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Magnetic Properties and Microstructures of Melt Spun Misch Metal-Ferroboron Alloys

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Magnetic properties and microstructures of melt spun misch metal-ferroboron alloys were investigated. The major phase is the tetragonal (rare earth)$_2$Fe$_{14}$B phase. Magnetic properties showed coercivity of 5.6 kOe, remanence of 7.85 kG, and so energy product 8.9 MGOe. Microstructures in optimum properties showed that matrix was composed of Ce-rich phase while second phase La-rich-oxygen phase with less amount of Fe element than matrix, and triple junction with La-rich phase contrary to matrix.

1. Introduction

The outstanding permanent magnetic properties of Nd-Fe-B alloys result from the formation of the tetragonal $Nd_2Fe_{14}B$ phase [1]. However, the high cost of rare earth, especially, Nd element keeps the price of Nd-Fe-B magnets much higher than that of ferrites. According to it, only much more abundant and less expensive misch metal might lead to permanent magnet that can compete strongly with ferrites. It was known that $(La, Ce)_2Fe_{14}B$ compound including both La and Ce elements forms tetragonal compound [2] but its magnetocrystalline anisotropy is not high as compared to that of $Nd_2Fe_{14}B$ alloy because both elements have not orbital moment [3]. Yamasaki et. al. [4] have found that the anisotropy field is maximum around x = 0.6 in $(La_{1-x}Ce_x)_2Fe_{14}B$ powders, and also reported [5] that $MM_{16}Fe_{75}B_9$ alloy quenched at the optimum rate of 20 m/sec exhibited coercivity of 9.4 kOe, remanence of 6.2 kG and maxmum energy product of 8.1 MGOe.

In this paper, magnetic properties and microstructures of melt spun $MM_{12}Fe_{76}B_{12}$ and $MM_{12}Fe_{82}B_6$ alloys with variable wheel speed were investigated.

2. Experimental

The master alloys of various composition were prepared by vacuum argon arc furnace with commercial grade in misch metal (MM) and ferroboron elements. It turned over 7～10 times to ensure homogeneous composition during arc melting. All alloys were made by four sorts because misch metal was composed of very delicate composition. A few piece of crushed master alloys were put in a quartz tube having an orifice of 0.7 mm diameter in high vacuum and high frequency induction furnace and melt spun in an argon atmosphere having 70 mmHg using a rotating Cu wheel with 200 mm diameter. The thicknesses and widths of the ribbons were about 25～40 μm and 2～3 mm respectively depending on the wheel speed of 10～40 m/sec. All ribbons used in this study were kept ambient atmosphere during 6 months. Magnetic measurements were carried out in a vibrating sample magnetometer (VSM) with a maximum field of 16 kOe and sometimes, Oxford VSM having a superconducting magnet with a maximum field of 120 kOe. All magnetization were measured after demagnetizing the samples in a 2000～3000 Oe with no premagnetization at room temperature. X-ray diffractometer was used to determine the crystral structure of melt spun ribbons and master alloys at room temperature. Transmission electron microscopy (Philips 200CX, VG Microscope HB601 STEM) was used to examine the microstructures of melt spun ribbons and master alloys. All samples were investigated at room temperature after heating up to 200 ℃ in order to evaporate remaining oxygen. Thin foils for electron transparency were prepared by ion milling method.

3. Results and Discussion

The X-ray powder diffraction patterns of melt spun ribbons with optimal magnetic properties in $MM_{16}Fe_{76}B_{12}$ alloys is

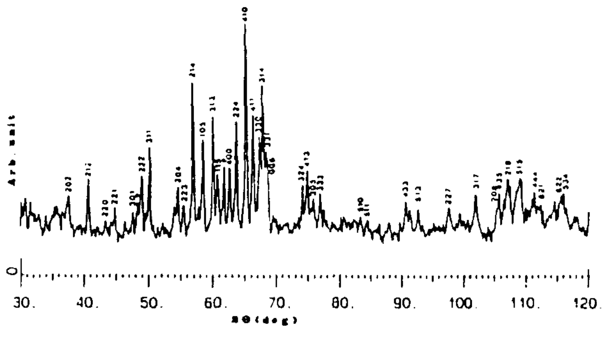


Fig. 1. X-ray diffraction pattern of melt spun $MM_{12}Fe_{76}B_{12}$ alloy with wheel speed of 25 m / sec.

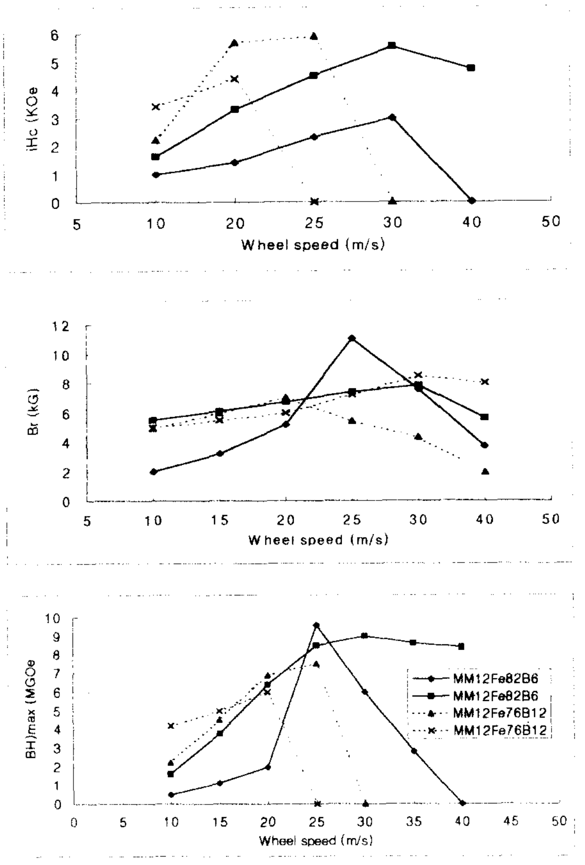
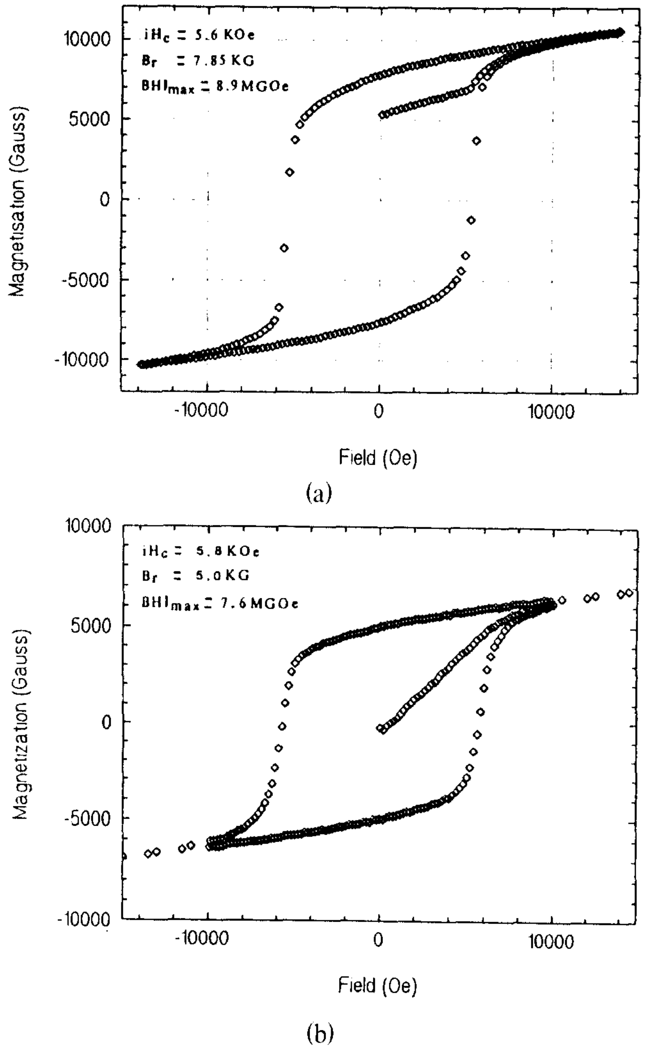


Fig. 2. Variations of magnetic properties with wheel speed.

shown in Fig. 1. This pattern confirms that the major phase in all samples studied is the tetragonal 2 : 14 : 1 phase with lattice parameter a = 8.77 Å, c = 12.20 Å. All but a few lines were indexed to 2 : 14 : 1 phase. The extra Bragg peaks presented are common to all samples. These lines may belong to second phase. It is very difficult to define because it shows low relative intensity but, two other obvious extra lines appeared at 2θ = 48.0, 61.7 and are marked by asterisks in Fig. 1. It may be assigned the form of misch metal-rich phase but it can suggest to not be alpha-Fe phase. Above results are very similiar with master alloy's results except two clear peaks. In $MM_{12}Fe_{82}B_6$ alloys, melt spun ribbons and master alloys showed extra peak that can be defined to alpha-Fe phase. As wheel speed increased, in general, relative peak intensity decreased and so revealed amorphous state. The magnetic properties of melt spun ribbons strongly depended on the quenching rate as reported in melt spun $Nd_2Fe_{14}B$ alloys [6] and exhibited dramatic changes despite little variation of amount of misch metal. Fig. 2 shows the coercivity $({}_iH_c)$, remanence (B_r) and maximum energy product $(BH)_{max}$ as a function of the quenching rate in terms of wheel surface speed. As B element increased, maximum properties were observed at lower wheel speed. Magnetic properties in as-cast samples did not show hysteresis loop, compared with melt spun ribbons. Optimal magnetic properties can be obtained with wheel speed in the range of 20 ~ 30 m / sec. Typical hysteresis loop for optimal magnetic properties are shown in Fig. 3 indicating H_c = 5.6 kOe, B_r = 7.85 kG, $BH)_{max}$ = 8.9 MGOe in $MM_{12}Fe_{82}B_6$ ribbons and H_c = 5.8 kOe, B_r = 5.0 kG, $BH)_{max}$ = 7.6 MGOe in $MM_{12}Fe_{76}B_{12}$ ribbons. The ratios of remanent to saturation magnetization (M_r / M_s) showed large values with



(a)

(b)

Fig. 3. Hysteresis loops in melt spun (a) $MM_{12}Fe_{82}B_6$ and (b) $MM_{12}Fe_{76}B_{12}$ alloys with wheel speed of 30 m / sec, 25 m / sec respectively.

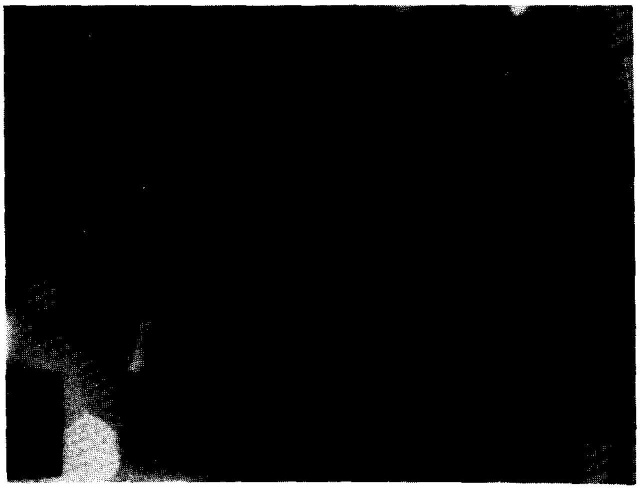


Fig. 4. Microstructure in melt spun $MM_{12}Fe_{76}B_{12}$ alloy with wheel speed of 25 m / sec.

range of 0.6 ~ 0.75. These values are higher than the quenched (Ce, La)-Fe-B ribbon [7], and melt spun-heat treated $MM_{17}Fe_{75}B_8$ ribbons [8]. The obtained high remanence may be introduced by Si element [9][10] contained in ferroboron element, due to ultra fine grain sizes. Obtained coercivity is very similar to (La, Ce)-Fe-B ribbon for the optimum quenched rate [5]. It suggests that the large coercivity is associated partly with the increase in magnetocrystalline anisotropy due to alloying Ce and La element [4]. Fig. 4 shows the microstructure corresponding to the melt spun $MM_{12}Fe_{76}B_{12}$ ribbon with wheel speed of about 25 m/sec. It consists of randomly oriented $MM_2Fe_{14}B$ grains and grain sizes are roughly 30 ~ 100 nm diameter. Sometimes, they have sharp grain boundaries and are polygonal structure like hot pressed Nd-Fe-B magnet [11] contrast to melt spun ribbon structure with nearly spherical grains with curved grain boundary [12]. An intergranular phase is not clearly seen in contrast to the melt spun Nd-Fe-B alloys. Fig. 5 shows the microanalysis of phases in $MM_{12}Fe_{76}B_{12}$ ribbon using STEM HB601UX. Matrix is composed of Ce-rich phase while second phase, La-rich-oxygen phase with insufficient Fe composition than matrix, and triple junction with La-rich phase contrary to matrix. It showed misfit of lattice image at grain boundary [13]. Also grain boundary shows intermediate phase between matrix and second phase. All phase exhibited peculiar phenomena in which oxygen strongly is in combination with rare earth elements with no relation of amount of oxygen. It shows possibility of an oxygen stabilized (rare earth)-Fe-oxygen phase which may be anisotropic as suggested by Schneider [14] and Hadjipanayis [15]. These results in microanalysis of ribbons are very similiar with results using SEM in master alloys except oxygen can not be analyzed within limit of resolution [13] Also, this would explain the low coercivity since it could act as a nucleation site for reverse domains because paramagnetic properties at room temperature [16]. In summary, our study in melt spun misch metal-ferroboron alloys supply possibility of permanent magnet which can be compete with ferrites and AlNiCo systems, and oxygen stabilized (rare earth)-Fe-oxygen compound with magnetic anisotropy.

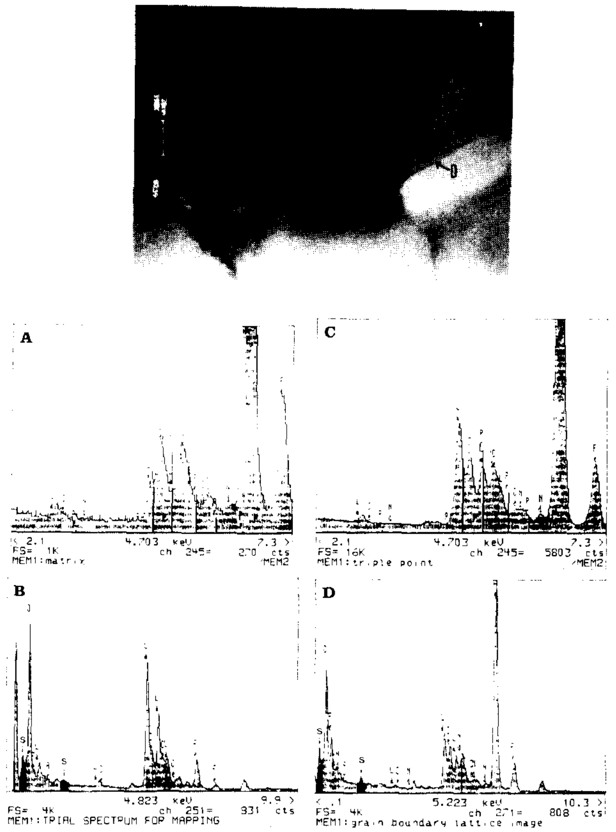


Fig. 5. Microanalysis in melt spun $MM_{12}Fe_{76}B_{12}$ alloy with wheel speed of 25 m / sec.

Acknowledgments

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