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SciVerse ScienceDirect
Acta Materialia 61 (2013) 4920–4927
Acta MATERIALIA
www.elsevier.com/locate/actamat

High-coercivity Nd–Fe–B thick films without heavy rare earth additions

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Received 2 September 2012; received in revised form 25 April 2013; accepted 26 April 2013
Available online 31 May 2013

Abstract

The magnetic properties and microstructures of two Nd–Fe–B thick films with different Nd contents have been studied. The films were deposited in the amorphous state and were crystallized by post-deposition annealing. Both films show a strong ⟨001⟩ fibre texture out-of-plane. The film with the higher Nd content has a large room temperature coercivity of 2.7 T, while the one with the lower Nd content has a room temperature coercivity of only 0.7 T. The difference in coercivity may be explained by the fact that the film with the higher Nd content exhibits a continuous Nd-rich grain boundary phase, giving better isolation of the $Nd_2Fe_{14}B$ grains with respect to magnetic exchange interactions. The extrusion of Nd-rich liquid to the top surface of the film with high Nd content during post-deposition annealing led to the formation of ripples in the Ta capping layer, indicating that the films are under compressive stress. This stress-induced flow of the Nd-rich material up through the film explains the excellent distribution of the Nd-rich grain boundary phase. Atom probe tomography has revealed the presence of Cu in the Nd-rich grain boundary phase, explaining the formation of the liquid phase at the relatively low temperature of 550 °C due to the eutectic reaction of Nd and Cu.

Keywords: Hard; Magnets; Coercivity; Thick films

1. Introduction

The demand for high-performance Nd–Fe–B-based magnets is growing because of their use in energy-related technologies such as hybrid and electric cars and gearless wind turbines [1]. In such applications, the magnets are required to operate at temperatures of up to 180 °C. At this temperature the coercive field of Nd–Fe–B magnets is typically below 0.5 T. The classic approach to increase the coercivity of sintered Nd–Fe–B-based magnets has been to replace a fraction of the Nd atoms with heavy rare earth (HRE) atoms such as Dy and/or Tb, with an overall HRE content of typically 4 at.%, so as to increase the magnetocrystalline anisotropy of the main $RE_2Fe_{14}B$ phase. From a scientific and technological point of view, the drawback of this approach is that HRE substitution leads to a decrease in the saturation magnetization of the main phase, since the magnetic moments of HRE elements couple antiparallel to those of iron atoms. Additionally, HREs are much scarcer than light rare earths. As a result, they are much more expensive and there are great concerns over future global supplies.

Much effort has recently gone into developing Nd–Fe–B-based magnets with high values of coercivity but reduced or even zero HRE content. In one approach, controlled diffusion of Dy along the grain boundaries, leading to the formation of a shell of high-anisotropy $(NdDy)_2Fe_{14}B$ at the surface of $Nd_2Fe_{14}B$ grains, has led to increased coercivity with significantly reduced HRE

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http://dx.doi.org/10.1016/j.actamat.2013.04.055

content in both sintered and hydrogenation–disproportionation–desorption–recombination (HDDR) processed magnets [2,3]. The improvement in coercivity achieved by the diffusion process reflects the prevalence for nucleation of reverse domains at the surface of individual grains. In a second approach, applied to both HDDR powders [4] and thin films [5], an increase in coercivity has been achieved in HRE-free magnets through the diffusion of an Nd-containing eutectic (e.g. Nd–Cu, Nd–Ag) into the regions between $Nd_2Fe_{14}B$ grains. In this case, the improvement in coercivity is attributed to a better decoupling of neighbouring grains. A record coercivity value of 3.0 T has been reported for the Nd–Ag diffused thin film samples [5]. In a third approach, coercivity has been increased by reducing the size of monocrystalline powders used to make textured bulk magnets [6]. In this so-called “pressless process”, exposure of the powder to oxygen is minimized to prevent degradation of the surface of individual particles, and coercivity values in excess of 2 T have been reported for HRE-free sintered magnets.

Thick high-performance hard magnetic films have much potential for applications in magnetic microsystems [7]. We previously reported on the influence of deposition temperature on the development of out-of-plane texture [8] and on magnetic interaction domain structures [9] in 5 μm thick Nd–Fe–B films. In this paper we demonstrate that very high coercivity values can be achieved in Nd-rich, HRE-free Nd–Fe–B thick films. Understanding the origin of the high coercivity in these thick films should serve in the development of HRE-free bulk Nd–Fe–B-based magnets.

2. Experimental details

Triode sputtering was used to deposit a Ta/Nd–Fe–B/Ta trilayer on a 525 μm thick Si substrate thermally oxidized to a depth of 100 nm. The magnetic layer was sputtered from a cast target of size 100 mm × 100 mm and of nominal composition $Nd_{16.8}Fe_{74.7}B_{8.5}$, upon which a piece of Nd of approximate size 5 mm × 5 mm was glued. The target was mounted on a Cu backing plate. The trilayer was deposited at 450 °C and then annealed in situ at 750 °C for 10 min. Note that both the film thickness and the composition of the magnetic layer vary across the surface of the substrate owing to a difference in the solid angle of sputtering of the different elements and the relatively large size of the substrate. Here we will compare the magnetic and structural properties of two samples from different regions of the substrate, having significantly different compositions (Nd:Fe ratios of 14.8:85.2 at.% and 19:82 at.%, respectively) and somewhat different values of thickness (Ta (80 nm)/Nd–Fe–B (3 μm)/Ta (80 nm) and (Ta (130 nm)/Nd–Fe–B (4.7 μm)/Ta (130 nm), respectively). The film composition was measured on a comparable film in the as-deposited amorphous state. Magnetic properties were measured at room temperature using a vibrating sample magnetometer and in the temperature range 300–650 K using an extraction magnetometer. The microstructures of the films were studied using scanning electron microscopy (SEM; ZEISS ULTRA plus) and transmission electron microscopy (TEM; FEI T20 operating at 200 kV, FEI $TITAN^3$ 80-300 aberration-corrected microscope operating at 300 kV), both coupled with energy-dispersive X-ray (EDX) analysis and by atom probe tomography (APT) using a laser-assisted three-dimensional atom probe (3DAP). TEM specimens were prepared by the focused ion beam (FIB) method. The needle-like specimens for the APT analysis were prepared by the microsampling technique using a Hitachi FB-2100 FIB and by the annular focused Ga ion beam technique using a Carl Zeiss CrossBeam 1540 EsB.

3. Results

The in-plane (ip) and out-of-plane (oop) hysteresis loops of both samples, measured at room temperature, are compared in Fig. 1a and b. Both films show highly anisotropic magnetic properties, indicating a strong out-of-plane ⟨0 0 1⟩ texture, owing to the choice of substrate temperature during deposition [8,10,11]. Comparing the coercivities in the oop direction, the sample with the lower Nd content is characterized by a relatively low value (0.7 T), while the film with the higher Nd content is characterized by the very high value of 2.7 T. Not surprisingly, the film with the higher Nd content has a lower magnetization (the value of magnetization at 8 T is 1.28 T, compared to 1.4 T of the lower Nd content film). The temperature dependence of the out-of-plane coercive field value of the high-coercivity film, measured in the range 300–650 K, is shown in the inset of Fig. 1b. Note that the relatively high value of 1.1 T was measured at 450 K. Hereafter, the low Nd content sample and the high Nd content sample will be referred to as the low-coercivity film and high-coercivity film, respectively.

While the low-coercivity film is characterized by a highly reflective surface, the high-coercivity film has a non-reflective, somewhat milky appearance. Low-resolution secondary electron plan-view imaging (Fig. 2a) revealed that the high-coercivity film is characterized by a network of distinct surface features (the surface of the low-coercivity film is featureless at this resolution). Note that in the as-deposited state the surface of the entire 100 mm wafer is highly reflective and does not exhibit these surface features, and that sections of the wafer which contain high-coercivity material after annealing lose their shiny aspect during the ramp-up step of the annealing process, at a temperature of about 550 °C. SEM imaging of the upper section of a fracture cross-section (Fig. 2b, secondary electron imaging) and the upper section of a FIB-cut cross-section (Fig. 2c and d, back-scattered electron imaging) revealed that the surface features of the high-coercivity film correspond to protruding features, or bumps, of typical height 2 μm. The thickness of the Ta capping layer is relatively uniform across the film, and the bumps correspond to the formation of ripples in the top Ta layer. The bumps are not always