Thermal annealing induced modification of structural and soft magnetic properties of Fe_{33.8}Co_{50.7}Nb_{5}B_{8.5}P_{2} alloy

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Abstract. Effect of thermal annealing treatment aimed to optimize the soft magnetic properties of Fe_{33.8}Co_{50.7}Nb_{5}B_{8.5}P_{2} alloy system has been investigated. Information on the correlation between micro-structure and magnetic properties have been obtained using differential scanning calorimetry (DSC), x-ray diffraction (XRD), and hysteresis measurements. Annealing treatment enhances the saturation induction in studied alloy composition. Whereas there is a moderate increment in the coercive behaviour with annealing temperature that may be ascribed to weakly exchange coupled nano grains.

1. Introduction
Owing to their excellent soft magnetic properties Fe-based nanocrystalline alloys obtained from partially crystallized amorphous precursors have been studied widely. Microstructure of these alloys consists of ferromagnetic nanocrystallites embedded in amorphous matrix. Coercivity of nanocrystalline alloys can be significantly reduced provided the magnetic anisotropy gets averaged over many randomly oriented grains. This happens if the average grain size is smaller than the exchange coherence length [1, 2]. So, a suitable alloy composition and post-preparation thermal annealing treatments play a very important role in order to achieve a uniform nano-granular structure.

Soft magnetic nanocrystalline alloys have been extensively studied specially the compositions based on FeSiNbBCu, FeZrNbCu and FeCoZrBCu under the patented trade names of FINEMET [3], NANOPERM [4] and HITPERM [5] respectively. Fe-Co based HITPERM alloy family was developed specially for high temperature applications that can be cast in air [6, 7]. Addition of Co to Fe-based amorphous precursor enhances the Curie temperature of the amorphous as well as that of the precipitated crystalline phase [8].

In the present work we report the investigations on the effects of thermal annealing treatment on the structural and soft magnetic properties of Fe_{33.8}Co_{50.7}Nb_{5}B_{8.5}P_{2} alloy in the form of ribbons.
2. Experimental details

Ribbons (4mm wide and 20μm thick) of nominal composition Fe$_{33.8}$Co$_{50.7}$Nb$_5$B$_{8.5}$P$_2$ were prepared in air by planar flow casting method using single Cu wheel. Differential scanning calorimetry (DSC) at a heating rate of 20 °C/min was done. Following the DSC results thermal annealing of the as cast ribbons was done at 400, 450 and 500 °C for 1 hr. In order to investigate the micro-structural parameters: Scherrer’s grain diameter ($D$), lattice parameter ($a$), crystalline volume fraction ($V_x$) and nearest neighbor distance ($X_m$), X-ray diffraction (XRD) patterns were recorded on Bruker advance diffractometer equipped with a fast counting detector and making use of Cu-K$_\alpha$ ($\lambda= 0.154$ nm) radiation. Room temperature hysteresis measurements on as cast and annealed samples were done using conventional induction technique based loop tracer working at 50Hz with a maximum applied magnetic field of ± 1000 A/m to obtain coercivity ($H_c$) and saturation induction ($B_s$).

3. Results and Discussion

DSC results reveal that the onset of crystallization of the studied alloy composition occurs at 416 °C. X-ray diffraction data was analyzed using a MATLAB® program that fits the data using one crystalline and an amorphous component based on pseudo Voigt line profiles. Table 1 represents the annealing temperature evolution of various structural parameters obtained by analyzing the XRD data. Perusal of Table 1 suggests the presence of crystalline phase in as quenched ribbons. As ribbons are prepared by rapid quenching of alloy melt on to a single copper wheel and, here the wheel side of the ribbon is rapidly cooled as compared to the shiny side. This may lead to growth of crystalline phase mainly in a thin layer near the surface region as is also observed earlier for metal-metalloid glass systems [9].

**Table 1:** Annealing temperature evolution of structural parameters obtained by XRD.

| Sample details | $<D>$ (nm) | $a$ (nm) | $V_x$ (%) | $X_m$ (nm) | Co % in Fe-Co Phase |
|----------------|------------|----------|-----------|------------|------------------|
| As-cast        | 20         | 0.2852   | 25        | 0.248      | 55               |
| Ann. 400 °C/1h | 12         | 0.2847   | 50        | 0.249      | 62               |
| Ann. 450 °C/1h | 9.5        | 0.2848   | 76        | 0.248      | 61               |
| Ann. 500 °C/1h | 10.5       | 0.2851   | 81        | 0.251      | 56               |

**Figure 1:** Hysteresis loops of as-quenched and annealed ribbons measured at 50 Hz with a maximum applied field of 1 kA/m. Inset: Magnified region of the loops around low field.
Moreover, presence of P reportedly favors the formation of high density nucleation sites by early precipitation of Fe-rich crystalline phase [10]. As can be seen from Table 1, the lattice parameter values indicate the precipitation of Fe-Co crystalline phase. The change in the lattice parameter values is indicative of the diffusion of Co from amorphous matrix to the Fe-Co nanocrystalline phase. Table 1 also contains information on the amount of Co (%) present in the Fe-Co nanocrystalline phase. For the observed change in the lattice parameter, values suggest that the amount of Co present in the crystalline phase corresponding to as cast and annealed samples range between 51 - 62%. Modest variation in the $X_m$ values suggests that the studied samples have similar mass densities.

It is interesting to note that average grain size is decreasing with increasing annealing temperature. Contrary to this, the volume fraction of crystalline phase is increasing as a function of thermal treatment. It may be interpreted in terms of diffusion of Nb in the nanocrystalline phase. There can also be a possibility of Nb pile up at the interface of Fe-Co nanocrystals and amorphous matrix which restricts the grain growth. It is also worth noting that B and P may not be able to be solidified with nanocrystalline Fe-Co phase. Thus, with increasing annealing temperature and hence the crystalline fraction, replacement of B by P in the amorphous matrix will increase as also observed in Fe-based nanocrystalline alloys [10]. This might also be a probable reason for the suppressed grain growth with higher annealing temperature.

Figure 1 represents the hysteresis curves corresponding to the as cast and the samples annealed at 400, 450 and 500 °C. Magnetic parameters obtained by hysteresis loop measurements are shown in Table 2. It should be noted that lowest value of coercive field (~33 A/m) corresponds to the sample annealed at 400 °C and this sample is not characterized by the smallest grain size and highest volume fraction. Best value of saturation induction (~1.46 T) was obtained for the sample annealed at 500 °C, but this sample also exhibited highest coercivity (~60 A/m). As can be seen from Table 2 the squareness ratio does not change much as is also reflected in terms of loops shape in Figure 1. Initial decrease in coercivity till annealing temperature of 400 °C may be associated with the relaxation of stresses. Further, it appears that this annealing treatment has resulted in optimized grain structure (~12 nm average grain diameter) where the nanograins are well exchange coupled through amorphous matrix.

Table 2: Annealing temperature dependence of magnetic parameters.

| Sample details | $H_c$ (A/m) | $B_s$ (Tesla) | $B_r/B_s$ |
|----------------|-------------|--------------|-----------|
| As-cast        | 52.4        | 0.94         | 0.43      |
| Ann.400 °C/1h  | 33.8        | 1.23         | 0.39      |
| Ann. 450 °C/1h | 38.1        | 1.23         | 0.43      |
| Ann. 500 °C/1h | 60.1        | 1.46         | 0.35      |

According to random anisotropy model [1] the average crystalline anisotropy in soft nanocrystalline alloys scale as $\propto 1/\sqrt{N}$ where N is the number of randomly oriented grains in exchange coupled volume. With increasing annealing temperature crystalline fraction increases. Consequently the number of exchange coupled grains should increase and eventually this would lead to lowering of magneto-crystalline anisotropy. As a result the coercivity should decrease. Contrary to this, the coercive field is increasing with increasing annealing temperature for the studied alloy system. It may be associated with the possibility that at higher annealing temperatures of 450 and 500 °C grain size is decreasing which may result in increasing lattice strain presumably due to increasing number of
structural defects. This may result in increasing magneto elastic anisotropy contributions that weakens the exchange coupling interaction among the Fe-Co nanograins despite of their reduced size and increased volume fraction.

4. Summary
Annealing temperature dependence of structural and magnetic properties of Fe$_{33.8}$Co$_{50.7}$Nb$_5$B$_{8.5}$P$_2$ alloy has been investigated using differential scanning calorimetry (DSC), x-ray diffraction (XRD), and magnetic measurements. Micro-structural evolution with annealing treatment is characterized by precipitation of single Fe-Co crystalline phase with average grain diameter ranging between 9-20 nm. Observed behaviour of coercive field is ascribed to the reduction of the internal stresses in the residual amorphous matrix during early stages of annealing. With increasing annealing temperature the growth of nanograins is suppressed ascribing to the diffusion of Nb and P through the amorphous matrix. Reduction in average size of nanograins appears to enhance the structural defects that lead to weaker exchange coupling among nano-grains. Annealing treatment appears to enhance the saturation induction values with moderate increment in coercivity.

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