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Effect of Ti and C additions on the microstructure and magnetic properties of $Nd_6Pr_1Fe_{80}B_{13}$ melt-spun ribbons

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Abstract

We have investigated the microstructure of $Nd_6Pr_1Fe_{80-x}Ti_xB_{13-y}C_y$ ($x = 0, 4$; $y = 0, 1$) melt-spun ribbons using transmission electron microscopy (TEM) and three dimensional atom probe (3DAP) analysis to correlate their hard magnetic properties with the microstructure. Optimally quenched and annealed $Nd_6Pr_1Fe_{76}B_{12}Ti_4C_1$ ribbon, which was composed of $Nd_2Fe_{14}B$ grains of about 16 nm mean diameter separated by Fe_3B grain boundary phase, showed a maximum energy product of 112 kJ/m^3 with coercivity of 510 kA/m. The addition of 4 at.% Ti significantly modified the solidification path by suppressing the formation of $Nd_2Fe_{23}B_3$ phase and promoting the formation of $Nd_2Fe_{14}B$ phase. TEM observations showed that the additions of Ti and C refined the microstructure, and 3DAP analysis indicated that the formation of TiC at the $Nd_2Fe_{14}B$ grain boundary is the reason for the refined grain size and enhanced remanence.

Keywords: Hard magnets; Nanocomposite; Melt spinning; Atom probe; $Nd_2Fe_{14}B$

1. Introduction

Nd–Fe–B-based nanocomposite magnets that are composed of a nanosized mixture of hard magnetic $Nd_2Fe_{14}B$ and soft magnetic α-Fe or Fe_3B show relatively good isotropic permanent magnetic properties with low rare earth content. The major compositional ranges of previously studied Nd–Fe–B-based nanocomposites are near $Nd_{4.5}Fe_{77}B_{18.5}$ for $Fe_3B/Nd_2Fe_{14}B$ nanocomposites [1,2] and near $Nd_8Fe_{87}B_6$ for α-Fe/$Nd_2Fe_{14}B$ composites [3,4]. Although the α-Fe/$Nd_2Fe_{14}B$ nanocomposites can achieve higher values of coercivity (H_c) and maximum energy product $(BH)_{max}$, commercial production of α-Fe/$Nd_2Fe_{14}B$ nanocomposite magnets has not been successfully implemented due to their poor processability. On the other hand, the microstructure of the $Fe_3B/Nd_2Fe_{14}B$ nanocomposites can be more easily controlled, because a fine uniform nanocomposite microstructure can be obtained by crystallizing fully amorphous precursors [5]. In contrast, only coarse α-Fe/$Nd_2Fe_{14}B$ nanocomposite microstructure can be obtained by crystallizing overquenched amorphous precursor [6]. Thus, $Fe_3B/Nd_2Fe_{14}B$ nanocomposites have been successfully commercialized as raw materials for bonded magnets [7]. One drawback of the $Fe_3B/Nd_2Fe_{14}B$ nanocomposite that is processed from a typical composition close to $Nd_{4.5}Fe_{77}B_{18.5}$ is its low coercivity. To increase the coercivity of the alloy, various additional elements have been investigated [5,7–10]. The most effective way was to substitute Cr for Fe [9,10], which increases the coercivity effectively but only at the expense of remanence and saturation magnetization.

Recently, a new compositional range, $Nd_{9.5-7}Fe_{bal}$-B_{10-13}, which is slightly lean in Nd and rich in B with respect to the stoichiometry of $Nd_2Fe_{14}B$ ($\sim Nd_{12}Fe_{82}B_6$), has attracted considerable research interest due to a good balance of coercivity and remanence [11–13]. In this alloy

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composition, the volume fraction of the $Nd_2Fe_{14}B$ is much larger than that of the $Fe_3B/Nd_2Fe_{14}B$ nanocomposite, but the types of additional constituent phases are not necessarily clear. Depending on the composition, α-Fe, ferroboron, and Fe_3B were reported [11–13]. In addition, various types of alloying elements have been explored to improve the magnetic properties [14]; in particular, Chang et al. reported that the addition of Ti and C was effective in increasing the coercivity. Further study by Hirosawa et al. [15] reported a coercivity increase without sacrificing much remanence even by the replacement of Fe with Ti. The promotion of $Nd_2Fe_{14}B$ phase formation by suppressing the formation of the metastable $Nd_2Fe_{23}B_3$ phase is believed to be one of the reasons for the beneficial effect of the Ti addition [16,17]. Changes in the grain growth kinetics by C and Ti additions were also reported. However, there is little understanding of the underlying mechanisms of Ti and C additions in improving the magnetic properties of these nanocomposite magnets.

In our recent work [18], we investigated the overall microstructural change caused by the addition of Ti and C to $Nd_9Fe_{77}B_{14}$ base alloys, mainly by energy filtered transmission electron microscopy (EF-TEM). In $Nd_9Fe_{73}B_{13}Ti_4C_1$, the nanocomposites were composed of $Nd_2Fe_{14}B$, α-Fe, and a B- and Ti-enriched amorphous grain boundary phase. In the work reported here, we investigated the effect of Ti and C additions on the hard magnetic properties of $Nd_6Pr_1Fe_{80-x}Ti_xB_{13-y}C_y$ ($x = 0$, 4; $y = 0$, 1) melt-spun ribbons with various processing and heat treatment conditions. These are the compositions of the commercial nanocomposite magnets having the trade name SPRAX assigned by NEOMAX Inc. Their microstructures and local chemistry have been characterized using EF-TEM and three-dimensional atom probe (3DAP) analysis to explain the hard magnetic property changes in terms of microstructural changes resulting from the additions of Ti and C.

2. Experimental

Ingots of $Nd_6Pr_1Fe_{80-x}B_{13-y}Ti_xC_y$ ($x = y = 0$; $x = 4$, $y = 0$; $x = 4$, $y = 1$) alloys were prepared from Fe, Nd, and Ti metals with purity greater than 99.5% and commercial-grade Fe–B and Fe–C alloys by induction melting in an argon gas atmosphere and casting onto a chilled hearth. Ribbons (100 μm thick) were prepared from small pieces of crushed ingots by the single-roller melt-spinning technique at a wheel surface velocity of 5–10 m/s in an argon gas atmosphere. The structure of the ribbons was preliminarily examined using X-ray diffraction (XRD) with monochromatic Cu K_α radiation.

The microstructure was investigated using a Philips CM200 TEM instrument operated at 200 kV for conventional observation and a JEOL JEM-2010F TEM instrument operated at 200 kV for high-resolution observation. Energy filtered images were obtained by the jump ratio technique using the Nd $N_{4,5}$-edge, the Fe $L_{2,3}$-edge, the B K-edge, the Ti $L_{2,3}$-edge, and the C K-edge of electron energy loss spectroscopy (EELS) acquired with a Gatan imaging filter (GIF). The TEM specimens were prepared by mechanical polishing, followed by the ion-milling technique using a Gatan model 691 PIPS machine at an accelerating voltage of 3.5 kV with an ion beam current of 20 μA. The ribbon specimens were mechanically ground to thin square rods and then electropolished by a microelectropolishing technique to prepare field ion microscopy (FIM) specimens. Atom probe analyses were conducted under ultrahigh vacuum conditions ($<2 \times 10^{-8}$ Pa) at a specimen temperature of 70 K using an energy-compensated 3DAP equipped with an Oxford Nanoscience delay line detector [19]. The magnetic properties of the ribbons were measured at room temperature with a vibrating sample magnetometer (VSM) after magnetizing the ribbons with a pulsed magnetic field of 16 T.

3. Results

3.1. Effect of cooling rate

One of the difficulties in the microstructural control of a Nd–Fe–B-based nanocomposite magnet is its sensitivity to the cooling rate that is controlled by varying the surface velocity of the Cu wheel of the melt-spinner. Thus, the effect of the wheel surface velocity on the microstructure must be examined before optimizing post-annealing conditions. Fig. 1(a) shows the hysteresis loops of as-quenched $Nd_6Pr_1Fe_{76}B_{12}Ti_4C_1$ ribbons prepared at wheel surface speeds of 5, 7.5, and 20 m/s. The ribbon melt-spun at a wheel surface speed of 20 m/s shows soft magnetic properties, indicating that the film is amorphous. The ribbon melt-spun at a wheel surface speed of 7.5 m/s clearly shows two-phase magnetic behavior whereas the specimen quenched at a wheel speed of 5 m/s shows a single-phase hard magnetic behavior. The specimens were annealed at 720 °C for 5 min in order to optimize the magnetic properties. The demagnetization curves for the samples after annealing are shown in Fig. 1(b). $(BH)_{max}$ values of 39, 50, and 112 kJ/m^3 were obtained from the annealed ribbons that were melt-spun at wheel surface speeds of 20, 5, and 7.5 m/s, respectively. These results clearly demonstrate that optimum quenching conditions are necessary for obtaining high $(BH)_{max}$ in the Nd–Pr–Fe–B–Ti–C composite magnets.

The XRD analysis (data not shown) showed the formation of $Nd_2Fe_{14}B$ and Fe_3B phases in the specimens spun at 5 and 7.5 m/s. It was observed that a further increase in wheel speed ($V_s > 10$ m/s) results in the formation of amorphous phase that crystallizes into soft magnetic $Nd_2Fe_{23}B_3$ phase (not shown here). Therefore, a wheel speed of 7.5 m/s for melt-spinning followed by annealing at 720 °C for 5 min was set as the optimum condition for obtaining the highest $(BH)_{max}$ values from the $Nd_6Pr_1Fe_{76}B_{12}Ti_4C_1$ alloy. Fig. 2 shows bright-field (BF) TEM images of optimally annealed $Nd_6Pr_1Fe_{76}B_{12}Ti_4C_1$ ribbon quenched at