Significant changes in crystallization kinetics of Nd$_2$Fe$_{14}$B/α-Fe nanocomposites induced by Nb addition

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Abstract. The effects of Nb addition on the crystallization kinetics, microstructure and magnetic properties of melt-spun Nd$_2$Fe$_{14}$B/α-Fe nanocomposite magnets have been studied. The analysis of crystallization kinetics for the alloys indicates that the growth of crystallites in the Nb-doped alloy needs more activation energy than that in the Nb-free alloy. This crystallization behaviour contributes to the formation of a finer and more homogeneous microstructure in the Nb-doped alloy than in the Nb-free alloy. And the Nb addition makes the grains more equiaxed shape. The intrinsic coercivity and the maximum energy product increase from 600 kA/m, 105 kJ/m$^3$ for Nd$_{10}$Fe$_{84}$B$_6$ alloy to 750 kA/m, 120 kJ/m$^3$ for Nd$_{10}$Fe$_{83}$Nb$_1$B$_6$ alloy, respectively.

1. Introduction
Nanocomposite magnets have attracted considerable attention due to their high remanence ratio, great energy product and low rare-earth content. The high performance is attributed to the intergrain exchange interactions between the hard-magnetic grains and the soft-magnetic grains. For the effective exchange coupling, a homogeneous and fine-grained microstructure is required.

Microalloying is an effective way to improve the magnetic properties by optimizing the microstructure and improving the intrinsic magnetic properties of magnetic phases [1-3]. The addition of Nb was reported to be advantageous in refining the grain size and improving the energy product of nanocomposite magnets [4-6]. On the other hand, Jin et al. [7] reported that some large grain clusters were observed in Nb-doped alloy, thus degrading the squareness of hysteresis loops. Ping et al. [8] reported that the Nb-doped ribbons prepared by annealing amorphous precursors exhibit coarser microstructures than the Nb-free ribbons prepared by melt spinning at a wheel speed of 20 m/s. Therefore, the effects of Nb in nanocomposite magnets need to be further studied.

One of the practical ways of preparing nanocomposite magnets is through the crystallization of amorphous phase into a mixture of hard and soft phases. Thus, the crystallization behaviour of the alloy plays a key role in the microstructure development. Hereafter, the influences of Nb addition on the crystallization behaviour of the Nd$_2$Fe$_{14}$B/α-Fe magnets have not been understood very well. The investigation on the crystallization kinetics [9,10] can provide an insight into the nucleation and growth mechanisms for the crystalline phases. However, work dealing with the crystallization kinetics of Nd$_2$Fe$_{14}$B/α-Fe magnets, especially the Nb-doped alloys, is limited. Our previous study [11] showed that the crystallization behaviour of the amorphous Nd-Fe-B alloy changes from a two-step process to a single-step process with the addition of Zr, leading to the difference in the activation energy of
crystallization between Zr-free and Zr-doped alloys, thus refining the microstructure and improving the magnetic properties of magnets. Nb is adjacent to Zr in the periodic table of elements. It raises an interesting question: whether or not the Nb addition has similar effect in the Nd$_2$Fe$_{14}$B/$\alpha$-Fe magnets?

In this paper, the effects of Nb addition on the crystallization kinetics, microstructure and magnetic properties of Nd$_2$Fe$_{14}$B/$\alpha$-Fe magnets are investigated.

2. Experiment

Alloy ingots with nominal compositions of Nd$_{10}$Fe$_{84}$B$_6$ and Nd$_{10}$Fe$_{83}$Nb$_1$B$_6$ were prepared by induction melting under purified argon. Alloy ribbons were obtained by melt spinning in an Ar atmosphere at a wheel speed of 35 m/s, and then annealed between 650 and 750 °C for 10 minutes under vacuum to develop the nanocrystalline microstructure. The magnetic properties were measured using a LakeShore 7410 vibrating sample magnetometer (VSM) with a maximum magnetic field of 2.5 T. X-ray diffraction (XRD, Rigaku D/max 2550Pc) with Cu K$_\alpha$ radiation was used to identify the phase composition of samples. The microstructures of samples were observed by a Philips CM200 transmission electron microscope (TEM). The crystallization behaviours of as-spun ribbons were traced using a SDT Q600 differential scanning calorimeter (DSC) at heating rates of 5, 10, 15, and 20 °C/min, respectively.

3. Results and discussion

Table 1 lists the magnetic properties (B$_r$, iH$_c$ and (BH)$_{max}$) and the corresponding annealing parameters for Nd$_{10}$Fe$_{84}$B$_6$ and Nd$_{10}$Fe$_{83}$Nb$_1$B$_6$. It can be seen that, for both alloys, the magnetic properties first increase and then decrease with increasing annealing temperature. The optimal annealing temperature at which the samples exhibit the optimized magnetic properties is 715 °C for both samples. At the optimal annealing temperature, the intrinsic coercivity iH$_c$ increases from 600 kA/m for the Nb-free sample to 750 kA/m for the Nb-doped sample, and the maximum energy product (BH)$_{max}$ increases from 105 kJ/m$^3$ to 120 kJ/m$^3$ correspondingly. The non-magnetic Nb element leads to the dilution of the overall magnetization, which may be the reason for the little decrease in the remanence for the Nb-doped alloy.

| Compositions     | Annealing condition | B$_r$ (T) | iH$_c$ (kA/m) | (BH)$_{max}$ (kJ/m$^3$) |
|------------------|--------------------|----------|--------------|------------------------|
| Nd$_{10}$Fe$_{84}$B$_6$ | 700 °C, 10min      | 0.91     | 592          | 101                    |
|                  | 715 °C, 10min      | 0.92     | 600          | 105                    |
|                  | 730 °C, 10min      | 0.89     | 590          | 100                    |
|                  | 700 °C, 10min      | 0.88     | 735          | 115                    |
| Nd$_{10}$Fe$_{83}$Nb$_1$B$_6$ | 715 °C, 10min | 0.90     | 750          | 120                    |
|                  | 730 °C, 10min      | 0.88     | 730          | 113                    |

The XRD studies revealed that the as-spun Nb-free and Nb-doped ribbons contain fully amorphous phase. Figure 1 illustrates the bright-field TEM images with selected area electron diffraction (SAED) patterns of both the optimally annealed samples. The SAED patterns show that the microstructures of both alloys are crystallographically isotropic, and the rings in SAED patterns can be indexed with those arising from the Nd$_2$Fe$_{14}$B and $\alpha$-Fe phases. It means that, for both alloys, the phase composition transforms from an as-spun amorphous state to a mixture of Nd$_2$Fe$_{14}$B and $\alpha$-Fe phases after optimal annealing. Figure 1a indicates that the Nd$_{10}$Fe$_{84}$B$_6$ has a heterogeneous microstructure consisting of large Nd$_2$Fe$_{14}$B and $\alpha$-Fe grains, and abnormally coarse grains with grain sizes of ~70 nm can be observed. A significant reduction in grain size with an improvement in microstructural homogeneity is observed in the Nb-doped alloy, as shown in Figure 1b, although this alloy still contains a few large grains ~50 nm. So the exchange coupling between the hard and soft magnetic phases is strengthened and the magnetic properties are improved. At the same time, it is
shown that the Nb addition optimizes the shape of grains, making the grains more equiaxed shape. It was reported [12] that a large stray field originating from the sharp edges of grains can reduce the coercivity. Thus, a microstructure with more equiaxed shaped grains is helpful to improve the coercivity in the Nb-doped alloy.

Figure 1. TEM bright-field images and selected area diffraction patterns of optimally annealed (a) Nd$_{10}$Fe$_{84}$B$_{6}$ and (b) Nd$_{10}$Fe$_{83}$Nb$_{1}$B$_{6}$ ribbons.

Figures 2 and 3 show the DSC curves for the crystallization behaviours of as-spun Nd$_{10}$Fe$_{84}$B$_{6}$ and Nd$_{10}$Fe$_{83}$Nb$_{1}$B$_{6}$ alloys at different heating rates, respectively. There are two exothermic peaks in the crystallization curves, which mean the crystallization behaviour is a two-step process for both alloys. According to our previous study [11] and other literature [13], the phase transformations of the as-spun Nd$_{10}$Fe$_{84}$B$_{6}$ and Nd$_{10}$Fe$_{83}$Nb$_{1}$B$_{6}$ ribbons during annealing take place with the same following sequences: Amorphous $\rightarrow$ Nd$_3$Fe$_{62}$B$_{14}$+α-Fe+Nd$_3$Fe$_{14}$B $\rightarrow$ α-Fe+Nd$_3$Fe$_{14}$B. For the both alloys, the first exothermic peak can be attributed to the formation of α-Fe phase, Nd$_3$Fe$_{14}$B phase and Nd$_3$Fe$_{62}$B$_{14}$ metastable phase from the amorphous phase, and the second one is related to the transformation from the Nd$_3$Fe$_{62}$B$_{14}$ metastable phase to the Nd$_3$Fe$_{14}$B and α-Fe phases.

Figure 2. DSC traces for as-spun Nd$_{10}$Fe$_{84}$B$_{6}$ alloy at different heating rates.

Figure 3. DSC traces for as-spun Nd$_{10}$Fe$_{83}$Nb$_{1}$B$_{6}$ alloy at different heating rates.

By measuring the peak positions of the crystallization exotherms shown in figures 2 and 3 at different heating rates, the average activation energies of crystallization (E$_c$) for the two amorphous alloys are calculated using the Kissinger method [14]. For the Nd$_{10}$Fe$_{84}$B$_{6}$ alloy, the average activation energy of crystallization is $281\pm5$ kJ/mol for the first exothermic peak and $365\pm5$ kJ/mol for the
second exothermic peak. For the \( \text{Nd}_{10}\text{Fe}_{84}\text{B}_6\) alloy, the average activation energy of crystallization is \(351\pm5\ \text{kJ/mol}\) for the first exothermic peak and \(398\pm5\ \text{kJ/mol}\) for the second exothermic peak.

To better understand the growth behaviour of crystalline phases in the amorphous alloy, the activation energy of crystallization at a given crystallized fraction \(x\), \(E_c(x)\), can be calculated by the Doyle equation \([15]\) using the DSC experimental data. The details of the calculation have already been published elsewhere \([9-11,15]\). Figure 4 shows the dependence of activation energy of crystallization on their crystallized fraction in Nb-free and Nb-doped alloys calculated from the DSC curves shown in figures 2 and 3. As illustrated in figure 4a, for both alloys, the activation energy of the first exothermic peak decreases with increasing the crystallized fraction. Obviously, the decrease of the activation energy in Nb-doped alloy is only from 390 to 340 kJ/mol, which is much smaller than that in the Nb-free alloy (from 390 to 270 kJ/mol). The activation energy of the second exothermic peak, as shown in Figure 4b, presents quite different behaviours in the two alloys. Significantly, in a wide range of crystallization fraction, the activation energy in the Nb-doped alloy is higher than that in the Nb-free alloy. These results imply that the growth of crystallites inNb-doped alloy needs more energy than that in the Nb-free alloy. Thus, the growth of crystallites in Nb-doped alloy would be relatively slower than that in the Nb-free alloy.

![Graph](image)

**Figure 4.** Dependence of activation energy on crystallized fraction in as-spun Nd\(_{10}\text{Fe}_{84}\text{B}_6\) and Nd\(_{10}\text{Fe}_{83}\text{Nb}_1\text{B}_6\) alloys: (a) the first crystallization exothermic peak; (b) the second crystallization exothermic peak.

The growth of crystallites in an amorphous alloy is strongly affected by the atomic diffusion. Due to the large atomic diameter, the diffusivity of Nb atoms is low. Moreover, after Nb addition there are more elements and atom radius (of which, \(R\text{Nd} > R\text{Nb} > R\text{Fe} > R\text{B}\)) variety in the as-spun ribbons. Thus the packing density of atoms would be enhanced, which also inhibits the atomic diffusion.

Previous studies \([6, 16]\) reported that Nb has very low solubility in both \(\alpha\text{-Fe}\) and \(\text{Nd}_2\text{Fe}_{14}\text{B}\) phases, the Nb atoms tend to enrich at the interface between the \(\alpha\text{-Fe}\) and \(\text{Nd}_2\text{Fe}_{14}\text{B}\) grains detected by three-dimensional atom probe (3DAP) and nano-probe energy dispersive spectroscopy. The segregation of Nb to the interfaces, in combination with the low atomic diffusion, could reduce the mobility of the interfaces. Thus the growth of crystallites in \(\text{Nd}_{10}\text{Fe}_{83}\text{Nb}_1\text{B}_6\) alloy needs more energy than that in the \(\text{Nd}_{10}\text{Fe}_{84}\text{B}_6\) alloy, leading to a finer and more equiaxed grain structure in the Nb-doped alloy than in the Nb-free counterpart.

However, the addition of Nb does not change the two-step crystallization process of amorphous phase. In the Nb-doped alloy, some \(\alpha\text{-Fe}\) and \(\text{Nd}_2\text{Fe}_{14}\text{B}\) grains precipitated earlier from the amorphous matrix in the first-step crystallization process still tend to grow larger during the decomposition of metastable phase. It is one of the reasons why the Nb-doped alloy still contains large grains in the present work and in the previous works \([7, 8]\). In addition, some Nb atoms may enter the metastable phase, leading to the difference in the activation energy of the second exothermic peak between the Nb-free and Nb-doped alloys. Further investigations are needed.
4. Conclusions
For both Nd$_{10}$Fe$_{84}$B$_6$ and Nd$_{10}$Fe$_{83}$Nb$_1$B$_6$ alloys, the crystallization behaviour is a two-step process. The analysis of crystallization kinetics for the two alloys indicates that the growth of crystallites in the Nb-doped alloy needs more activation energy than that in the Nb-free alloy. These crystallization behaviours result in a finer and more homogeneous microstructure in the Nb-doped alloy than in the Nb-free alloy. And the Nb addition makes the grains more equiaxed shape. The Nd$_{10}$Fe$_{83}$Nb$_1$B$_6$ alloy annealed at 715 °C for 10min exhibits the improved magnetic properties, $B_r$=0.90T, $H_c$=750kA/m, $(BH)_{max}$=120kJ/m$^3$. The intrinsic coercivity and the maximum energy product increase by 25% and 14%, respectively, compared with those of Nd$_{10}$Fe$_{84}$B$_6$ alloy.

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