Contents lists available at ScienceDirect

Scripta Materialia

In-situ high-temperature domain structures of die-upset Nd–Fe–B magnets

Yikun Fang [a,b,*], Xiaolu Yin [a], Ralph Skomski [a], Hongsheng Cheng [b], Kuikui Song [b], Minggang Zhu [b], Zhaohui Guo [b], Wei Li [b], Sy-Hwang Liou [a]

[a] *Department of Physics and Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska–Lincoln, Lincoln, NE 68588, USA*
[b] *Division of Functional Materials Research, Central Iron and Steel Research Institute, Beijing 100081, China*

ARTICLE INFO

ABSTRACT

Magnetic domains of a die-upset Nd–Fe–B magnet with an energy product of about 50 MGOe are investigated by using *in-situ* magnetic force microscopy (MFM), varying temperature from room temperature to 240 °C. For both as-prepared and magnetized Nd–Fe–B samples, the domain-pattern evolution during thermal demagnetization is monitored by MFM. The temperature dependence of the evolution of reverse domains is explained by micromagnetic models. At all temperatures, the magnetization reversal in the technological relevant magnetized limit proceeds by nucleation.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

The large demand for hybrid electric vehicles and wind turbines for electricity generation has led to renewed interest in the development of Nd–Fe–B magnets, particularly concerning their performance at elevated temperatures ($T > 150$ °C) [1]. The understanding of the temperature dependence of domain structures in $Nd_2Fe_{14}B$ is of great importance, because $Nd_2Fe_{14}B$ has a relatively low Curie temperature ($T_c = 312$ °C). The magnetocrystalline anisotropy decreases rapidly as the temperature approaches T_c [2], accompanied by a reduction in coercivity and by changes in domain structure and reversal mechanism. It is great of interest to investigate the high temperature domain structures in these materials from both fundamental research and practical application points of views.

To fully exploit the potential of $Nd_2Fe_{14}B$ [3–6], it is necessary to have the magnetic grain *c*-axis aligned. One method of achieving this goal is die-upsetting, where the *c*-axis of the grains is stress-induced and parallel to the press direction [7–11] and where the texture formation is caused by preferential grain growth via dissolution and precipitation [12–14].

Previous studies of the die-upset Nd–Fe–B have shown that the magnetic domains at room temperature, referred to as interaction domains, are much larger than the grain size [15–17], because the grains are coupled due to intergranular exchange. The grains included in the interaction domain are almost in single-domain because their size (50–400 nm) is comparable to the single domain grain size for $Nd_2Fe_{14}B$ [18].

Many high-performance permanent magnets, for example in motors, operate above room temperature. It is therefore desirable to directly observe domain structures at elevated temperatures, rather than making indirect conclusions, for example from hysteresis loops. Magnetic force microscopy (MFM), a surface technique, has been widely used to reveal the magnetic domains of bulk permanent materials [17,19–24]. Surprisingly, it has not been possible so far to record *in-situ* MFM images of die-upset Nd–Fe–B magnet above room temperature. In this paper, we directly monitor the magnetic domains of a bulk die-upset Nd–Fe–B magnet at elevated temperature.

The die-upset Nd–Fe–B magnets were prepared by using hot compaction and subsequent hot deformation. Melt-spun powder of $Nd_{13.62}Fe_{75.70}Co_{4.45}B_{5.76}Ga_{0.47}$ was hot-pressed in vacuum at 550 °C and 113 MPa to obtain pieces of fully dense isotropic precursors. The precursors were hot-deformed in argon at temperatures from 600 to 900 °C, to achieve a height reduction of 70%. Cylindrical samples approximately 6 mm in diameter and 4 mm in height were cut from the center of die-upset magnets, and then their magnetic properties were measured parallel to the loading direction at room temperature, using a hysteresograph. The microstructure of the magnets was studied by field-emission scanning-electron microscopy (SEM), and the crystal structure of the magnets was investigated by X-ray diffraction (XRD) with Cu K_α radiation. The temperature dependence of saturation magnetization of the samples was measured by vibrating sample

---

* Corresponding author at: Division of Functional Materials Research, Central Iron and Steel Research Institute, Beijing 100081, China.
E-mail addresses: ykfang@126.com, ykfang@cisri.com.cn (Y. Fang).

magnetometry (VSM) in a magnetic field of 30 kOe. The samples for the MFM experiments are cubes of approximately $4 \times 4 \times 4$ mm³ taken from central region close to that used for the magnetic measurements. One surface of each of the cubes, with the surface normal in the same direction as the loading direction, was polished with standard metallographic polished techniques using a water-free lubricant.

Fig. 1(a) shows the demagnetizing curve in the second quadrant of the hysteresis loop. The remanence B_r, intrinsic coercivity H_{cj}, and maximum energy product $(BH)_{max}$ are 14.2 kGs, 12.9 kOe, and 50 MGOe, respectively. This energy product equals the previous energy-product record for die-upset Nd–Fe–B, achieved by Saito et al. [10] and Liu et al. [11]. The inset in Fig. 1(a) is the XRD pattern of the die-upset Nd–Fe–B along the loading direction. Reflections such as (006), (105), (004) and (008) become dominate and the relative intensity ratio of (006)/(105) is about 1.86, indicating a strong c-axis crystallographic alignment in the magnets. The microstructure of the sample perpendicular to the loading direction [Fig. 1(b)] consists of elongated nanocrystalline grains with their length perpendicular to the loading direction. Their width and length are about 60 and 400 nm, respectively. The strong c-axis alignment and the fairly regular microstructure are one of the reasons for the excellent magnetic properties of the magnet.

To image the magnetic domains of the samples, we have used a Digital Instruments EnviroScope MFM operating in the tapping/lift mode and equipped with a downwards-magnetized highly coercive Fe–Pt tip [23]. The sample stage of the EnviroScope MFM consists of a thermoelectric unit capable of varying the stage temperature T from room temperature (~23 °C) to about 300 °C. The MFM chamber was pumped down to about 6.7×10^{-3} Pa to avoid the oxidation of the sample.

In our experiments, we found that the magnetization direction and magnitude of the MFM tips is not significantly changed below 200 °C. Therefore, we carried on our in-situ MFM experiments only below 200 °C. For higher temperatures, between 200 and 300 °C, the sample was first heated to the corresponding temperature and then cooled down to 180 °C and the MFM images were captured at the same scan area. All MFM images were obtained by

the same tip with a lift-height of 50 nm. The average domain width was measured using the stereological method proposed by Bodenberger and Hubert [25,26].

We have captured in-situ MFM images of the as-prepared (thermal demagnetized) die-upset Nd–Fe–B permanent magnet at room temperature and at 180 °C in zero applied magnetic field (see Fig. 2). The as-prepared sample is almost in a virgin state (thermal demagnetized). The two images are taken by the same tip and for almost the same area. The root-mean-square values of the phase shift, ϕ_{rms}, of the Fig. 2(a) and (b) are about 12.0° and 6.25°, respectively. The domain patterns between room temperature and 180 °C are exactly same as those of regular maze pattern, but show weaker contrast at higher temperature. The average domain width (w) remains 530 nm, which is much larger than the grain size. Consequently, many grains participate in the formation of an interaction domain in which the grains exhibit the similar orientation of magnetization. The weaker contrast is probably due to the decreased magnetization of magnet and MFM tip at high temperature.

The domain pattern reflects the competition between magnetostatic energy and domain wall energy. As assuming the reverse domain is conical with height of h and radius of b, the corresponding energy gain (E) on domain formation is as follows:

$$E = -\frac{1}{3}\pi b^2 h \mu_0 M_s^2 + \pi\gamma b\left(\sqrt{b^2 + h^2}\right) \tag{1}$$

The first term represents magnetostatic energy with M_s (the saturation magnetization), and the second term represents domain wall energy with γ (the domain wall energy density). The relation between b and h is obtained by minimizing the energy with respect to b, $\partial E/\partial b = 0$. This yields $b = \sqrt{6}\pi\gamma/\mu_0 M_s^2$, which means the corresponding domain size is as large as $2b = 214$ nm. The calculated domain size is significantly smaller than the MFM domain size (Fig. 2), which greatly depends on the real structure and sample history. One example is the fully magnetized state, where the domain size should approach infinity. This is because domain size is, by definition, an equilibrium property. In non-equilibrium, states with much larger domain size can be stabilized by micromagnetic energy barriers. The height of the energy barriers is largely determined by the magnetocrystalline anisotropy K_1. Other considerations in explaining the larger actual domain size are the underestimation of the magnetostatic self-interaction in the calculation and the formation of branch domains [26].

In order to investigate the high-temperature domain structures, we studied the sample in the remanent state, which was obtained by magnetizing the as-prepared sample to a field of 70 kOe along the loading direction (easy axis) and then gradual reducing to zero magnetic field. Fig. 3(a–f) show the domain patterns of the magnetized die-upset Nd–Fe–B bulk sample at different temperatures. These in-situ magnetic domain images were captured at the same area. As shown in Fig. 3(a), the magnetization of the sample is nearly fully aligned, so it is virtually free of domains at room temperature. With increasing the temperature, the reverse domains start to show up at 80 °C with size ranging about 1 μm, and then grow and spread throughout the sample. The facilitated nucleation of reverse domains is probably caused by the rapid weakening of magnetocystalline anisotropy in the magnet, especially at the grain boundaries. For the same reason, the feature size of the reverse domain become slender as the temperature increases. The width of the reverse domains shrinks from 1 μm (at 80 °C) to 400 nm (from 160 to 240 °C). Note that the direct creation of magnetic domain by thermal activation is extremely unlikely, because K_1V is huge, even at elevated temperatures, where K_1 is relatively small.

The magnetized state is quite different from the as-prepared (thermal demagnetized) state. The large positive magnetic field
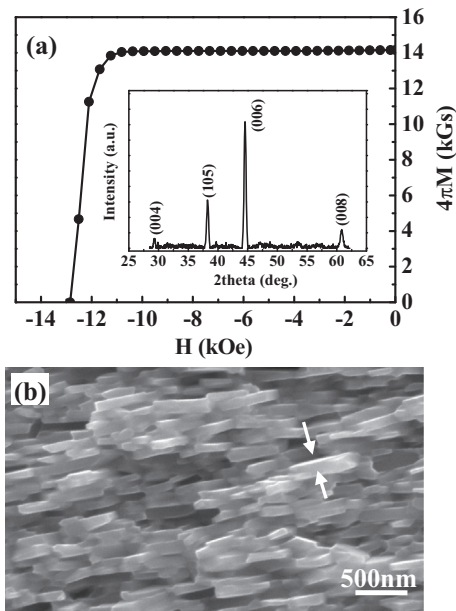

Fig. 1. Die-upset Nd–Fe–B sample: (a) demagnetization curve at room temperature and (b) SEM image along the loading direction (marked by arrows). The inset in (a) is the XRD pattern of the sample.