

A. CHROBAK*, M. KUBISZTAL**, G. HANECZOK**, D. CHROBAK**, P. KWAPULIŃSKI**, Z. STOKŁOSA**, J. RASEK**

PHASE STABILITY AND STRUCTURAL RELAXATION IN Fe-Nb-B AMORPHOUS ALLOYS

STABILNOŚĆ FAZOWA I RELAKSACJA STRUKTURALNA W STOPACH AMORFICZNYCH Fe-Nb-B

In the present paper the phase stability in the $\text{Fe}_{86-x}\text{Nb}_x\text{B}_{14}$ ($2 \leq x \leq 8$) group of amorphous alloys was examined by applying i) DSC measurements, ii) Young modulus versus temperature and iii) magnetic after effects. It was shown that different physical quantities i.e. i) the optimized magnetic permeability, ii) the heat of amorphous – crystalline transition and iii) the change of Young modulus taking place during structural relaxation of amorphous Fe-Nb-B alloys exhibit the remarkable maximum for $x = 6$ at.% Nb. The degree of amorphisation measured by the heat transition (energetic difference between amorphous and crystalline state) or by change of the Young modulus (intensity of structural relaxation) is the main reason of structural changes favorable for soft magnetic properties enhancement effect. Intensity of magnetic after effects, corresponding to the free volume content, decreases with increasing Nb content.

Keywords: amorphous alloys, optimization effect, nanoperm alloys, structural relaxation

W niniejszej pracy badano stabilność fazową w amorficznych stopach $\text{Fe}_{86-x}\text{Nb}_x\text{B}_{14}$ ($2 \leq x \leq 8$) poprzez zastosowanie takich technik pomiarowych jak pomiary kalorymetryczne DSC, pomiary modułu Younga w funkcji temperatury oraz pomiary przenikalności magnetycznej po rozmagnesowaniu próbek. Z otrzymanych wyników wynika, że różne wielkości fizyczne (zoptymalizowana przenikalność magnetyczna, ciepło krystalizacji, zmiana modułu Younga w trakcie relaksacji strukturalnej) wykazują charakterystyczne maksimum dla próbek o zawartości $x = 6\%$ Nb. Na tej podstawie sformułowano wniosek, że stopień amorficzności badanych stopów, mierzony jako ciepło przemiany ze stanu amorficznego do krystalicznego (energia swobodna zamrożona procesie produkcji próbek) oraz zmiana modułu Younga (natężenie relaksacji strukturalnej), jest decydującym czynnikiem dla korzystnych, z punktu widzenia optymalizacji miękkich właściwości magnetycznych, przemian strukturalnych. Zmiana przenikalności magnetycznej po rozmagnesowaniu, odpowiadająca stężeniu mikropustek w strukturze amorficznej, maleje wraz ze wzrostem stężenia niobu.

1. Introduction

Amorphous and nanocrystalline *nanoperm* type alloys are very interesting from both scientific and practical point of view. It is known that magnetic properties of such materials can be significantly improved by applying a suitable thermal annealing leading to structural relaxation and nanocrystallization [1–11]. The so-called optimization annealing can cause an increase of magnetic permeability more than 10 times which is usually explained by formation of iron nanograins in amorphous surroundings. Magnetic anisotropy of the optimized microstructure averages to zero giving the mentioned above increase of magnetic permeability [2, 3].

Recently, we have reported that in the Fe-Nb-B amorphous alloys the main role in the optimization ef-

fect plays structural relaxation i.e. annealing out of free volume leading to formation of small iron clusters [6]. Therefore, the aim of this paper is to study structural changes and phase stability in the $\text{Fe}_{86-x}\text{Nb}_x\text{B}_{14}$ ($2 \leq x \leq 8$) group of amorphous alloys.

The optimization effect observed in [6, 7] is shown in Fig. 1. Samples were annealed for 1h at temperatures $300 < T_a < 900$ K and magnetic permeability was measured at room temperature. Let notice that for $x = 6$ at.% Nb and $T_a = 700$ K (denoted as the 1h optimization temperature T_{op}) magnetic permeability increases about 14 times (from 2400 to 33000) and this phenomenon occurs in the so-called relaxed amorphous phase free of α -Fe nanograins [6, 12]. Niobium as an alloying addition causes a slowing down of diffusion processes and significantly increases crystallization temperature [12] so

* INSTITUTE OF PHYSICS, UNIVERSITY OF SILESIA, 40-007 KATOWICE, 4 UNIWERSYTECKA, POLAND

** INSTITUTE OF MATERIALS SCIENCE, UNIVERSITY OF SILESIA, 40-007 KATOWICE, 12 BANKOWA, POLAND

for these chemical compositions the relaxed amorphous structure free of nanograins can be easily observed. This fact is of great importance because such material is not as brittle as a nanostructured one and applications of these kinds of alloys can be significantly broadened.

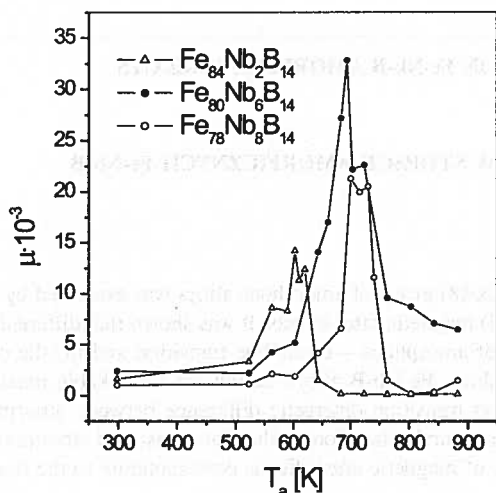


Fig. 1. Relative initial magnetic permeability determined at room temperature for samples annealed for 1h at temperatures T_a [7]

According to [6] iron clusters (acting as sub-nanograins) which are magnetically coupled and coherent with the amorphous surrounding are a characteristic feature of the relaxed amorphous phase. A microstructure with iron clusters of dimensions smaller than the ferromagnetic exchange length gives a random distribution of magnetic anisotropy and leads to the increase of magnetic permeability. It is a simple consequence of the averaging anisotropy energy to zero. According to [6, 12] annealing of the $Fe_{80}Nb_6B_{14}$ alloy at temperatures $T_a \leq 760$ ($T_{op} = 700$ K) for 1 hour causes formation of nanograins and finally the full crystallization.

In general, the driving force for crystallization is a free energy frozen during fabrication. After fast quenching during fabrication the amorphous material is in a metastable state trapped into an energetic local minimum and continuously tends to a new energetic equilibrium via atomic jumps over an overall energetic barrier called the activation energy. Energetic factors responsible for the structural changes can be determined by applying several measurement techniques (differential scanning calorimetry (DSC), magnetic balance, Young modulus versus temperature, magnetic after effects etc.) [1–8, 11, 13]. In any way in order to improve our knowledge it is necessary to study in detail all factors responsible for the driving force for crystallization and a slowing down of diffusion processes.

2. Material, experimental procedure and results

The examined alloys – $Fe_{86-x}Nb_xB_{14}$ ($2 \leq x \leq 8$) – were obtained by melt spinning technique in a form of strips with thickness and width of about 25 μm and 10 mm, respectively. As quenched samples were in amorphous state which was confirmed by X-ray measurements and high resolution electron microscopy techniques [12]. The phase stability and the structural relaxation was examined by applying the following measurements: i) heat transition of amorphous – crystalline state Q_T (the area under the exothermal peak of differential scanning calorimetry – DSC, Perkin-Elmer DSC-7, temperature range of 300–850 K, heating rate 5 K/min), ii) Young modulus E of as quenched samples versus temperature (vibrating-reed apparatus for which $f^2 \propto E$; f is the frequency of free vibration, maximal deformation was of the order of 10^{-5} , temperature range of 300–800 K, heating rate 5 K/min) and iii) magnetic after effects $\Delta\mu/\mu$ measured at room temperature for samples annealed for 1h at temperatures T_a ranging from 300 K to 900 K (were $\Delta\mu = \mu(t_1) - \mu(t_2)$; $t_1 = 30$ s and $t_2 = 1800$ s are times after demagnetization; Maxwell-Wien bridge, frequency of about 1 kHz, magnetic field 0.5 A/m).

Fig. 2 shows a family of DSC curves obtained for samples with different Nb content. The DSC signal was recalculated by subtracting the base line and taking the samples mass into consideration. As it was expected in all cases a typical DSC exothermal peak due to primary crystallization is observed. The shift of this peak into higher temperatures with increasing Nb content is well documented (for $x = 2$ at.% Nb $T_x = 720$ K and for $x = 8$ at.% Nb $T_x = 805$ K). Moreover, the height as well as the area of the peak depend on the Nb content.

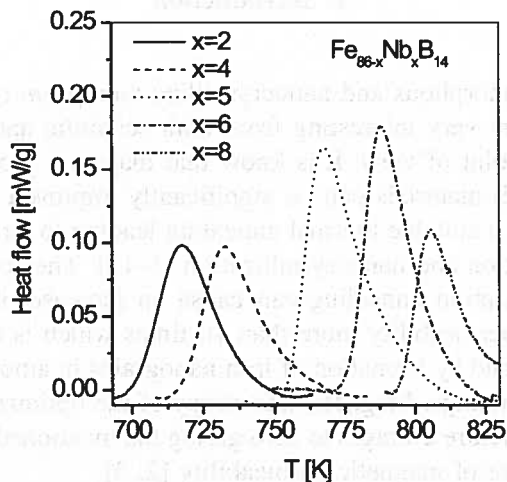


Fig. 2. Experimental DSC maxima measured for $Fe_{86-x}Nb_xB_{14}$ amorphous alloy (heating rate 5 K/min)

Figure 3 shows an example of DSC and Young modulus curve determined with heating rate 5 K/min for samples containing 6 at.% of Nb. The Young modulus $E(T)$ decreases in the temperature range 300–400 K as it is expected for a solid state. An anomalous behavior is observed in temperature range 400–600 K where $E(T)$ significantly increases. It reveals a change of mean interatomic distances and is due to structural relaxation in amorphous phase. Finally, at $T > 750$ K a strong rise of $E(T)$, corresponding to the crystallization, is observed. The latter as it can be seen is correlated with the DSC exothermal maximum ($T_x = 788$ K).

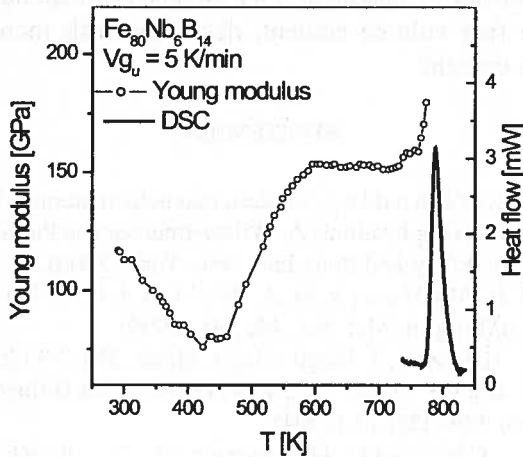


Fig. 3. Young modulus versus temperature and DSC curve determined for $\text{Fe}_{89}\text{Nb}_6\text{B}_{14}$ amorphous alloy

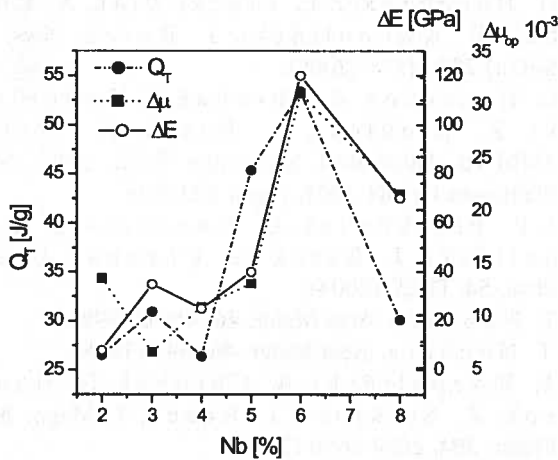


Fig. 4. The heat transitions amorphous – crystalline state Q_T , the change of Young modulus during structural relaxation ΔE and the change of magnetic permeability reflecting the optimization effect plotted versus Nb content

Figure 4 shows different physical quantities sensitive to structural changes (local atomic rearrangements) taking place during structural relaxation and crystallization plotted versus Nb content i.e. i) Q_T (heat transition of amorphous to crystalline state calculated from DSC curves as the area under exothermal maximum), ii) ΔE (the change of $E(T)$ during the structural relaxation i.e.

$\Delta E = E(600\text{K}) - E(300\text{K})$) and iii) $\Delta\mu_{op}$ (the change of magnetic permeability during the structural relaxation i.e. $\Delta\mu_{op} = \mu_{op} - \mu_{asq}$; μ_{op} and μ_{asq} are magnetic permeability determined for the optimized microstructure (for sample annealed at T_{op} for 1 h) and for the as quenched state, respectively).

The heat transition Q_T can be considered as the energy between amorphous and crystalline phase and raises from 25 J/g to 55 J/g for $x = 2$ to $x = 6$ at.% Nb content and falls down for $x = 8$ at.% of Nb. As it can be seen the ΔE and $\Delta\mu/\mu_{op}$ exhibit similar behavior.

This result does not correspond to a change of the activation enthalpy with Nb content which for x ranging from 5 to 8 at.% Nb is almost constant and equals 4 eV [12].

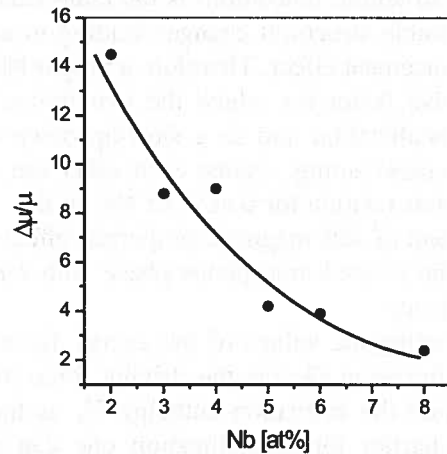


Fig. 5. Magnetic after effects for the as quenched samples versus Nb content

Figure 5 presents magnetic after effects $\Delta\mu/\mu$ determined for the as quenched samples. As it can be seen the $\Delta\mu/\mu$ curve continuously decreases with increasing Nb content.

3. Discussion

On account of wide practical applications of amorphous alloys based on iron as modern soft magnets the experimental studies of the enhancement of soft magnetic properties effect are of great importance. Especially interesting are those studies referring to the context of structural changes in amorphous phase. Generally, in amorphous structure there are two opposing factors. The first is a natural force leading to the crystallization or better to transition amorphous state – crystalline state. The second one originating from some alloying additions leads to a slowing down of diffusion processes i.e. acts just in opposite to the first one.

As we recently reported [6] Nb as an alloying addition shifts the crystallization into high temperature re-

gion which allows formation of the relaxed amorphous phase as a precursor of nano and full crystallization [6, 12]. Besides, it should be another factor making possible formation of iron clusters coherent with amorphous surrounding and magnetically coupled [6, 8, 14]. Let notice that the optimization curve (see Fig.1) shows a remarkable maximum situated at $x = 6$ at.% of Nb. Similarly, in Fig. 4 both the heat transition Q_T and the Young modulus ΔE show the maximum for the same Nb content. We point out this observed correlation between different physical quantities is the main results of the present paper.

One can suggest that a degree of amorphisation measured as the energy difference between amorphous and crystalline state or by a change of Young modulus (intensity of structural relaxation) is the main reason causing a favorable structural changes leading to soft magnetic enhancement effect. Therefore a proper Nb content is a decisive factor for which the two forces (leading to the crystallization and to a slowing down of diffusion processes) acting against each other are really in advantageous relation for 6 at.% of Nb. In this point the enhancement of soft magnetic properties effect can take place in the relaxed amorphous phase with a relatively high efficiency.

Comparing the values of the energy frozen during sample fabrication Q_T (as the driving force to crystallization) and the activation enthalpy H_a as the overall energetic barrier for crystallization one can conclude $H_a \gg Q_T$. For instance, for sample with $x = 6$ at.% Nb $H_a = 4$ eV [12] and $Q_T = 0.03$ eV (see Fig. 4). In spite of the low value of Q_T , the phase transition needs much more energy, for example in the form of heat.

Amorphous structure can be also characterized by the so called free volume content, which according to [15, 16], is responsible for time instability of amorphous structure. Magnetic relaxation is due to atomic pairs formed in the vicinity of free volume in amorphous structure. This was monitored by measuring the magnetic permeability after effects ($\Delta\mu/\mu$ curve, see Fig. 5). The free volume content decreases with increasing Nb content. Moreover, there is no maximum for $x = 6$ at.% Nb on the contrary to the results presented in Fig. 4. This indicates that free volume content does not directly influence on the degree of amorphisation of the tested alloys.

4. Conclusions

The main conclusions of the paper can be summarized as follows:

- Different physical quantities i.e. i) the optimized magnetic permeability, ii) the heat of amorphous – crystalline transition and iii) the change of Young modulus taking place during structural relaxation of amorphous Fe-Nb-B alloys exhibit the remarkable maximum for $x = 6$ at.% Nb.
- The degree of amorphisation measured by the heat transition (energetic difference between amorphous and crystalline state) or by change of the Young modulus (intensity of structural relaxation) is the main reason of structural changes favorable for soft magnetic properties enhancement effect.
- Intensity of magnetic after effects, corresponding to the free volume content, decreases with increasing Nb content.

REFERENCES

- [1] R. C. O'Hanley, Modern magnetic materials, Principles and applications, A. Willey-Interscience Publication, John Willey and Sons Inc., New York (2000).
- [2] M. E. McHenry, M. A. Willard, D. E. Laughlin, Prog. in Mat. Sci. **44**, 291 (1999).
- [3] G. Herzer, J. Magn. Mater. **294**, 99 (2005).
- [4] G. Haneczok, J. Rasek, Defects and Diffusion Forum **224–225**, 13 (2004).
- [5] A. Chrobak, G. Haneczok, Z. Stokłosa, P. Kwapuliński, J. Rasek, G. Chełkowska, Phys. Stat. Sol. (a) **196**, 248 (2003).
- [6] G. Haneczok, J. E. Frąckowiak, A. Chrobak, P. Kwapuliński, J. Rasek, Phys. Stat. Sol.(a) **202**, 2574 (2005).
- [7] G. Haneczok, A. Chrobak, P. Kwapuliński, Z. Stokłosa, J. Rasek, N. Wójcik, SMM'16, Düsseldorf September 9–12, 2003, Verlag Stahleisen GmbH 2004, pages 603–608.
- [8] J. E. Frąckowiak, G. Haneczok, P. Kwapuliński, J. Rasek, A. Chrobak, Czech. J. Phys. **54**, D109 (2004).
- [9] T. Naohara, Acta Mater. **46**, 4601(1998).
- [10] T. Naohara, Acta Mater. **46**, 397 (1998).
- [11] P. Kwapuliński, A. Chrobak, G. Haneczok, Z. Stokłosa, J. Rasek, J. Magn. Mater. **304**, e654-e656 (2006).
- [12] A. Chrobak, D. Chrobak, G. Haneczok, P. Kwapuliński, Z. Kwolek, M. Karolus, Mater. Sci. Eng. A **382**, 401 (2004).
- [13] T. Kulik, Journal of Non-Crystalline Solids **287**, 145 (2001).
- [14] J. Marcin, A. Wiedenmann, I. Škorvák, Physica B **276–278**, 870 (2000).
- [15] H. Kronmüller, Phil. Mag. B **48**, 127 (1983).
- [16] H. Kronmüller, Phil. Mag. B **48**, 2 (1982).