JOURNAL OF MATERIALS SCIENCE **36** (2001) 4125–4129

Influence of annealing and hydrogenation-dehydrogenation processes on internal stresses and barkhausen noise of $Fe_{83}B_{17}$ amorphous alloy

L. CENIGA, F. KOVÁČ
Institute of Materials Research, Watsonova 47, 043 53 Košice, Slovak Republic
E-mail: ceniga@saske.sk, kovacf@saske.sk

Internal stresses as a consequence of structural changes of the $Fe_{83}B_{17}$ amorphous alloy during annealing and hydrogenation-dehydrogenation processes were investigated by structurally sensitive properties as a stress induced anisotropy, a coercive force, a demagnetizing factor and Barkhausen noise parameters.

1. Introduction

An investigation of amorphous alloys has been performed for several years due to their excellent soft magnetic properties. In spite of a low anisotropy of amorphous alloys [1, 2], their structure is considered to be clustered [3, 4] what can be, also reflected by a distribution of internal stresses. To obtain information about the internal stresses, an investigated amorphous alloy structure was changed during annealing and hydrogenation-dehydrogenation processes.

2. Experimental method

The samples of the $Fe_{83}B_{17}$ amorphous alloy were prepared by the spinning wheel technique in a form of the 10 mm wide and 20 μm thick ribbons [5–7]. The first series of the 150 mm long samples were isothermally annealed at different temperature in argon protective atmosphere for 1 hour with the 5 deg/min cooling rate in the end.

The $Fe_{83}B_{17}$ amorphous alloy of an as-cast state was also hydrogenated electrolytically at room temperature for 2 hours [8–19]. The sample dehydrogenation was effected spontaneously in air at room temperature. The hydrogen content was not measured but on the basis of the results of the paper [8] it could be estimated that H/M ratio after the hydrogenation could be about 0.01. In the case of the hydrogenation-dehydrogenation process, the first series of measurement began with measurement of magnetic and Barkhausen noise parameters in the as-cast state and then the sample was hydrogenated. The hydrogenation time is given in the Figs 5 and 6 as negative time on the time axis. The magnetic parameters were then measured at an interval of 30 minutes during 20 hours of the first day of the dehydrogenation and once a day during next 29 days of the dehydrogenation [17, 20].

The magnetic parameters to be measured at room temperature were [20, 21]: the whole quasi-static hysteresis curve and the anhysteresis curve from which values of the coercive field, H_c, the total and stress induced anisotropy energy, K_i and K_σ, determined from the area over the virgin curve and the demagnetizing curve, respectively, the total demagnetizing factor, D, as a sum of the inner and geometrical demagnetizing factor, D_i and D_g, respectively, were evaluated. The K_σ parameter was induced by a value and a heterogeneous distribution of internal stresses [13, 14]. The D_g was calculated from the sample geometry [15], $D_g = 15.3 \times 10^{-5.}$

The Barkhausen noise parameters to be measured at room temperature were [17, 19–23]: the power spectrum, $S(f)$, the number and total number of Barkhausen pulses per a volume unit, n and N, respectively. The external magnetic field intensity for the Barkhausen noise measurement varied in the -1000–$+1000$ A m^{-1} range. The n parameter was registered and increased during the magnetization process along one branch of the hysteresis loop (Figs 3 and 8) and then the N parameter represents a value of the n parameter to be reached at 1000 A m^{-1}.

3. Results and discussion

3.1. Annealing process

An annealing process of metal alloys is connected with a relaxation process characterized by internal stresses decrease and a precipitation process which could be generally attributed to low and high annealing temperature, respectively [23]. In the case of amorphous alloys, the precipitation process is represented by an amorphous structure crystallization which is usually preceded by forming of regions of such chemical composition which is suitable for crystallization of individual phases, e.g. the regions of higher concentration of B-atoms than in surroundings is formed for crystallization of the Fe_2B phase [24].

The relaxation process expressive influence which was observed in the temperature range to about 240°C (Figs 1 and 2) was a reason of the internal

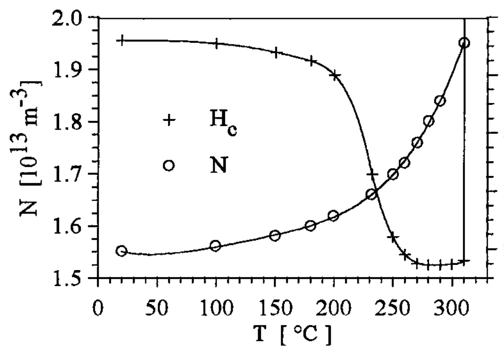

Figure 1 The coercive field, H_c, and the total number of the Barkhausen pulses per a volume unit, N, vs. annealing temperature.

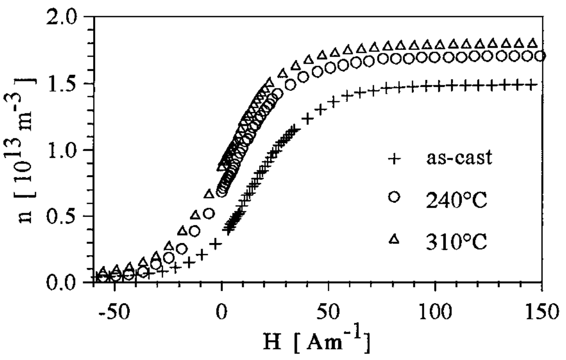

Figure 3 The BP number per a volume unit, n, during magnetization process.

stresses reduction causing the concave decrease of the H_c, K_i, K_σ parameters [21, 23]. The changes of the concave course to the convex course of the H_c, K_i, K_σ parameters at about 240°C could indicate the presence of the concentration-suitable regions in the amorphous structure [21, 23]. The rapid increase of the H_c, K_i parameters was connected with the crystallization process which created crystalline grains within these regions [21, 23]. The $K_i - K_\sigma$ difference in the temperature range to about 310°C was constant and small so it could be concluded that the K_i parameter was mainly of an origin of the K_σ parameter [21, 23]. The K_i increase above 310°C was a consequence of a crystalline lattice anisotropy [21, 23]. On the other hand, the K_σ increase above 310°C was caused by a presence of crystal line lattice defects which increased the internal stresses [21, 23]. The values of the H_c, K_i, K_σ parameters at 320°C are 540 A m^{-1}, 675 J m^{-3}, 195 J m^{-3}, respectively.

Modifying the Fe-B structure by the annealing, the D_g factor was unchanged so a possible change of the D factor would be only due to the D_i change [17, 18]. The D_i factor is given by the demagnetizing field due to magnetic inhomogeneities inside the material, e.g. non-magnetic inclusions or clusters [17, 18]. The almost constant course of the D factor in the temperature range to 310°C could indicate homogeneous structure of the Fe-B amorphous alloy unlike the results published in the paper [23]. The D increase above 310°C could be attributed to the crystallization process because of crystalline lattice anisotropy [23].

The Fig. 3 shows courses of the n parameter during the magnetization process for the as-cast and annealed states. It is evident that the n parameter was almost constant above 60 A m^{-1} of the external magnetic field intensity, H, [17, 21, 23] so a contribution of domain walls irreversible motion to a total magnetization was then expressive in the range to 60 A m^{-1} [17, 21, 23]. The H was the linear function of time so the n parameter was also time-dependent and then $dn/dt \propto dn/dH$ [17, 21, 23]. The $S(f)$ parameter (Fig. 4), $S(f) \propto dn/dt$ [17, 21, 23], was always registered at the external field intensity equal to the sample coercive field [17, 21, 23]. The inexpressive changes of the n gradient at $H = H_c$ for the measured sample states were then responsible for the inexpressive changes of the $S(f)$ intensity [17, 21, 23].

The small shift towards lower frequencies and the smaller slope of the $S(f)$ parameter by the annealing process could indicate that the Barkhausen pulses of the annealing states are characterized by a shorter duration and by a higher slope of their increasing part [17, 21, 23]. As a consequence of the internal stresses decrease, the $\partial U/\partial x$ function barriers, which influence domain walls motion and are not influenced by external magnetic field but by internal stresses [22], also decreased what was reflected by the N increase [17, 21].

The $S(f)$ shift corresponded to the shift of maximum and inflexion points of the $S(f)$ courses, ω_m and ω_i (Table I), respectively, which were found from curves fitting these courses. It is evident from the Table I that the obtained experimental values were in a good agreement with the theoretical predictions which were published in the paper [20], presenting the relation, $\omega_i = \omega_m \frac{3+\sqrt{5}}{2}$.

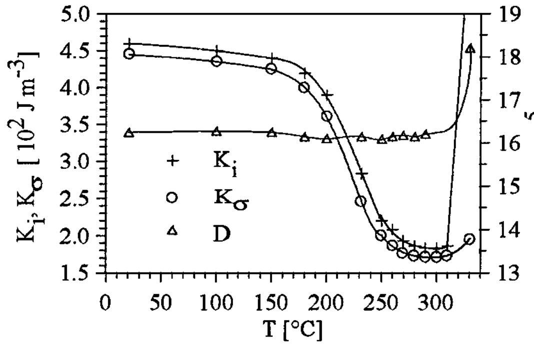

Figure 2 The total and stress induced anisotropy energy, K_i and K_σ, respectively, vs. annealing temperature.

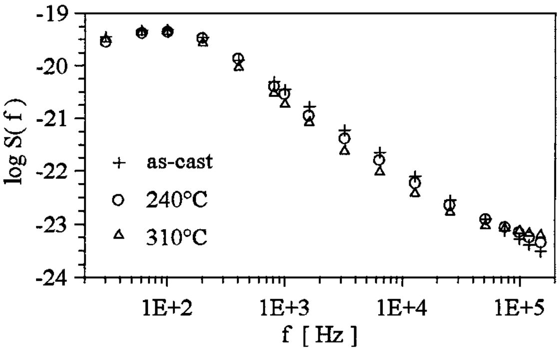

Figure 4 The Barkhausen noise power spectrum, $S(f)$.

TABLE I Maximum and inflexion points of Barkhausen noise power spectra, ω_m and ω_i, respectively

	As-cast	240°C	310°C	Hydrogenated	9 days	30 days
ω_m [2πHz]	525	413	374	218	387	478
ω_i [2πHz]	1432	1128	1157	609	1089	1303

During the annealing process all parameters were measured in the temperature range to 310°C within which the samples were characterized by soft magnetic properties [17, 21].

3.2. Hydrogenation-dehydrogenation process

Hydrogen atoms, which occupy the Bernal's holes in the amorphous matrix [19] and increase internal stresses, caused the H_c, K_i, K_σ rapid increase (Figs 5 and 6) [12–19]. The chemical components of the $Fe_{83}B_{17}$ sample have not high affinity to the hydrogen atoms, which could then move in the sample and could escape of the sample easily [12–19]. It could be then postulated that most of the hydrogen atoms left the sample at room temperature during 20 hours (Figs 5 and 6) [12–19]. The decreasing hydrogen content was then a reason of the magnetic parameters decrease [12–19].

After 20 hours of the dehydrogenation the H_c parameter reached higher values than before the hydrogenation. This fact could indicate that either the hydrogen atoms caused some defects remained in the amorphous structure during and after the hydrogenation, e.g. microcracks [17], or a rest of the hydrogen atoms remained in the sample even after 20 hours of the dehydrogenation [12–19]. The K_i, K_σ small irreversible decrease after 20 hours of the dehydrogenation could be attributed to a relaxation-like effect [12–19]. Due to big internal stresses around hydrogen atoms, matrix atoms were pushed away into regions of lower internal stresses. This relaxation-like effect was similar to that during a low-temperature annealing process [12–19].

The decrease and the increase of the D parameter after the hydrogenation and during the dehydrogenation, which were observed in the case of Fe-V-B, Fe-Cr-B, Fe-Ni-Zr amorphous alloys [8–10], indicated a presence of clusters consisting of weakly-coupled atoms which connections were destroyed and reformed as a consequence of the increase and the decrease of the internal stresses, respectively. In accordance with that, the $Fe_{83}B_{17}$ amorphous structure could be considered to be stable because of no changes of the D parameter during the hydrogenation-dehydrogenation process. The chemical composition of the investigated amorphous alloy, which represents an eutectic point composition of the Fe-B system [17], is perhaps seemed to be a reason of the stability.

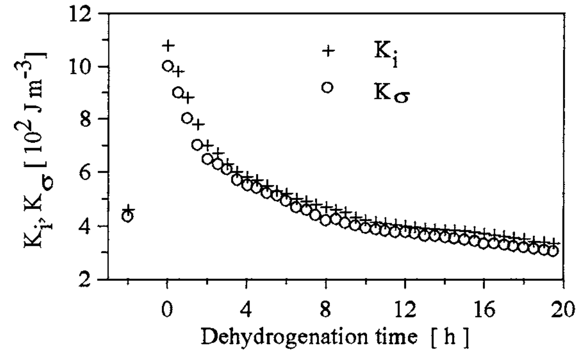

Figure 6 The total and stress induced anisotropy energy, K_i and K_σ, respectively, vs. dehydrogenation time.

The N/N_{ac} course during the dehydrogenation is shown in the Fig. 7 and for the as-cast sample $N_{ac} = 1.55 \times 10^{13}$ m^{-3} (Fig. 1). After the hydrogenation, the $\partial U/\partial x$ function barriers, which were situated in places of the hydrogen atoms occurrence, increased, so the domain walls motion was influenced only by them and not by the lower barriers situated between them [22]. This fact could explain the N/N_{ac} rapid decrease after the hydrogenation [17].

The Fig. 8 shows the courses of the n parameter during the magnetization process for the as-cast, hydrogenated states and after 9 and 30 days of the dehydrogenation of the sample. The contribution of domain wall irreversible motion to the total magnetization in the case of the hydrogenation-dehydrogenation process was also expressive in the range to 60 A m^{-1} likewise as in the case of the annealing (Fig. 3). In contrast to the annealing process (Figs 3 and 4), the expressive changes of the n gradient at $H = H_c$ were observed what was a reason of the expressive changes of the $S(f)$ intensity (Fig. 9). The expressive shift towards lower frequencies (Table I) and the expressive smaller

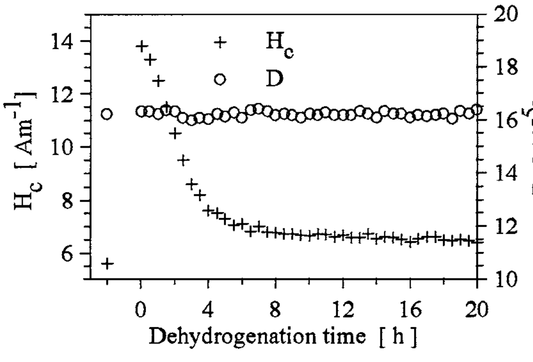

Figure 5 The coercive field, H_c, and the total demagnetizing factor, D, vs. dehydrogenation time.

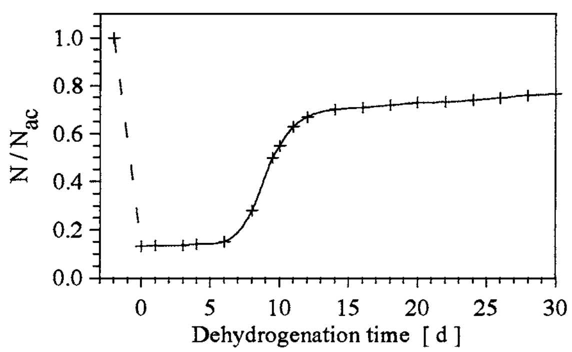

Figure 7 The N/N_{ac} vs. dehydrogenation time.

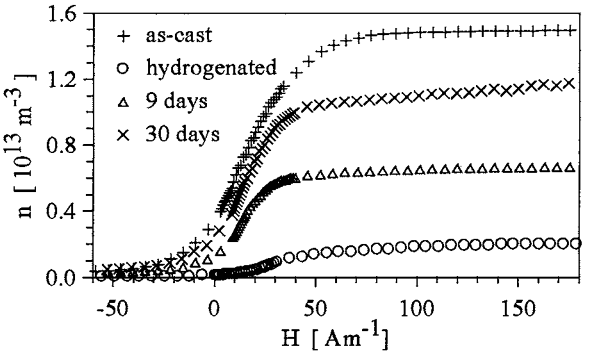

Figure 8 The BP number per a volume unit, *n*, during magnetization process.

slope of the $S(f)$ parameter after the hydrogenation were reflected by a shorter duration of the Barkhausen pulses and by a higher slope of the Barkhausen pulses increasing part, respectively [17, 20, 23]. In the case of the hydrogenation-dehydrogenation process, the obtained values of the maximum and inflexion points were also in a good agreement with the theoretical relation [20].

In contrast to the H_c, K_i, K_σ changes during 20 hours of the dehydrogenation, the expression time delay of the N/N_ac, n, $S(f)$ reactions to the dehydrogenation was observed [17]. It is evident that the H_c, K_i, K_σ parameters reached after 20 hours almost the same values as before the hydrogenation (Figs 5 and 6) but the N, n, $S(f)$ parameters changed after 6–7 days of the dehydrogenation (Figs 7–9). The K_i, K_σ parameters represent an average value of the internal stresses over a sample. The Barkhausen noise parameters are sensitive to a presence of centres of very big internal stresses above all and then these parameters are not influenced by the decrease of the average value of the internal stresses. On the other hand, due to small amount of the centres, the K_i, K_σ parameters are not perhaps expressively influenced by their presence. Only after 6–7 days of the dehydrogenation, these centres were maybe destroyed what was expressed by the N, n, $S(f)$ changes. The N, n, $S(f)$ expressive changes could be caused by the more intensive dehydrogenation although no expressive changes of the H_c, K_i, K_σ parameters were measured during next 29 days of the dehydrogenation [17]. The hydrogen atoms rest [12–19] and perhaps the microcracks, forming after the hydrogenation [17, 20], could be responsible for the N, n, $S(f)$ expressive irreversible changes which were observed even after 30 days of the dehydrogenation [17, 20].

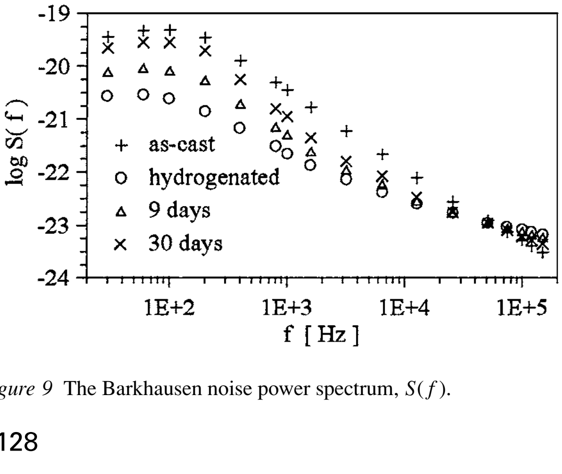

Figure 9 The Barkhausen noise power spectrum, $S(f)$.

4. Conclusions

The results obtained from the investigation of an influence of the annealing and hydrogenation-dehydrogenation processes on the magnetic properties and the Barkhausen noise parameters are as follows:

- the H_c, K_i, K_σ concave-convex decrease during the annealing process in the temperature range to about 310°C was a consequence of the amorphous structure relaxation characterized by more intensity in the temperature range to about 240°C,
- along with the structural relaxation in the temperature range above 240°C, the observed convex decrease of these parameters was caused by forming of the regions of such chemical composition which was suitable for crystallization of individual phases [24],
- the rapid increase of these parameters was connected with the crystallization process which created crystalline grains within these regions [24],
- the small shift towards lower frequencies and the smaller slope of the $S(f)$ parameter were reflected by a shorter duration of Barkhausen pulses and by a higher slope of their increasing part of the annealed state [17, 20, 23],
- after the hydrogenation, the expressive changes of all investigated parameters were observed,
- during the dehydrogenation, the relaxation-like effect appeared being similar to a low-temperature annealing process,
- the magnetic properties changes during the dehydrogenation caused by the decrease of the internal stresses average value were not followed by the changes of the Barkhausen noise parameters which were a consequence of changes of the internal stresses fluctuation.

Acknowledgement

This work was supported by the Slovak Grant Agency VEGA (No. 2/1063/21, 1/8128/01).

References

1. K. CSACH, A. KASARDOVÁ, V. OCELÍK, J. MIŠKUF and V. Z. BENGUS, *Acta Physica Slovaca* **46** (1996) 141.
2. V. OCELÍK, K. CSACH, A. KASARDOVÁ, J. MIŠKUF, V. Z. BENGUS and P. DUHAJ, *Key Eng. Mat.* **97–98** (1994) 97.
3. A. KASARDOVÁ, V. OCELÍK, K. CSACH and J. MIŠKUF, *Phil. Mag. Lett.* **71** (1995) 257.
4. J. MIŠKUF, K. CSACH, V. OCELÍK, V. Z. BENGUS, E. D. TABACHNIKOVA and P. DUHAJ, *Met. Mat.* **3** (1999) 153.
5. A. LOVAS, L. F. KISS, B. VARGA, P. KAMASA, I. BALOGH and I. BAKONYI, *J. Phys. IV. France* **8** (1998) 29.
6. B. VARGA, K. TAKÁCS, A. LOVAS, P. KAMASA, F. ZHOU and J. VANDLIK, *J. Mat. Scien. Technol.* **14** (1998) 323.
7. P. KAMASA, L. K. VARGA, É. KISDI-KOSZÓ and J. VANDLIK, in Proceedings of the 9th International Conference on Rapidly Quenched and Metastable Alloys, Bratislava, March 1996, edited by P. Duhaj, P. Mrafko, P. Svec (Elsevier, Amsterdam, 1997) p. 280.

8. É. KISDI-KOSZÓ, L. F. KISS, L. K. VARGA, P. KAMASA, and P. DUHAJ, *Mater. Sci. Eng. A* **226–228** (1997) 689.
9. I. JACYNA-ONYSZKIEWICZ and P. KAMASA, *J. Phys. IV France* **8** (1998) 315.
10. P. KAMASA, P. MYSLINSKI, B. VARGA and Z. JURASZ, *Acta Phys. Slov.* **48** (1998) 857.
11. I. BAKONYI, E. TÓTH-KADAR, J. THÓTH, L. POGANY, T. TARNÓCZI and P. KAMASA *J. Phys. Cond. Matter.* **11** (1999) 963.
12. L. NOVÁK, É. KISDI-KOSZÓ and P. DUHAJ, in Proceedings of the 9th International Conference on Rapidly Quenched and Metastable Alloys, Bratislava, March 1996, edited by P. Duhaj, P. Mrafko, P. Svec (Elsevier, Amsterdam, 1997) p. 216.
13. L. POTOCKÝ, É. KISDI-KOSZÓ, I. NAGY, L. NOVÁK, A. LOVAS and J. TAKÁCS, *Anales de Fisica B* **86** (1990) 193.
14. É. KISDI-KOSZÓ, L. POTOCKÝ, M. HRABČÁK, L. NOVÁK and A. LOVAS, *JMMM* **92** (1990) 181.
15. J. ZIMAN, B. ZAGYI and L. NOVÁK, *Phys. Stat. Sol. B* **171** (1992) 177.
16. Z. JURÁNEK, P. KOLLÁR, L. POTOCKÝ, L. NOVÁK and É. KISDI-KOSZÓ, *Acta Phys. Slov.* **38** (1988) 261.
17. L. CENIGA and L. NOVÁK, *Acta Phys. Polonica* **97** (2000) 575.
18. L. NOVÁK, É. KISDI-KOSZÓ, M. KONČ and M. ZATROCH, *JMMM* **160** (1996) 261.
19. L. NOVÁK, É. KISDI-KOSZÓ, A. STANČÁKOVÁ, L. KAFKOVÁ and M. KONČ, *Key Eng. Mat.* **81–83** (1993) 337.
20. L. CENIGA, K. ŠTERBÁKOVÁ, L. NOVÁK and M. ZENTKOVÁ, *Czech. J. Phys.* **49** (1999) 549.
21. L. CENIGA, L. NOVÁK and É. KISDI-KOSZÓ, *JMMM* **196–197** (1999) 154.
22. E. KNELLER, "Ferromagnetismus" (Springer-Verlag, Berlin, 1962) p. 102.
23. L. CENIGA, L. NOVÁK and A. ZENTKO, *Acta Phys. Polonica* **97** (2000) 611.
24. O. M. BARABASH and U. N. KOVAL, "Structure and Properties of Metals and Alloys—Crystalline Structure of Metals and Alloys" (НаукоаR умка, Kiev, 1986) p. 324 (in Russian).

Received 15 August 2000
and accepted 24 April 2001