Microstructure and magnetic properties of melt-spun Alnico-5 Alloys

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Abstract

The aim of this work is to investigate the effect of very fine grain sizes on the spinodal decomposition in the Alnico system. Commercial Alnico 5 was melted and melt-spun with varying copper wheel speeds, which led to a grain size of 1-2 μm . This value was further reduced to sub-micrometer size by a small addition of Boron (1at.%). The spinodal decomposition was induced through a two-step annealing treatment under magnetic field in the range of 600-900°C. It was found that the size of the spinodal structures is not influenced much by increased wheel speeds but becomes smaller with the addition of Boron. However, the difference in coercivity between the samples with and without Boron is only 50 Oe (4 kA/m). To study the influence of the annealing treatment two sets of samples are compared, one with the highest coercivity (366 Oe / 29 kA/m) and the other one with lower coercivity (180 Oe / 14.5 kA/m). We found with Scanning transmission electron microscopy Energy-dispersive X-ray spectroscopy (STEM EDX) a much sharper chemical interface between the α_1 and α_2 precipitates in the former sample, which we attribute to be the main reason for the higher coercivity.

1. Introduction

Permanent magnets are crucial components in many commercial applications with the most important ones in motors and generators. Nowadays, the magnets with the highest energy content rely on rare earth elements, e.g. the Nd-Fe-B system. However, the recent rare-earth crisis calls for the development of rare-earth-lean/free permanent magnets [1,2,3]. A prominent example for non-rare earth magnets are the so-called Alnico magnets, which are the first modern permanent magnets discovered by Mishima [4] already in 1931. They do not contain rare-earths and have a relatively high energy product. The magnetic hardness originates from the shape anisotropy of FeCo-rich magnetic rods (α_1 phase) which are embedded in a non-magnetic NiAl-rich matrix (α_2 phase) [5]. This microstructure is obtained through spinodal decomposition after a special heat-treatment. However, the low coercivity H_c (< 2 kOe) of Alnico magnets limits their use for high temperature applications. The theoretical value of H_c based on rod shape anisotropy is expected to be much higher (> 7 kOe) [6]. Recent studies by Zhou et al. [7] revealed that the morphology of the rods is inhomogeneous and the matrix is weakly magnetic, both of which can lead to the low coercivity. Sun et al. [8] reported the coercivity-spinodal structure relation in Alnico 5-7 and Alnico 8 commercial magnets. A similar study was carried out by Xing et al. [9] in Alnico 9 type alloys. All of the above reports are on bulk commercial magnets.

It has been shown theoretically that there exists a critical wavelength λ_c (which corresponds to the grain size of the homogeneous initial alloy) below which the spinodal decomposition is suppressed [10]. This value is approximately 100 nm. Consequently, Akdogan et al. [11] could not induce spinodal decomposition in Alnico thin films with a grain size of 20 nm. Above the critical wavelength the morphology of the spinodal features, and therefore the magnetic properties, are supposed to vary greatly with grain size. Regarding this issue, in the present work we varied the grain size in Alnico melt-spun ribbons through varying copper wheel speeds and by a small addition of Boron (1 at.%). We investigate the correlation between grain size, coercivity, and spinodal structures.

2. Experimental details

A commercial Alnico5 magnet was used as sample material in this study. The magnet was melted and subsequently melt-spun. Samples with different grain sizes were prepared by varying the copper wheel speed of the melt-spinner from 5-60 m/s. To further reduce the grain size another set of samples was prepared with the addition of a small amount of B (1 at.%), which was added prior to melting. Spinodal decomposition was induced by subjecting the as-spun samples to heat-treatment at temperatures in the range of 600-900 °C. The ribbons were heat-treated under vacuum at temperatures 700-900 °C (for 2-30 minutes) and then were cooled to 600 °C with a cooling rate ~100 K/min. The heat-treatment was continued at this temperature for 120 minutes. During the decomposition heat treatment the samples were under a magnetic field of 1 T, applied along the length of the ribbons. The magnetic properties were measured with Quantum Design VersaLab vibrating sample magnetometer. Microstructural characterization of the ribbons was carried out by electron microscopy. A JEOL JSM 7600F scanning electron microscope operated at 15 keV was used in electron backscattering (BSE) mode to image the surface microstructure. A 200 kV Jeol JEM 2100F (scanning) transmission electron microscope (STEM) equipped with an Oxford X-max80 EDX detector was used to determine the microstructure on the nanometer scale. For the TEM studies the samples were demagnetized and mounted on Cu rings using Ag-bonded epoxy. Ion thinning was done in a Gatan Dual Ion Mill Model 600 using Ar^+ ions at 3.5 keV and 0.5 keV ion energies, respectively. Annular dark-field (ADF) scanning transmission electron microscope (STEM) images and energy-dispersive X-ray (EDX) spectra were obtained using a 0.7 nm spot size being a compromise between spatial resolution and EDX counts (detector dead time around 10%). Quantification of EDX spectra was carried out using the Cliff-Lorimer k-factor method.

3. Results and discussion

Backscattered SEM images of as-spun (5 and 60 m/s) and heat-treated samples at 900 °C for 30 min and aged at 600 °C for 2 hours are shown in figure 1. By examining

SEM images of several different regions of the ribbons a drastic reduction of the grain size is clearly visible, from 5-10 μm to roughly 1 μm and below in the samples produced at 5 m/s and 60 m/s copper wheel speed, respectively. After the heat treatment to induce the spinodal decomposition the grain size is almost doubled to around 10 μm and 1-2 μm in the ribbons produced at 5 m/s and 60 m/s, respectively (not shown).

The developed spinodal structures within the grains are shown in the high resolution SEM images (figure 1, bottom). A typical interpenetrating block structure can be observed in our samples, which is in contrast to the work by Akdogan et al. on Alnico thin films[11]. As mentioned in the introduction, the grain size in these films was only around 20 nm and a spinodal decomposition could not be induced. The brighter block like shapes correspond to FeCo-rich α_1 phase and the dark interspacing phase represents the AlNi-rich α_2 phase. The spinodal structures have approximately the same size in both samples. It can be concluded that grain sizes in the range of several micrometers have only a weak influence on the morphology of the spinodal structures. The respective hysteresis loops of the optimally heat-treated ribbons show a H_c of 226 Oe for the 5 m/s sample compared to 201 Oe for the 60 m/s ribbons (figure 2). The reason for the small difference in H_c might be the slightly smaller spinodal features in the 5 m/s sample and a changed aspect ratio of the FeCo needles.

Figure 3 shows the BSE SEM images of the cross-section of ribbons melt-spun at 60 m/s without and with 1 at.% B addition. The samples are in as-spun state (top) and after spinodal decomposition (bottom). The grain size decreased significantly with B addition to values below 1 μm . Also, from the high resolution SEM images it can be seen that the spinodal morphology in the ribbons with B is significantly finer compared to that of the ribbons without B. Also, with B a minor secondary phase is formed with a size about 50 nm (black dots seen in the figure), which we found to be Ti-rich with STEM EDX. Hysteresis loops of the heat-treated ribbons with and without B are shown figure 4. The H_c values of the samples with and without B are 255 and 201 Oe, respectively. The reasons for the difference in coercivity might be the finer spinodal morphology in the B-containing sample or the occurrence of more secondary phases.

Summarizing the results of the above two experiments: The grain size of Alnico ribbons was decreased by an order of magnitude by increasing the copper wheel speed from 5 m/s to 60 m/s to values, from 5 – 10 μm to about 1 μm . The ribbons with bigger

grains have a slightly finer spinodal morphology than the smaller grained ribbons, although the difference is not pronounced. It seems that in the range of μm the grain size does not strongly influence the size of the spinodal structures. When the grain size was decreased by B addition, a significantly finer spinodal structure developed compared to samples without B. Consequently, the coercivity of the B containing samples is higher compared to the ribbons without B. However, this difference could also be due to the difference in chemical composition and amount of secondary phases than with grain size.

Details of the spinodal structure are further investigated by High angle annular dark field (HAADF)-STEM and STEM-EDX studies. Two samples of Alnico5 melt-spun at the same wheel speed of 26 m/s, but heat-treated at different conditions, having best (Alnico+) and worst (Alnico-) H_c values are selected for this study. The hysteresis loops of the ribbon samples heat-treated at 800 °C for 4 min (Alnico+) and at 800 °C for 30 min (Alnico-) and then aged at 600 °C for 120 min are shown in figure 5. The coercivities differ greatly between 366 and 180 Oe for Alnico+ and Alnico-, respectively. HAADF-STEM images of both ribbons are shown in figure 6. The images show spinodal structures precipitating along the magnetic field direction. The dark spots seen are found to be Ti-rich precipitates. It was mentioned before that in the samples with B addition more of these precipitates can be found. The morphology of the spinodal structures shows distinct differences between the two samples. While the spacing of the lamellae (α_1 phase) is roughly the same there is more matrix phase (α_2 phase) in Alnico-, i.e. the α_1 -lamellae are thinner. Compositional profiles across the phases have been recorded with EDX linescans perpendicular to the longitudinal direction of the lamellae (figure 6, bottom). The FeCo-rich lamellae and the NiAl-rich matrix phase can be clearly distinguished for both the samples. The difference in the concentrations across the phases, i.e. the ratio of peak and valley is more pronounced in Alnico+ sample than in Alnico- sample. Compositional profiles in Alnico+ also depict plateau like regions for Fe and Co unlike the sharp peaks and valleys in Alnico-. In other words, the chemical interface between both phases is sharp in Alnico+ and less defined in Alnico-. The quantitative composition of the two phases was measured with EDX point scans and is shown in Table 1.

To get a first estimate for the coercivity of Alnico a well-established relation for the coercivity of a fully aligned array of single domain particles is commonly used [5]:

$$H_c = (1 - p)(N_z - N_x)M_s$$

Here p is the volume fraction of the FeCo-rich α 1-lamellae, $(N_z - N_x)$ denotes the difference in demagnetization factors between the principal directions of the lamella (i.e. the shape anisotropy contribution) and M_s is the saturation magnetization of the α 1-lamellae. M_s will increase with increasing content of Fe and Co, consequently the coercivity should be proportional to the Fe and Co concentration in the α 1-phase. Since they are, within the error limits, almost the same for both samples we doubt that they are responsible for the relatively big difference in coercivity. However, the formula was derived for an ideal separation of the magnetic phases. This separation is regarded as a necessity for a high coercivity and therefore it is likely that the main reason for the decreased coercivity is the less defined chemical interface rather than the absolute change in composition. Similar conclusions were drawn by Xing et al. [9] in commercial Alnico 5-8 magnets and by Sun et al. [12] in commercial Alnico 9 magnets. The other influencing factors, the volume fraction p and the shape anisotropy $(N_z - N_x)$ are hard to precisely determine from our STEM images and EDX line scans but seem to be rather equal.

4. Conclusions

The influence of the microstructure on spinodal structures and the magnetic properties of melt-spun Alnico ribbons have been studied. The grain size of the ribbons was decreased from 5-10 μm to about 1 μm by increasing the copper wheel speed from 5 m/s to 60 m/s, and further decreased by addition of 1 at.%B to less than 1 μm . The size of the spinodal features was about the same in the ribbons without B, which means that grain size above a certain threshold (which was theoretically shown to be >100 nm in another work [10]) does not influence the spinodal decomposition anymore. Through addition of B the spinodal features became significantly smaller. This, however, resulted only in a small increase in coercivity of about 50 Oe. The coercivities obtained in all samples are about half of those in anisotropic bulk samples, even though the aspect ratio of spinodals are the same as in bulk [8,9]. In a second part we set out to compare an optimally heat treated sample with high coercivity with one with low coercivity. With

STEM EDX linescans a much sharper compositional contrast between the α_1 lamellae and the α_2 matrix phase was found in the former sample, which we attribute to be the main reason for the higher coercivity.

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Figure 1: BSE SEM images of microstructures observed from the side of the ribbons(top) and from the cross-section (middle) of as-spun samples prepared at 5 m/s and 60 m/s wheel speed. Spinodal structures in the same ribbons after subsequent heat-treatment (bottom, seen from cross-section).

Figure 2: Hysteresis loops of the samples melt-spun at 5 and 60 m/s wheel speeds after spinodal decomposition.

Figure 3: (Top) BSE SEM images taken from the cross section of the as-spun samples without B and with 1 at.% B addition. (Bottom) Spinodal structures in the same ribbons after heat-treatment.

Figure 4: Comparisons of hysteresis loops for samples with and without the addition of 1 at.% B produced at 60 m/s after spinodal decomposition.

Figure 5: Hysteresis loops of Alnico+ (800 °C for 4 minutes then 600 °C 120 minutes; $H_c = 366$ Oe) and Alnico- (800 °C for 30 minutes then 600 °C 120 minutes; $H_c = 180$ Oe) ribbons.

Figure 6: Differences in microstructure and chemical composition in high coercivity Alnico+ and low coercivity Alnico- (cp. figure 5).

Table 3: Composition of lamellae and matrix phase in Alnico+ and Alnico- measured by EDX (in at.%). Note that since a Cu ring was used for mounting the sample the measured Cu concentration might be slightly too high due to stray radiation.

Sample	Lamella		Matrix		Difference Lamella - Matrix	
	Alnico+	Alnico-	Alnico+	Alnico-	Alnico+	Alnico-
Al	14.5 ± 2.5	10.9 ± 2.2	23.9 ± 3.0	17.1 ± 1.0	9.4 ± 3.9	6.2 ± 2.4
Fe	50.3 ± 4.4	53.2 ± 3.9	34.5 ± 5.3	38.4 ± 2.4	15.8 ± 6.9	14.8 ± 4.6
Co	21.6 ± 0.7	22.8 ± 0.6	19.1 ± 0.8	21.6 ± 0.3	2.5 ± 1.1	1.2 ± 0.7
Ni	10.0 ± 2.1	10.0 ± 1.9	17.1 ± 2.4	17.8 ± 1.4	7.1 ± 3.2	7.8 ± 2.4
Cu	2.3 ± 0.4	2.1 ± 0.5	4.2 ± 1.4	3.7 ± 0.6	1.9 ± 1.5	1.6 ± 0.8