Mater. Sci. Eng.*, 375-377 (2004) 385.

[2] ALCALÁ, E. M. – LÓPEZ, E. – AROCA, C. – SÁNCHEZ, M.C. – SÁNCHEZ, P.: *Eur. Phys. J. B*, 14 (2000) 473.

[3] ELIAZ, N. – ELIEZER, D.: *Advanced Performance Materials,* 6 (1999) 5.

[4] AKIHISA. I.: *Acta. Mater.*, 48 (2000) 279.

[5] SPIVAK, L. V. – SKRYABINA, N. Ye.: *International Journal of Hydrogen Energy*, 24 (1999) 795.

[6] NOVÁK, L. – ZIMAN, J. – KOVAĽAKOVÁ, M. – KLADIVOVÁ, M.: *Acta Electrotechnica et Informatica*, 12 (2012) 72.

[7] KOVAĽAKOVÁ, M. – NOVÁK, L. – ŠEVČOVIČ, L.: *Proceedings of the 10th International Workshop on Applied Physics of Condensed Matter.* , Slovak University of Technology, (2004) 138.

[8] KOVAĽAKOVÁ, M. – KOLLÁR, P. – NOVÁK, L. – ŠEVČOVIČ, L.: *J. Magn. Magn. Mater.,* 304 (2006) e648.

BIOGRAPHIES

Mária Kladivová graduated in mathematical physics in 1980. In 2008 she received the PhD. degree from Pavol Jozef Šafárik University in Košice. She has been working at the Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice since 1995. Study of ferromagnetic materials is a dominant field of her current research interest.

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