Alnico Thin Films with High Coercivities up to 6.9 kOe

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Abstract. The spinodal decomposition has been investigated in Alnico thin films prepared by sputtering. The as-made bcc thin films were heat treated both by the complex heat treatment of bulk Alnico magnets and by a simple annealing at different temperatures in the range of 600-900 °C. The simple heat treatment gave a coercivity of 2.6 kOe at 600 °C and 6.9 kOe at 800 °C. The maximum coercivity observed is approximately ten times larger than the bulk Alnico V value. Electron diffraction patterns can be mostly indexed to a new fcc phase with a=7.79 Å. The traditional Alnico heat treatment gave a similar coercivity (6.7 kOe after full heat treatment) and similar diffraction patterns. The coercivity was found to depend strongly on the film thickness. In samples with thickness above 100 nm, the coercivity declined dramatically and at 150 nm it was only 500 Oe. These findings suggest structural transformations in films which are drastically different from the spinodal decomposition observed in bulk Alnico.

1. Introduction
Alnico alloys are important permanent magnets and widely used in many applications [1]. Alnico is the first modern permanent magnet discovered by Mishima in 1931 [2]. The magnetic hardness of Alnico magnets results from the shape anisotropy of magnetic precipitates which are formed when cast Alnico alloys are subjected to a special heat treatment. The homogenized alloy consists of a single BCC structure (α-phase) which with heat treatment undergoes spinodal decomposition into two BCC phases (α1 and α2 phases). The α1 phase is an Al(Ni)-rich weakly magnetic phase (matrix phase) and the α2 phase is an Fe(Co)-rich strongly magnetic phase (in the form of rod shaped precipitates) [3]. There are only few studies exist on the behavior of Alnico in confined geometries [4-7]. None of these studies reported any effect of the confined geometry on spinodal decomposition. In this study, we extensively studied the structural, microstructural and magnetic properties of thin Alnico films produced by magnetron sputtering.

2. Experiment
A 1 mm thick sputtering target was cut from a commercial Alnico V magnet. Thin film samples for magnetic measurements and transmission electron microscopy (TEM) were sputtered on 500 μm thick Si(100) substrates at a rate of 0.35 Å/sec with a dc power of 10.7 W. The base pressure in the sputtering chamber was 3x10^-7 Torr and high purity Ar (99.9999%) was used for the deposition with a pressure of 5 mTorr. Thin film samples with a thickness in the range of 50-300 nm were prepared. The films were coated with carbon in order to prevent oxidation. The films were subjected to different heat treatments;(i) a simple annealing in the temperature range of 600-1000 °C,(ii) a complex heat treatment consisting of 30 min annealing at 900 °C followed by cooling to 600 °C and annealing at this temperature for a few hours. The TEM samples were additionally thinned (from the substrate side)
down to 15 \mu m with a dimple grinder first and then by ion milling. Microstructure characterization and composition analyses of the thin films were performed with a JEOL JEM-3010 TEM. Magnetic measurements were done with a Lakeshore vibrating sample magnetometer with a maximum field of 10 kOe. For the heat treatment, the samples were sealed in quartz tubes under Ar atmosphere.

3. Results and discussion

3.1. Simple Annealing

Figure 1 shows the bright field (BF) image and selected area electron diffraction (SAED) pattern of the as-made Alnico thin films. The BF image shows continues film with a very fine grain structure and the SAED pattern was indexed to the BCC structure with a = 2.88 Å. Therefore, the as-made samples had the \( \alpha \)-phase.

![Figure 1: BF and SAED pattern of the as-made thin films.](image)

The microstructure and corresponding SAED pattern of the 100 nm film annealed at 900 °C for 30 min. is shown in Figure 2 a and b. The diffraction pattern was indexed using a Process Diffraction program [8] by converting the SAED image to a classical XRD data (Figure 2 c). The pattern matches closely with a spinel FCC structure (\( a = 7.79 \) Å). A similar phase has been seen in the Alnico system before with a little difference in lattice constant [9]. Due to the fact that only a couple of papers [9-11] had been written on a similar FCC phase in the literature before, this phase is probably a metastable phase that occurs and disappears at some stage of the heat treatment process. Heidenreich R. D. and Nesbitt E. A. [9] have seen this effect for the similar phase they reported. In contrary, after full heat treatment of Alnico thin films with annealing at 600 °C for 10 h, the new FCC phase is still observed. High resolution XRD studies are scheduled to check this phase further. The grain size of this new phase varies from 30 to 100 nm. High resolution TEM image (Figure 2 d) shows clear lattice fringes with a \( d \)-spacing of 4.6 Å corresponding to the first peak of the new FCC phase (111).

The heat treated sample showed a high coercivity of 6 kOe which is 7-8 times than the coercivity of bulk samples [12].
The 100 nm thick sample was also subjected to annealing at different temperatures of 600, 800 and 1000 °C for 30 min and the corresponding coercivities are 2.6, 6.9 and 5.9 kOe, respectively. The coercivity values of the annealed films are much higher when compared to those of the Alnico V magnets (0.7 kOe [12]).

The out-of-plane hysteresis loop showed a different coercivity suggesting the presence of a texture in the thin film samples. The films with different thicknesses 50, 100, 150, 200 and 300 nm were annealed at 900 °C for 30 min and the coercivities were 6.1 kOe, 5.5 kOe, 500 Oe, 200 Oe and 150 Oe, respectively. The coercivity rapidly declines as the film thickness increases from 100 to 150 nm.

### 3.2. Complex heat treatment

The standard heat treatment for Alnico was also applied to the thin films. The same FCC phase has also been observed with the nanoparticulate microstructure. TEM analysis and magnetic data of this portion of the work will be published elsewhere.

The hysteresis loops of as-made sample and samples annealed at 900 °C followed by 6 h of annealing at 600 °C are shown in Figure 3. As expected, the as-made sample has a negligible coercivity because the α-phase is magnetically soft. The sample after 900 °C annealing showed a large coercivity of 5.6 kOe, five times greater than then the highest coercivity observed in bulk Alnico V. Step in the demagnetization curve can be explained by the wide distribution in grain size. The coercivity of the sample after full heat treatment is 6.7 kOe, seven times larger than bulk Alnico.
4. Conclusions
The crystal structure and magnetic properties of the Alnico-type thin films are drastically different from the bulk alloys. The bulk Alnico alloys after the complex multi-step heat treatment exhibit a coercivity of 720 Oe [12] (up to 2 kOe if Ti is added to the alloys [13]). The coercivity of annealed films is 6.7 kOe, more than seven times larger. The annealed films showed a new phase which can be mostly indexed to a new spinel FCC phase (the possibility of the presence of minority phases cannot be excluded at this time). However, this phase alone cannot explain the high coercivity values because of its low magnetic anisotropy. We are currently examining other possibilities for the origin of the giant hardness, including strain anisotropy caused by the epitaxy between the film and the Si substrate and/or the presence of precipitates of another phase which have not yet been identified. Also the carbon coating (which was used primarily to prevent oxidation) could lead to high coercivity and the formation of the metastable phase through diffusion into the film during the heat treatment.

Acknowledgements
The authors would like to thank A. M. Gabay for helpful discussions. Work supported by NSF DMR-0739624.

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