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Architecture and magnetism of alnico

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Abstract

A rare-earth supply crisis has stimulated an intensive search for alternative permanent magnets. Alnico materials, alloys containing Al, Ni, Co and Fe, are functional nanostructured alloys, which show great potential for replacing the best commercial Nd-based rare-earth alloys for applications above 200 °C. However, their coercivity is ~2–3× below theoretical limits. The coercivity of alnico depends on the nanostructure developed during spinodal decomposition. In this work, atom probe tomography, combined with advanced electron microcopy, indicate that the microstructure of alnico is sensitive to the introduction of alloying elements such as Ti and Cu, as well as the crystallographic orientation of the parent phase with respect to the direction of the imposed magnetic field during spinodal decomposition. The alnico coercivity mechanism involves interplay of size, chemistry and possibly stress at interfaces. Control of these parameters should allow reduction of the spatial dimension of the FeCo-rich precipitates and the interaction between them, which should in term increase the coercivity of alnico alloys.

Keywords: Magnetic, Microstructure; Spinodal decomposition; Atom-probe tomography; TEM

1. Introduction

Neodymium-based permanent magnets (PMs) are widely used for microphones, motors, wind generators and hybrid-car traction drive motors [1,2]. However, in order to be able to operate at temperatures above 180 °C, which are typical for most traction motors utilized in electric vehicles, these PMs require significant additions of dysprosium (Dy). Driven by high costs, supply chain disruptions and inadequate Dy resources, there has been significant interest in finding alternatives to current Nd-based PMs [1,2]. For demanding high-temperature applications, such as traction motors [1], the temperature performance of the magnetic alloy in terms of magnetization in zero field, referred to as the residual induction (B_r), its resistance to a demagnetizing field, characterized by intrinsic coercivity (H_{ci}), and maximum energy (BH_{max}), set the design parameters for devices which utilize the material.

Alnico, alloys of Fe with Al, Ni and Co, are among the oldest manufactured functional nanostructured materials and represent a possible near-term replacement for Nd-based PMs, given their lower cost and nearly flat temperature dependence of magnetic properties up to 400 °C [1].

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Developed between 1930 and 1970 [3–7], this class of PMs takes advantage of the spinodal decomposition of the alloy into a magnetic Fe–Co-rich (α_1) phase and an Al–Ni-rich (α_2) phase during cooling. Unlike most of the rare-earth-based magnetic alloys, the development of alnico alloys occurred prior to the advent of many modern analytical tools. Much of the prior characterization work defined the general nanoscale features [8–14], but failed to identify the detailed atomic-scale differences in the phase assemblages of the various grades of alnico alloys, and salient features that gave rise to control of the magnetic properties. Current commercial alloys contain a number of minor alloy additives and receive a complex heat treatment arising from ad hoc optimization over the years. For example, thermal annealing is performed within the spinodal region in the presence of a magnetic field, and the resulting duplex nanoscale structure of the α_1 phase is elongated along the applied field direction [3]. The anisotropic growth of the α_1 phase gives rise to the anisotropic hysteretic response to an applied magnetic field characteristic of aligned PMs. This effect, termed shape anisotropy, is fairly weak compared to magnetocrystalline anisotropy, which is responsible for the higher BH_{max} observed in high-end commercial rare-earth-based PMs [15]. In this paper, we demonstrate how changes in chemistry and processing give rise to distinctly different nanoscale structures, which are crucial for understanding differences in magnetic properties, especially remanence and coercivity. Insights provided by modern computational tools provide potential optimization pathways to both chemistry and processing to bring these alloys closer to their theoretical potential.

2. Experimental procedure

Using a suite of techniques with resolutions ranging from the atomic to the micron scale, we have investigated three commercial optimized alnico alloys, 5–7, 8 and 9, supplied by Arnold Magnetic Technologies Corp (Table 1). The highest Fe content alnico 5–7 has the highest B_r (13.5 kG), but the lowest H_{ci} (740Oe). The highest Co content alnico 8 has the lowest B_r (7.4 kG) and the highest H_{ci} (1900 Oe). Alnico 9 has the highest energy product of ~10.5 MOe with B_r (11.2 kG) and H_{ci} (1375 Oe) in between the other two alloys (Table 1). Alnico 5–7 and 9 are grain-aligned alloys with most grains aligned along the [0 0 1] direction, produced by casting into a heated mold with a chilled bottom plate (Fig. 1a and c). Alnico 8 (Fig. 1b) is crystallographically isotropic and produced by casting without any imposed temperature gradient. The cast alloys are heat-treated at about 1250 °C to fully solutionize the alloy, then air-cooled to ~800 °C. Alnico 5–7 and 9 are isothermally annealed at ~800 °C with an applied magnetic field along their casting direction, whereas the field was applied along the cylinder axis for alnico 8. Depending on the magnet grade, the alloys undergo an extended "draw" cycle with slow cooling and holding at temperatures of ~640 °C.

Table 1
Commercial alnico alloy composition.

	Composition (wt.%)							B_r	H_{ci}
Samples	Fe	Co	Ni	Al	Cu	Nb	Ti	(kG)	(Oe)
5–7	49.9	24.3	14.0	8.2	2.3	1.0	0.0	13.5	740
8	30.0	40.1	13.0	7.1	3.0	0.0	6.5	7.4	1900
9	35.5	35.4	13.1	7.0	3.2	0.5	5.0	11.2	1375

Atom probe tomography (APT) was performed with a LEAP 4000X HR in voltage-pulsed mode on samples prepared using a FEI Nova 200 dual-beam focused ion beam (FIB) system. Samples were extracted from interior of grains (polished transverse sections) by a standard lift-out technique [16] so as to provide multiple interphase interfaces along the sample axis. Samples of the appropriate orientation were first located on the polished transverse sections using electron backscattered diffraction imaging, also known as OIM, with an EDAX GENESIS system on an Amray 1845 field emission scanning electron microscope. Two or three samples were characterized for each composition.

Transmission electron microscopy (TEM) analysis was performed on transverse (observation along the magnetic field direction during annealing) as well as longitudinal (observation perpendicular to the magnetic field direction during annealing) orientations. TEM samples with a 1 mm long and 1 μm wide electron-transparent region were prepared by mechanical wedge-polishing followed by a short duration, low-voltage Ar ion-milling in a liquid-nitrogen cold stage. An FEI Titan G2 80-200 scanning transmission electron microscope with Cs probe corrector and ChemiSTEM™ technology, and an FEI Tecnai F20 (200 kV, field emission gun) with a Lorentz lens and biprism were used for microstructural characterization. Lorentz microscopy is a widely used TEM technique for direct observation of magnetic domain structure with high spatial resolution [17]. Domains are revealed as lines of light and dark contrast as a result of deflection of the electron beam by a magnetic field inside the TEM sample [17]. Electron holography is a unique nanoscale phase-imaging TEM technique for acquiring electrostatic and magnetic field information. Quantitative field measurements can be achieved by relating the relative phase shift of the electron wave that has passed through the TEM sample with that of a wave which has passed through a vacuum. In-plane magnetic induction maps of the material can be extracted [18,19].

3. Results

3.1. Microstructure overview

The morphology of these three alloys can be observed by orientation imaging microscopy (OIM), as OIM images reveal both grain size and orientation. Inverse [0 0 1] pole figure maps of alnico 5–7, 8 and 9 along their transverse