Synthesis and magnetic properties of Fe-B-Nd-Nb nanocomposite magnets

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Abstract. Magnetic properties of Fe-B-Nd-Nb quaternary alloys were investigated in terms of the Fe concentration and the quenching rate. High energy products reaching 98 kJ/m$^3$ with high coercivities of 570-750 kA/m were obtained by a conventional rapid quenching technique followed by heat treatment. The nanocomposite magnets are attractive for future applications since their magnetic performance can be improved by optimization of the quenching rate and the heat treatment condition.

1. Introduction
Recently, bulk metallic glasses were produced for the first time in an Fe-Nd-B-based system [1] and the best glass former with a critical diameter of 4 mm was obtained by the addition of Nb, i.e., for the alloy composition of Fe$_{65.28}$B$_{24}$Nd$_{6.72}$Nb$_{4}$. The addition of Nb was also reported to be very effective for grain refinement of nanocomposites, leading to the enhancement of the coercivity [2]. According to Zhang et al.[1], an optimum magnetic performance occurs for Fe$_{64.32}$B$_{22.08}$Nd$_{9.6}$Nb$_{4}$ where the coercivity reaches a very high value of 1100 kA/m after crystallization of the metallic glass by a subsequent heat treatment. However, in contrast to the excellent coercivity value, the energy product is not high, i.e., 33 kJ/m$^3$, which is due to its low remanence magnetization of 0.44 T.

In general, the magnitude of the saturation magnetization of a magnet is determined by the Fe concentration, therefore, one efficient way to improve the remanence is to raise the Fe concentration of a magnet. According to Zhang et al.[1], bulk metallic glasses are formed in a region with 66 - 70 at%Fe and 5 - 9 at%Nd at the constant Nb concentration of 4 at%Nb. Therefore, in order to realize higher energy products, it is necessary to improve the remanence at the expense of the glass forming ability. In the present work, we aimed at obtaining higher remanence while maintaining the coercivity at a substantial level, putting aside the glass forming ability. Our final goal is not to produce bulk metallic glasses but to obtain high performance magnets with high coercivity in a bulk form. In the present work, we have exploited an Fe-rich part of the Fe-B-Nd-Nb quaternary system at the constant Nb concentration of 4 at%Nb after the work of Zhang et al. [1] and investigated the variation of the magnetic behaviour with the Fe concentration as well as the quenching rate. Investigations have been performed on melt-spun and annealed samples with different quenching rates, i.e., different rotating speeds of the Cu wheel. Optimization of the magnetic property by changing the heat treatment condition will be a future work and is now underway.
2. Experimental

Alloy ingots of nominal compositions Nd$_{9}$Fe$_{77}$B$_{10}$Nb$_{4}$ and Nd$_{9}$Fe$_{73}$B$_{10}$Nb$_{4}$ were prepared by using high purity raw materials of Nd (3N), Fe (4N), B (2N5) and Nb (3N) in an arc furnace under an Ar atmosphere. The alloys were then melt spun onto a Cu wheel rotating with 800 and 1000 rpm (rotations per minute), i.e., the surface velocity of 10 and 12.5 m/s, respectively, under the Ar atmosphere and then annealed at 993 K for 6 min. Characterization of the samples was performed by using an X-ray diffractometer (Rigaku Ultima III). Differential scanning calorimetry (DSC) analyses have been performed on the melt-spun samples with a heating rate of 0.33 K/s using DSC 3300S (Mac Science). The magnetic properties were measured in magnetic fields up to 4000 kA/m by using a superconducting quantum interference device (SQUID, Quantum Design).

3. Results and discussion

In figures 1 and 2 the Cu Kα X-ray diffraction patterns of as melt-spun and annealed Nd$_{9}$Fe$_{77}$B$_{10}$Nb$_{4}$ and Nd$_{9}$Fe$_{73}$B$_{14}$Nb$_{4}$ alloy ribbons produced with two different quenching speeds, i.e., 10 and 12.5 m/s, are presented. Due to the low quenching rates, the as-spun alloys are mostly crystallized, composed of the Nd$_{2}$Fe$_{14}$B and α-Fe phases, and the existence of an amorphous phase is not obvious from the patterns in the figure 1. Here, the pattern of the 73 at%Fe sample is mostly composed of the Nd$_{2}$Fe$_{14}$B phase, implying that the Nd$_{2}$Fe$_{14}$B phase is the primary crystallization phase [4]. For the 77 at%Fe samples, it is seen that the formation of the α-Fe phase is promoted when the quenching rate is low. Upon annealing at 993 K for 6 min, the volume fraction of the α-Fe phase increases relatively as seen in the figure 2. It is also seen from the figure that the residual amorphous phase mostly transforms into α-Fe phase during annealing.

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** X-ray diffraction patterns of as-spun Nd$_{9}$Fe$_{77}$B$_{10}$Nb$_{4}$ and Nd$_{9}$Fe$_{73}$B$_{14}$Nb$_{4}$ alloys.

**Figure 2.** X-ray diffraction patterns of Nd$_{9}$Fe$_{77}$B$_{10}$Nb$_{4}$ and Nd$_{9}$Fe$_{73}$B$_{14}$Nb$_{4}$ alloys annealed at 993 K for 6 min.

DSC curves of the as melt-spun Nd$_{9}$Fe$_{77}$B$_{10}$Nb$_{4}$ and Nd$_{9}$Fe$_{73}$B$_{14}$Nb$_{4}$ alloys are presented in figure 3. In all the alloys, two exothermic reactions due to two-step crystallizations are noticed, suggesting that the melt-spun alloys contain a certain amount of residual amorphous phase, which presumably transforms into the Nd$_{2}$Fe$_{14}$B and the α-Fe phases upon heating. It is seen that the crystallization behaviour is greatly affected by changing the Fe/B concentration ratio.
In figure 4 the demagnetization curves of the annealed Nd\textsubscript{9}Fe\textsubscript{77}B\textsubscript{10}Nb\textsubscript{4} and Nd\textsubscript{9}Fe\textsubscript{73}B\textsubscript{14}Nb\textsubscript{4} alloys prepared with quenching rates of 10 and 12.5 m/s are presented. The magnetic properties are summarized in the table 1. The curves exhibit behaviours of a magnetically single phase, indicating that the Nd\textsubscript{2}Fe\textsubscript{14}B and $\alpha$-Fe phases are magnetically coupled by the exchange interaction forming a spring magnet. The coercivity is found to sensitively depend on the quenching speed, indicating that the optimization of the quenching speed plays a key role in increasing the coercivity. On the other hand, the remanence is improved by the increase of the Fe content as expected, which is attributed to the increase of the volume fraction of the $\alpha$-Fe phase due to the Fe rich compositions. Although the coercivity values are smaller than that (1100 kA/m) reported for Fe\textsubscript{64.32}B\textsubscript{22.08}Nd\textsubscript{9.6}Nb\textsubscript{4}, a significant improvement of the remanence has been achieved by raising the Fe concentration in the present work. The resulting energy products $BH_{\text{max}}$ are 81, 98 and 97 kJ/m\textsuperscript{3} for Nd\textsubscript{9}Fe\textsubscript{73}B\textsubscript{14}Nb\textsubscript{4}, Nd\textsubscript{9}Fe\textsubscript{77}B\textsubscript{10}Nb\textsubscript{4} with 10 m/s and 12.5 m/s, respectively. These values are considerably high, nearly three times higher than the value (33 kJ/m\textsuperscript{3}) reported by Zhang et al. [1]. The high $BH_{\text{max}}$ obtained for the Nd\textsubscript{9}Fe\textsubscript{77}B\textsubscript{10}Nb\textsubscript{4} alloys is comparable to those of the Nd-Fe-B-C-Ti nanocomposite magnets with the same Nd content [3] which have been developed for commercial bond magnets. Since the coercivity is higher for the slower quenching speed of 10 m/s, it may open up a way to obtain bulk magnets with higher coercivity by a conventional casting method.

### Table 1. Magnetic properties of the annealed Nd\textsubscript{9}Fe\textsubscript{77}B\textsubscript{10}Nb\textsubscript{4} and Nd\textsubscript{9}Fe\textsubscript{73}B\textsubscript{14}Nb\textsubscript{4} alloys.

|                  | $iHc$ (kA/m\textsuperscript{-1}) | $Mr$ (T) | $BH_{\text{max}}$ (kJ/m\textsuperscript{3}) |
|------------------|---------------------------------|---------|---------------------------------|
| Nd\textsubscript{9}Fe\textsubscript{77}B\textsubscript{10}Nb\textsubscript{4} (12.5 m/s) | 750    | 0.73    | 81                              |
| Nd\textsubscript{9}Fe\textsubscript{73}B\textsubscript{14}Nb\textsubscript{4} (10.0 m/s) | 685    | 0.82    | 98                              |
| Nd\textsubscript{9}Fe\textsubscript{77}B\textsubscript{10}Nb\textsubscript{4} (12.5 m/s) | 570    | 0.82    | 97                              |

### 4. Conclusion

An Fe-rich part of the Fe-B-Nd-Nb quaternary system has been investigated in order to improve the remanence of the Fe-B-Nd-Nb magnet while keeping the coercivity at a substantial level. As a result, high energy products reaching 98 kJ/m\textsuperscript{3} with substantially high coercivity values of 685 kA/m have
been obtained by a conventional melt-spinning and annealing process. Optimization of the magnetic property with respect to the quenching rate and the heat treatment conditions is expected to further improve the magnetic performance of the Fe-B-Nd-Nb quaternary magnet.

5. References
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