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Aplications of rietveld refinement in Fe-B-Nb alloy structure studies

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The paper presents in a short view the theoretical background of the Rietveld refinement method and some application of it in the structure studies of the alloys. The Fe-B-Nb magnetic alloys obtained by melt spinning method [1] were choosen as a searching materials for the presentation of the Rietveld refinement results.

1. INTRODUCTION

The Rietveld refinement is the well-known method [2,3] of structure determination of polycrystalline materials. There are planty of papers describing the theory and practical aspects of that method [4], aplications of that procedure in structure determination [5], quantitative phase analysis [6], crystallite size and lattice strain determination [7] and so on.

In general the Rietveld method uses the least-squares refinement for the receiving the best fit between the experimental data and the calculated pattern based on the simultaneously refined models for the crystal structure, diffraction optics effects, instrumental factors and others specimen characteristics which can be modelled.

The calculated intensities y_{ci} are determined by summing the contributions from neighboring Bragg reflections plus the backgroung:

$$y_{ci} = s\sum_k L_k \left|F_k\right|^2 \phi(2\theta_i - 2\theta_k) P_k A + y_{bi} \qquad (1)$$

where: s is the scale factor, k represents the Miller indices, h, k, l for the Bragg reflection, L_k containes the Lorentz, polarization and multiplicity factors, ϕ is the reflection profile function, P_k is preferred, A is an absorption factor, F_k is the structure factor for the k-th Bragg reflection, y_{bi} is the background intensity at the i-th step. Analitycal reflection profile functions available in some of the most widely used programmes are described e.g. by the pseudo-Voigt function: $pV = \eta L + (1-\eta)$, where $\eta = NA + NB^* 2\theta$, the Pearson VII function: $PVII = (C_5 / H_k)\left[1 + 4(2^{1/m} - 1)(2\theta_i - 2\theta_i)^2 / H_k^2\right]$, where $m = NA + NB/2\theta + NC/(2\theta)^2$ and standard Gaussian, Lorentzian and modified Lorentzian functions [5].

The dependence of the breadth H of the reflection profiles is defined as full-width-at-half-maximum (FWHM) by the equation:

$$H^2 = U\tan^2\theta + V\tan\theta + W\,, \qquad (2)$$

where: U, V, W are the refinable parameters.

The R-factors are used as the numerical criteria of fit: R-p – the pattern R-factor, R-wp – the weight pattern R-factor, R-exp – the R-expected factor :

$$Rp = 100S\left|y_{oi} - y_{ci}\right| / S\left|y_{oi}\right|, \qquad (3)$$

$$Rwp = 100\left\{Sw_i\left(y_{oi} - y_{ci}\right)^2 / Sw_i\left(y_{oi}\right)^2\right\}^{1/2}, \qquad (4)$$

$$\mathrm{Re}\,xp = 100\left\{(n - P + C) / Sw_i(y_{oi})^2\right\}^{1/2} \qquad (5)$$

and S - the „goodness of fit" defined as the ratio: $S = Rwp / \mathrm{Re}\,xp$, where N is the total number of data points, P is the number of parameters adjusted and C is the number of constraints applied. Beside the R-values which are good indicators of the progress of a particular refinement the differential plot at the diffraction pattern (Fig.2) is a good visualisation of the refinement results.

2. MATERIAL AND METHODS

The $Fe_{79}B_{14}Nb_7$ alloys were choosen as a searching material. The alloys were obtained by melt spinning technique in the form of ribbons with thickness and width of about 25 μm and 10 mm, respectively. The samples were annealed for 1 h in the temperature range from 300 to 900 K. The X-ray diffraction patterns of all the samples were performed on the Philips Diffractometer X'Pert PW 3040/60. The copper radiation ($\lambda_{K\alpha}$ = 1.5418 Å), the graphite monochromator on the diffracted beam and the step scanning mode in a range of 30-90° 2θ, the step of 0.04° 2θ and counting time of 4 s. were used (Fig. 1).

After the crystallization process the crystallite size and the lattice strain were calculated basing on the Williamson-Hall method [7] which was successfully applied to many others nanomaterials and semi-amorphous materials (~ 10 Å) [9,10,11]. The line breadth was defined by the full width at half maximum (FHWM). For the determination of the physical line broadening the Fe-B standard was used. For the calculation of the lattice strain and the crystallite size of αFe the diffraction lines 110, 200 and 211 were selected. The analysis of the line broadening was performed by the Philips software X'Pert Plus.

The Rietveld refinement was performed for all samples using the DBWS version programme [12]. The lattice constants, diffraction line profile, background and other structural and instrumental factors were refined. The some results of the refining are presented in the Fig. 3.

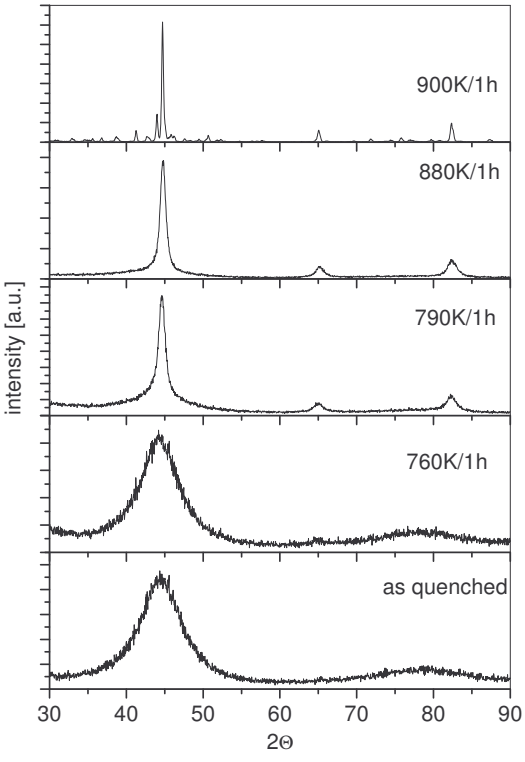


Fig.1. The X-ray diffraction patterns of the annealed $Fe_{79}Nb_7B_{14}$ alloy.

3. RESULTS AND DISCUSSION

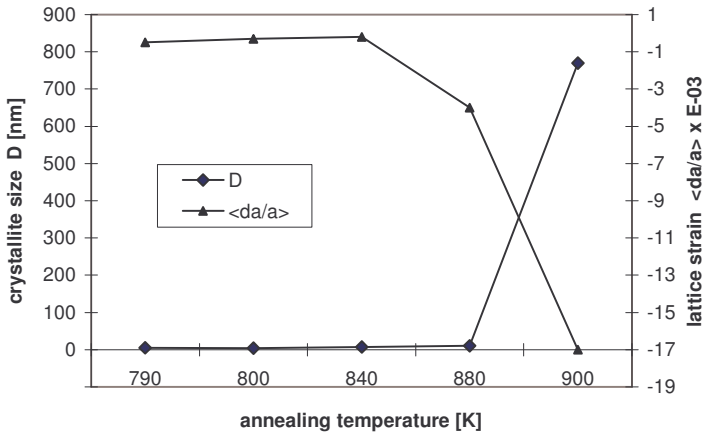
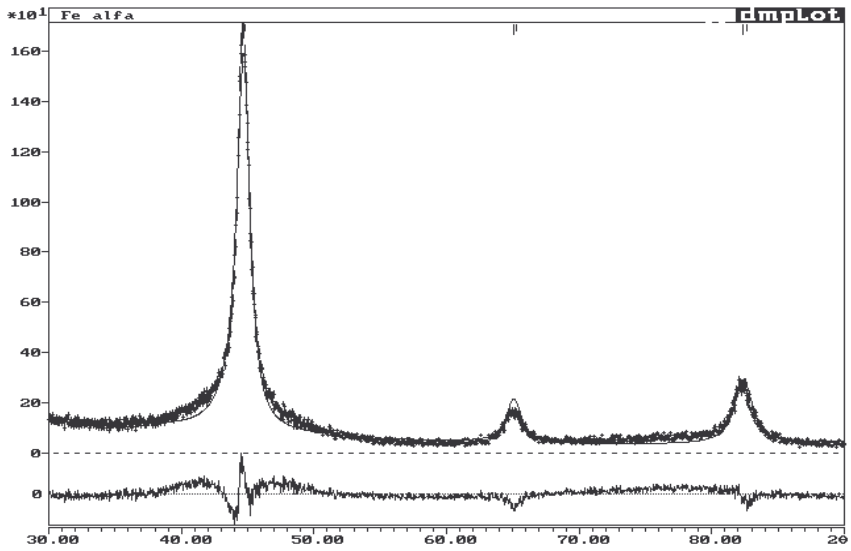


Fig. 2. The crystallite size and the lattice strain of the annealed $Fe_{79}B_{14}Nb_7$ alloys.

The X-ray diffraction patterns obtained for all alloys are presented in Fig. 1. It can be seen that the $Fe_{79}Nb_7B_{14}$ alloys were in the amorphous state till 790 K annealing temperature, where the first diffraction lines (typical for αFe phase) were detected. The full crystallisation (αFe and Fe_3B phases) was observed in the sample annealed at 900 K/1h (see Fig.1).

The values of the crystallite size and the lattice strain of the alloys are presented in Fig. 2 and in Table 1.

Below the full crystallisation - for annealing temperatures T_a < 900 K - the size of nanocrystallites varies from 5 to 10 nm. The annealing temperature of 900 K/1h gives the mean crystallite size of about 770 nm, what is a typical value of polycrystalline phase. The values of the lattice strain varies in a range of $-0.5\ 10^{-3}$ to $-4.0\ 10^{-3}$ for nanostructured phase and is of about $-17.0\ x10^{-3}$ for the polycrystalline phase.



The Rietveld refinement was performed for nanocrystalline alloys annealed in a temperature range of 790-900 K. The example result of refining is presented in Fig. 3. The received values of R-factors - typical for other nanomaterials [9, 10, 11] are presented in Table 2 and they are in a range of: Rp: 13 - 18 %, Rwp: 17 22 %, rexp: 8 – 9 % and S: 1.9 – 2.3 %.

Fig. 3. The example of the Rietveld refinement plot obtained for $Fe_{79}B_{14}Nb_7$ alloy annealed at 800 K.

Table 1. The crystallite size and the lattice strain obtained for annealed $Fe_{79}B_{14}Nb_7$ alloys.

annealing temperature [K]	crystallite size [nm]	lattice strain [10^{-3}]
790	5	-0.5
800	4	-0.3
840	7	-0.2
880	10	-4.0
900	770	-17.0

Table 2. The values of R-factors obtained for nanocrystalline $Fe_{79}B_{14}Nb_7$ alloys.

annealing temperature [K]	Rp [%]	Rwp [%]	Rexp [%]	S
790	15	19	8	2.2
800	13	17	8	1.9
840	14	19	9	2
880	18	22	9	2.3

4. CONCLUSIONS

i) the annealing at temperatures from 790 K to 880 K leads to formation of the nanostructure of αFe with the crystallite size 5 – 10 nm, ii) annealing above temperature of 900 K/1h the full crystallisation is observed (αFe grains of about 1000 nm plus borides Fe_3B and Fe_2B), iii) the values of lattice strain are in a range from -0.5 to -17 $x10^{-3}$, iv) the obtained, for nanocrystalline $Fe_{79}B_{14}Nb_7$ alloys, values of R-factors are in ranges of: Rp: 13 - 18 %, Rwp: 17 – 22 %, rexp: 8 – 9 % and S: 1.9 – 2.3 %.

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