Effect of Heat Treatment on the Phase Transformation and Magnetic Properties of the Rapidly Solidified \( \text{Pr}_{9}\text{Fe}_{58}\text{Co}_{13}\text{Zr}_{1}\text{Nb}_{4}\text{B}_{15} \) Alloy Ribbons

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The rapidly solidified ribbon samples of the \( \text{Pr}_{9}\text{Fe}_{58}\text{Co}_{13}\text{Zr}_{1}\text{Nb}_{4}\text{B}_{15} \) alloy subjected to short time annealing at temperatures ranging from 923 K to 1033 K were investigated. The phase analysis supported by the Rietveld refinement was used to identify the phase constitution. The results of Rietveld calculations were confirmed by transmission electron microscopy and \( M(T) \) studies. Measurement of recoil curves allowed the determination of switching field distributions and \( \delta M \) plots for samples annealed at various temperatures.

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1. Introduction

\( \text{Pr}–\text{Fe}–\text{B} \) magnets of low Pr concentration seem to be an attractive alternative to more popular Nd–Fe–B counterparts due to a possibility of their applications at low temperatures. The argument for that is the fact that the hard magnetic Nd\(_2\)Fe\(_{14}\)B phase undergoes a significant reduction of magnetocrystalline anisotropy below 150 K due to the spin reorientation in this phase [1]. Replacement of Nd by Pr in the alloy composition results in a decrease of the spin-reorientation temperature down to 25 K [2] and maintaining good performance of hard magnetic devices above this temperature. Additionally, Betancourt and Davies [3] reported that addition of Nb and Zr led to the improvement of magnetic properties of nanocomposite (Pr–Nd–Fe–B) magnets by restraining the growth of metastable phases and increasing the content of the hard magnetic phase [4].

In our recent work [5], we have reported on rapidly solidified ribbons of \( \text{Pr}_{5}\text{Fe}_{58}\text{Co}_{13}\text{Zr}_{1}\text{Nb}_{4}\text{B}_{23–x} \) \( (x = 0, 2, 5, 8) \) alloys. It was shown that as-cast ribbons were fully amorphous and revealed soft magnetic properties. The differential scanning calorimetry (DSC) and differential thermal analysis (DTA) studies have revealed high values of the activation energy for crystallization \( E_a \) for all alloy compositions that indicate good thermal stability of an amorphous phase. The \( E_a \) reaches 498 kJ/m\(^3\) for \( x = 2 \) alloy and decreases with increasing Fe content down to \( E_a = 420 \) kJ/m\(^3\) for \( x = 8 \) alloy. Furthermore, the large supercooled liquid region before crystallization \( \Delta T_c \) of \( \approx 100 \) K for \( x = 2, 5 \) and 8 alloys is related to simultaneous crystallization of two phases. Short time annealing resulted in crystallization and thus changes of the magnetic properties. The ribbons annealed for 5 min at temperatures ranging from 923 to 1033 K exhibited high coercivities. Our studies have shown that magnetic properties depend both on the heat treatment temperature and the chemical composition of the alloy. The highest value of coercivity \( (\approx 1100 \) kA/m) was measured for \( \text{Pr}_{9}\text{Fe}_{58}\text{Co}_{13}\text{Zr}_{1}\text{Nb}_{4}\text{B}_{15} \) alloy ribbons. In the present work, detailed studies of evolution of the phase constitution and microstructure with the annealing temperature and the impact of these factors on the magnetic properties of the \( \text{Pr}_{9}\text{Fe}_{58}\text{Co}_{13}\text{Zr}_{1}\text{Nb}_{4}\text{B}_{15} \) rapidly solidified ribbons are presented.

2. Samples preparation and experimental methods

The ribbon samples of \( \text{Pr}_{9}\text{Fe}_{58}\text{Co}_{13}\text{Zr}_{1}\text{Nb}_{4}\text{B}_{15} \) alloy were produced by the controlled atmosphere single roll melt-spinning technique at the velocity of the copper roll surface of 25 m/s. Subsequently the samples were sealed off in a quartz tube under low pressure of argon and heat treated at temperatures ranging from 923 K to 1033 K for 5 min. The phase constitution of devitrified ribbons was determined by the qualitative analysis of X-ray diffraction (XRD) patterns supported by the Rietveld refinement. The XRD patterns were collected using the Bruker D8 Advance diffractometer with Cu \( K_\alpha \) radiation equipped with a LynxEye detector (linear focus of 25 mm, primary beam divergence slit \( \approx 0.6 \) mm) with Soller slits on a primary and diffracted beam. The measurements were performed in the Bragg–Brentano configuration with a \( K\beta \) filter on the detector side. The 2θ step size was 0.02 deg and step time 5 s. The Rietveld refinements were performed using DIFFRAC SUITE TOPAS 4.2 software [6] in 2θ range from 30 deg to 90 deg. The profile shapes were modeled with the TCHZ function. Additionally the quantitative phase structure analysis was performed by the PONKCS method [7].

The microstructure was examined by transmission electron microscopy (TEM). To determine the Curie temperatures \( T_C \) of constituent phases, the magnetization \( J \) versus temperature \( T \) measurements, using the Faraday magnetic balance, over the temperature range 300–850 K and at a heating rate of 10 K/min were performed. Hysteresis loops were measured using LakeShore VSM 7307 operating in external magnetic fields up to 2 T at room
3. Results and discussion

The X-ray diffraction patterns measured for samples annealed at various temperatures with the phase identification are presented in Fig. 1. For the sample annealed at 923 K, two crystalline phases were identified: the paramagnetic Pr$_{1+x}$Fe$_4$B$_4$ (1:4:4) and hard magnetic Pr$_2$(Fe,Co)$_{14}$B (2:14:1). However, the peak positions of these phases are strongly overlapped. Although these two phases were identified for all annealing temperatures, the presence of the amorphous phase was not clear for temperatures higher than 923 K. Annealing at 1013 K resulted in crystallization of the additional soft magnetic α-Fe phase.

![Fig. 1. The XRD patterns measured for Pr$_9$Fe$_{58}$Co$_{13}$Zr$_1$Nb$_4$B$_{15}$ alloy ribbons annealed at various temperatures for 5 min, with marked crystalline phases.](image)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$R_{exp}$</th>
<th>$R_{wp}$</th>
<th>GOF</th>
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<tbody>
<tr>
<td>923 K</td>
<td>0.493</td>
<td>0.727</td>
<td>1.472</td>
</tr>
<tr>
<td>953 K</td>
<td>0.486</td>
<td>0.809</td>
<td>1.668</td>
</tr>
<tr>
<td>1003 K</td>
<td>0.508</td>
<td>0.857</td>
<td>1.687</td>
</tr>
<tr>
<td>1033 K</td>
<td>0.499</td>
<td>1.081</td>
<td>2.174</td>
</tr>
</tbody>
</table>

For detailed determination of the phase constitution, and in order to address the issue of amorphous phase presence in the annealed samples, the series of the Rietveld refinements were performed. The refined patterns with corresponding difference curves are presented in Fig. 2. The criteria of fit $R$ are collected in Table I. In Table II the starting and final model parameters values are presented. In the starting model, the presence of two crystalline phases 1:4:4 and 2:14:1 for all annealing temperatures was considered. Quantification of the amorphous phase is not possible in traditional Rietveld analysis [8]. One of commonly used methods to overcome this problem is the technique known as PONKCS [7] (Partial Or No Known Crystal Structure) that can be classified as an internal standard method. The PONKCS analysis is based on determining the ZMV parameter for the amorphous phase. This parameter is easily derived when the structure of phase is well known ($ZM$ is the mass and $V$ the volume of the unit cell) [9]. Using these ZMV values, one can calculate the weight fractions of constituent phases. However, any phase that is not included in the model will not be considered in these calculations. Therefore, if an amorphous or any unidentified crystalline phase has not been incorporated in the model, only the relative fractions of known phases can be calculated. The method will return the sum of analyzed phases as 100% regardless of the sample components not numbered in the starting model. For amorphous phase structural details are not available. However, it is possible to represent the amorphous phase with a group of peaks (peaks phase). The value of ZMV for such a phase can be derived by measuring the diffraction pattern for the mixture of a known amount of the phase of interest with the well-characterized internal standard. Such a ZMV value has no physical significance and serves as a calibration value for the later phase concentration calculations in samples under investigation. In the present work, the diffraction pattern was measured for defined mixture of as-cast amorphous ribbons with the standard α-Fe. The amorphous phase was incorporated into the starting structural model by treating the amorphous bump as
Crystallite sizes ($L_{\text{vol}}$) and weight fractions of constituent phases calculated by the Rietveld method for Pr$_5$Fe$_{58}$Co$_{13}$Zr$_1$Nb$_4$B$_{15}$ alloy ribbons annealed at various temperatures.

| Phase name | Pr$_2$(Fe,Co)$_4$B | PrFe$_4$B$_4$ | α-Fe | Pr$_2$O$_3$ | amorphous
<table>
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</thead>
<tbody>
<tr>
<td>space group</td>
<td>$P4_2/mnm$</td>
<td>$Pc$</td>
<td>$I$</td>
<td>$I$</td>
<td>$a$-3</td>
</tr>
<tr>
<td>$L_{\text{vol}}$ [nm]</td>
<td>$L_{\text{vol}}$ [nm]</td>
<td>$L_{\text{vol}}$ [nm]</td>
<td>$L_{\text{vol}}$ [nm]</td>
<td>$L_{\text{vol}}$ [nm]</td>
<td></td>
</tr>
<tr>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
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<td></td>
</tr>
<tr>
<td>923 K</td>
<td>41.2±1.4</td>
<td>33.5±0.5</td>
<td>7.2±0.3</td>
<td>13.8±0.6</td>
<td>52.8±0.4</td>
</tr>
<tr>
<td>953 K</td>
<td>37.9±0.6</td>
<td>49.3±0.4</td>
<td>12.9±0.5</td>
<td>10.9±0.4</td>
<td>39.8±0.4</td>
</tr>
<tr>
<td>1003 K</td>
<td>36.3±0.5</td>
<td>65.1±0.6</td>
<td>50.1±5.7</td>
<td>8.5±0.6</td>
<td>14.6±0.2</td>
</tr>
<tr>
<td>1033 K</td>
<td>36.5±1.8</td>
<td>56.1±1.4</td>
<td>45.1±13.9</td>
<td>5.5±0.6</td>
<td>27.9±0.8</td>
</tr>
</tbody>
</table>

A corresponding electron diffraction pattern with distinguishable diffused ring confirms the presence of amorphous phase. Additionally, smaller nanocrystals of $\approx$ 10 nm diameters are marked in Fig. 4b. Measured grain sizes are in good agreement with the results of the Rietveld analysis.

The dependencies of reduced magnetization on the temperature for all samples are presented in Fig. 5. For the lowest annealing temperature, two stages of dependence were measured confirming the presence of the amorphous phase. For higher annealing temperatures no such inflection was observed. Although, according to the Rietveld analysis the amorphous phase still exists in the samples. This is probably due to the increase of the weight fraction of the hard magnetic phase and reduction of the amorphous phase content. For annealing temperatures 1003 K and 1033 K the magnetization keeps relatively high values above the Curie temperature of the hard magnetic phase which confirms presence of the α-Fe phase.

The Curie temperature was determined as the minimum of the temperature first derivative of magnetization. Its value reaches 665 K for sample annealed at 623 K and is higher than for pure Pr$_2$Fe$_{14}$B ($T_c = 558$ K). It was established for nanocrystalline Pr$_{10}$Fe$_{84}$B$_8$ ribbons that the Curie temperature of Pr$_2$Fe$_{14}$B phase increases by the “peaks-phase” signal consisting of three broad TCHZ peaks. From the refinement, the ZMV parameter for the amorphous phase was determined. Subsequent calculations have shown that the amorphous component was present in the samples annealed up to 1003 K. The amorphous phase content decreases with increasing annealing temperature. For the samples annealed at 1003 K and 1033 K the α-Fe phase had to be incorporated into the starting model to obtain the best fit. In the case of sample annealed at 1033 K the difference curve has shown that at least one additional crystalline phase had to be included to the model. Furthermore, detailed identification and subsequent Rietveld refinement have shown the presence of Pr$_2$O$_3$ phase in this sample.
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Fig. 3. Crystallite sizes ($L_{vol}$) (a) and weight fractions of constituent phases (b) dependences on annealing temperature for Pr$_9$Fe$_{58}$Co$_{13}$Zr$_1$Nb$_4$B$_{15}$ ribbons.

≈ 9 K with each 1% of Co for Fe substitution [11] which is in good agreement with this result.

The hysteresis loops measured for ribbons annealed at various temperatures (a) and magnetic parameters dependences on annealing temperature (b) are presented in Fig. 6. The squareness of hysteresis loop (SQR) defined by the ratio of the reverse field required to reduce $J$ by 10% from the remanence to $J_{H_c}$, were calculated for the measured demagnetization curves. The SQR values are 0.26, 0.35, 0.25, and 0.06 for the samples annealed at 923, 953, 1003, and 1033 K, respectively. Although the demagnetization curves have very favorable shapes for the annealing temperature up to 1003 K, the SQR are rather low due to the step around the zero field shown in the inset of Fig. 6a.

Furthermore, a pronounced increase of coercivity $J_{H_c}$ with the annealing temperature is observed. The $J_{H_c}$ reaches the maximum value of 1089 kA/m for the sample annealed at 1003 K. This is accompanied by a slight increase in saturation polarization with the annealing temperature from $J_r = 0.79$ T for 923 K to $J_r = 0.91$ T for 1033 K. After heat treatment at 1033 K, the coercivity drops to 541 kA/m and the shape of demagnetization curve changes causing significant decrease of $(BH)_{max}$.

The series of recoil curves were measured for initially saturated ($D$) and demagnetized ($R$) samples and the irreversible remanence dependences on the reverse field $M_{irr}^D(H)$ and $M_{irr}^R(H)$ were constructed. Subsequently, the first derivatives of $M_{irr}(H)$ with respect to the applied magnetic field $(dM_{irr}/dH)$ gave the switching field distributions (SFD) presented in Fig. 7. These dependences reflect the rate of irreversible remanence changes with the increase of maximum applied recoil field [12]. The profile of SFD peak can indirectly provide information about the homogeneity of the microstructure of the samples. The SFD peaks for samples annealed at 953 K
Fig. 6. The hysteresis loops measured for Pr$_9$Fe$_{58}$Co$_{13}$Zr$_1$Nb$_4$B$_{15}$ alloy ribbons annealed at various temperatures (a) and magnetic parameters (saturation polarization $J_s$, remanence $J_r$, coercivity $J_H$ and maximum energy product ($BH_{\text{max}}$)) dependences on annealing temperature (b).

and 1003 K are narrow and sharp with the maxima at 950 and 1100 kA/m. These values are close to $J_H$ of the samples. Such shapes indicate that the magnetization reversal occurs in a narrow field range and that the grains of the hard magnetic phase have uniform sizes. For the samples annealed at 1033 K the peak becomes slightly wider with the maximum shifted to lower fields ($\approx$ 800 kA/m).

In order to determine at which points of hysteresis loops the interactions between grains enhance or reduce magnetization of the samples, the $\delta M(H)$ dependence can be calculated based on the modified Stoner–Wohlfarth relation (Eq. (1)) [13]:

$$\delta M(H) = I_D(H)/I_R(\infty) + 2I_R(H)/I_R(\infty) - 1.$$  

(1)

For the sample annealed at 1003 K, $\delta M$ values increase to a sharp peak and decrease rapidly around the coercivity (Fig. 8). These positive $\delta M$ values indicate the existence of strong exchange coupling between grains. This is due to the high weight fraction of hard magnetic phase (65 wt%) and the presence of soft magnetic phases: the amorphous and the nanocrystalline $\alpha$-Fe of very fine crystallite sizes. After the annealing at 1033 K, the increase of weight fraction of $\alpha$-Fe phase at the expense of amorphous phase accompanied by the growth of grain sizes of

Fig. 7. The switching field distributions calculated for the Pr$_9$Fe$_{58}$Co$_{13}$Zr$_1$Nb$_4$B$_{15}$ alloy ribbons annealed at various temperatures.

Fig. 8. The $\delta M$ plots for the Pr$_9$Fe$_{58}$Co$_{13}$Zr$_1$Nb$_4$B$_{15}$ alloy ribbons annealed at various temperatures.
α-Fe led to a decrease of the level of exchange interactions. This has an effect in considerable reduction of the coercivity of the sample and changes of the demagnetization curve. The $\delta M$ peak becomes wider and its maximum shifts towards lower fields. Above 800 kA/m the dipolar interactions between grains become dominant.

4. Conclusions

Detailed studies of the phase constitution of Pr$_9$Fe$_{58}$Co$_{13}$Zr$_1$Nb$_4$B$_{15}$ ribbon samples subjected to short time annealing have shown changes in the volume fractions of constituent phases with the annealing temperature. The Rietveld refinement of XRD scans using the PONKCS method made it possible to reveal presence of amorphous phase in samples annealed at temperatures up to 1003 K. This method allowed us to determine the weight fractions of constituent phases and their crystallite sizes. The largest content of hard magnetic phase of mean crystallite diameters of $\approx 36$ nm and small amount of very fine crystallites ($\approx 8$ nm) of soft magnetic α-Fe was detected for the sample annealed at 1003 K. This is accompanied by the best hard magnetic properties of this ribbon. Positive values of $\delta M$ parameter indicate the existence of strong exchange coupling between grains in this sample. Lower values of $JH_c$ and $(BH)_{\text{max}}$ for ribbons annealed below 1003 K have the origin in large fraction of the amorphous phase. The worsening of magnetic properties of samples annealed at 1033 K is related to the formation of large grains of α-Fe and to the presence of Pr$_2$O$_3$ phase.

References