Physica B 407 (2012) 3291–3294

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Microstructure and hard magnetic properties in bulk rods of $Nd_{60}Fe_{30}Al_{10}$ glass forming alloys

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ARTICLE INFO

Available online 17 December 2011

Keywords:
Bulk glassy alloys
Hard magnetic
Strong wall pinning

ABSTRACT

The $Nd_{60}Fe_{30}Al_{10}$ alloy exhibits a large glass forming ability which allows to obtain relatively thick cast rods containing large volume fractions of amorphous phases. In this work the microstructure and the hard magnetic properties of as-cast rods are characterized. The alloy is processed by suction casting into a chilled copper mould to obtain cylinders 5 mm diameter and 50 mm length. This diameter is selected because it is an upper limit for this processing route, beyond which the hard properties largely deteriorate. A room temperature coercivity of 0.34 T is obtained. The sample microstructure is heterogeneous, with very different size scales near the surface and along the central zone. However, in both regions a large fraction of an amorphous ferromagnetic phase is observed; it is found that paramagnetic nanocrystalline phases – mainly Nd or Nd-rich particles, embedded in the amorphous matrix – are somewhat coarser in the central zone. These larger nanocrystals, less efficient to pin domain walls, are proposed to be responsible for the lower coercive fields observed, as compared with those found in cylinders 1–3 mm diameter where no inhomogeneities are found. This conclusion is supported by microstructure, calorimetric and magnetic observations.

1. Introduction

Bulk metallic glassy alloys can be vitrified into a completely amorphous state from liquid, at cooling rates near 10 K/s or slower. In 1996 Inoue [1] first reported appreciable room temperature coercivities ($\sim$0.4 T) in as cast bulk rods (1–12 mm diameter) of $Nd_{60}Fe_{30}Al_{10}$ magnetic alloys. The hard magnetic properties are observed for a relatively wide range of sample thickness (150 μm–5 mm [2]) but they decline in thinner ribbons, melt spun at higher cooling rates and also in thicker chilled mould cast rods. In cylinders processed by suction casting into a chilled copper mould a limit diameter is generally found at 5 mm; beyond this thickness the bulky rods become magnetically softer, and coercivity largely decreases, as shown in Fig. 1 [2–4].

The microstructure of the as cast $Nd_{60}Fe_{30}Al_{10}$ rods is known to consist of large (micrometric) dendrite like particles of dhcp Nd surrounded by a composite matrix, containing crystalline Nd-rich phases embedded in a Fe-rich amorphous phase [5,6]. These Nd-rich crystals are generally identified as particles of the equilibrium δ phase [7].

These three microstructure elements, the dhcp Nd crystals, the δ-type particles and the Fe rich amorphous matrix, are also found in ribbons melt spun at wheel speeds, up to 30 m/s [8,9], being the only difference the particle sizes and the relative volume and composition of the amorphous phase. As the crystalline phases detected are all paramagnetic at room temperature it is concluded that the hard magnetic properties arise in the composite matrix, containing the amorphous phase. For the entire range of cooling rates investigated [5,6,8], the coercivity is proposed to be controlled by the strong pinning of domain walls in the ferromagnetic amorphous phase, by nanocrystals of the Nd-rich (δ-type) phase.

In this work we investigate the microstructure of a 5 mm diameter cylinder obtained by suction casting, and its relationship with the reduced coercivity observed.

2. Experimental procedures

$Nd_{60}Fe_{30}Al_{10}$ alloys were prepared by induction melting of the pure elements on a water-cooled copper boat, under a Zr-gettered argon atmosphere. The melt alloy was then cast by suction into water chilled Cu moulds of 50 mm length and diameters between 1 mm (C1) and 5 mm (C5). X-ray diffraction profiles were recorded in a Philips PW 3830 diffractometer, operated in

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doi:10.1016/j.physb.2011.12.090

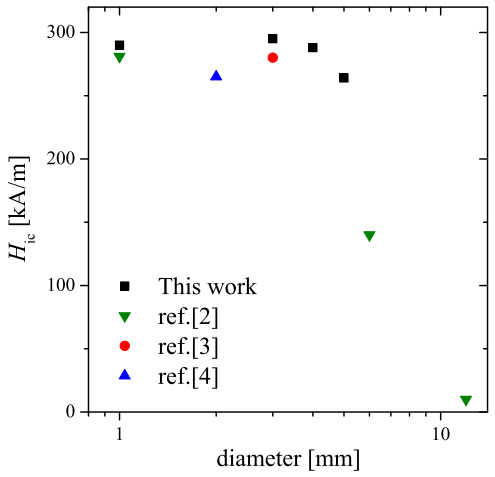

Fig. 1. Room temperature coercive field as a function of the sample diameter, for suction cast $Nd_{60}Fe_{30}Al_{10}$ alloys.

Bragg-Brentano geometry, with Cu K_α radiation ($\lambda = 1.5418$ Å). Samples for scanning electron microscopy (SEM) were etched for 10 s at 293 K in a solution of 0.5 vol% of hydrofluoric acid in distilled water. For transmission electron microscopy, samples were mechanically thinned and ion milled. Measurements were performed in a Philips CM200UT TEM operating at 200 kV. Magnetic measurements were performed at room temperature, in a Vibrating Sample Magnetometer with applied field up to 1.5 T. Conventional magnetic viscosity experiments were also conducted [10] to estimate the mean fluctuations field $\mu_0 H_F$ and the apparent activation volume V_{ac} corresponding to the magnetization switching mechanism operating in each microstructure. The viscosity values S were estimated by fitting the expression $M(t) = S \ln(t/t_0)$ to the magnetization time decay, under constant applied field.

3. Results and discussion

The X-ray diffraction patterns corresponding to samples C1 and C5 are shown in Fig. 2; the maxima are indexed as arising in dhcp Nd and in the δ-type $Nd_6Fe_{13-x}Al_{1+x}$ phase [11]. These results indicate that, in both samples, the ferromagnetic phase is either amorphous or it has crystal sizes below the detection limit of X-rays (about 8 nm). Fig. 3 shows the continuous differential thermal analysis (DTA) curves corresponding to C1 and C5 rods, both in the as cast state; the endothermic contributions observed between 500 K and 720 K, attributed to relaxation or pre-precipitation effects in the amorphous phase [12] are still detected in C5 and they only disappear after 5 h at 823 K (C5TT). These results confirm that an appreciable amount of amorphous phase is still present in C5 as cast rods.

The hysteresis loops corresponding to samples C1 and C5 are displayed in Fig. 4. A clear single magnetic phase is found for the rod with smaller diameter, while for sample C5 an incipient biphasic behavior is observed, largely reducing the maximum energy product (see Table 1). The smaller coercivity of C5 is accompanied by a slight reduction in the saturation polarization. The hard magnetic properties and the thermal relaxation parameters corresponding to the samples investigated are listed in Table 1. The microstructure of sample C5 at different size scales is shown in Fig. 5. The SEM image of a transversal section – Fig. 5a – shows that these samples are not homogeneous; the peripheral region (A) near the external surface (mean depth of about 70 μm) shows a quite uniform contrast while the central zone (B) exhibits

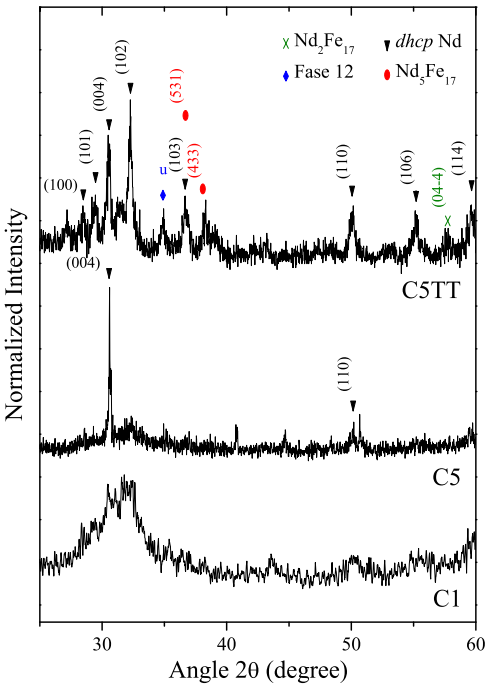

Fig. 2. X-ray diffraction patterns of samples C1 and C5 in the as cast condition. The peaks correspond to hcpNd and to the δ-type $Nd_6Fe_{13-x}Al_{1+x}$ phases [11].

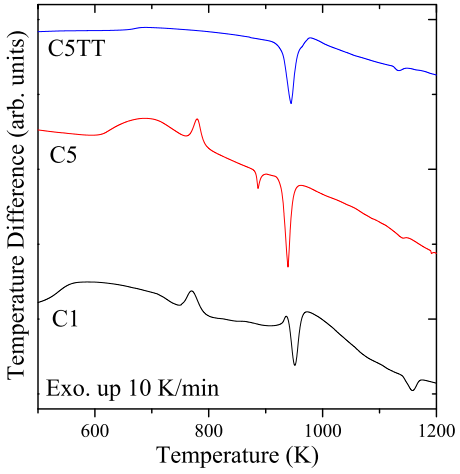

Fig. 3. DTA curves corresponding to samples C1 and C5, showing relaxation and pre-precipitation effects between 500 K and 750 K. These effects are absent in C5TT.

a typical eutectic-like morphology. This nonuniform microstructure is not observed in ribbons nor in rods with diameters below 5 mm. The crystalline phases in this eutectic-like structure are mainly dhcp Nd and some dendrite particles of the equilibrium δ phase. Even when a relatively large volume of this ferromagnetic eutectic-like structure (about 94 vol%) is found in samples C5, no drastic changes in the hard magnetic properties are observed. This suggests that the microstructure promoting the strong domain wall pinning is still present in the central coarse microstructure. Fig. 5b shows a TEM micrograph corresponding to the central eutectic-like phase. This region contains Nd and Nd-rich (likely δ-type phase) crystalline precipitates in contact with large portions of "amorphous" matrix. When these amorphous zones are closely observed, Fig. 5c and d, it is found that they actually are a nanocomposite, constituted of quite small Nd-rich crystals

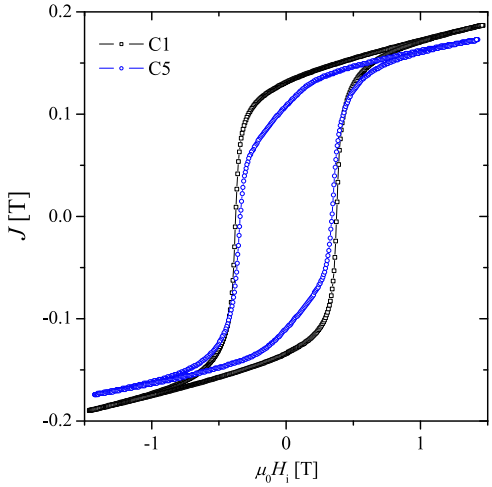

Fig. 4. Room temperature hysteresis loops of samples C1, a single magnetic phase, and C5 exhibiting an incipient two-phase character.

Table 1
The room temperature hysteresis parameters, the coercive field $\mu_0 H_c$, the saturation magnetization J_s and the remanent magnetization J_r of the samples investigated. Also shown are the maximum energy product $(BH)_{max}$, the mean fluctuations field $\mu_0 H_F$ and the apparent activation length $V_{ac}^{1/3}$.

Sample	C1	C5
$\mu_0 H_c$ (mT)	370.5	332
J_s (mT)	186.8	173.2
J_r (mT)	131.6	108.6
$(BH)_{max}$ (kJ/m^3)	3.23 ± 0.02	2.04 ± 0.02
$\mu_0 H_F$ (mT)	14.4	11.8
$V_{ac}^{1/3}$ (nm)	7.3	8

immersed in an amorphous phase. Similar microstructure ingredients have been reported in melt spun ribbons of the same composition [5,8,9] but with smaller sizes. For example, Nd-rich clusters of 1–3 nm in size [9] in samples melt spun at 25 m/s.

In the present case, the mean size of these paramagnetic crystallites is above 5 nm, indicating that the particles acting as domain wall pinning centers are coarser. The amorphous matrix between crystallites often shows a band contrast, with a period of about 1.5 ± 0.1 nm. The origin of this contrast is unclear; a similar band contrast is exhibited by the μ phase for an orientation perpendicular to the basal plane. This μ phase is reported to be a polytypism with 12R type stacking sequence of hexagonal cells with parameters $a = 1.65$ nm and $c^* = 1.25$ nm, leading to a primitive vector $c = 12 \times 1.25 = 15$ nm [13].

4. Conclusion

The temperature and hard magnetic properties of bulk $Nd_{60}Fe_{30}Al_{10}$ rods of 5 mm diameter are examined and compared with those associated to thinner rods, 1 mm diameter, which shows the optimal energy product $(BH)_{max}$. Up to 4 mm diameter the rod microstructures are uniform; for 5 mm diameter rods two zones, with different size scales appear. The peripheral region, near the external surface, exhibits a quite uniform contrast at medium magnification, similar to that found in ribbons and thinner rods. On contrary, the central zone shows a coarse, eutectic-like structure. In this central region, it is observed that paramagnetic nanocrystalline phases – mainly Nd or Nd-rich crystalline phases embedded in the amorphous phase – are somewhat larger. These bigger and more dispersed nanocrystals, less efficient to pin domain walls, are proposed to be responsible for the lower coercive fields observed.

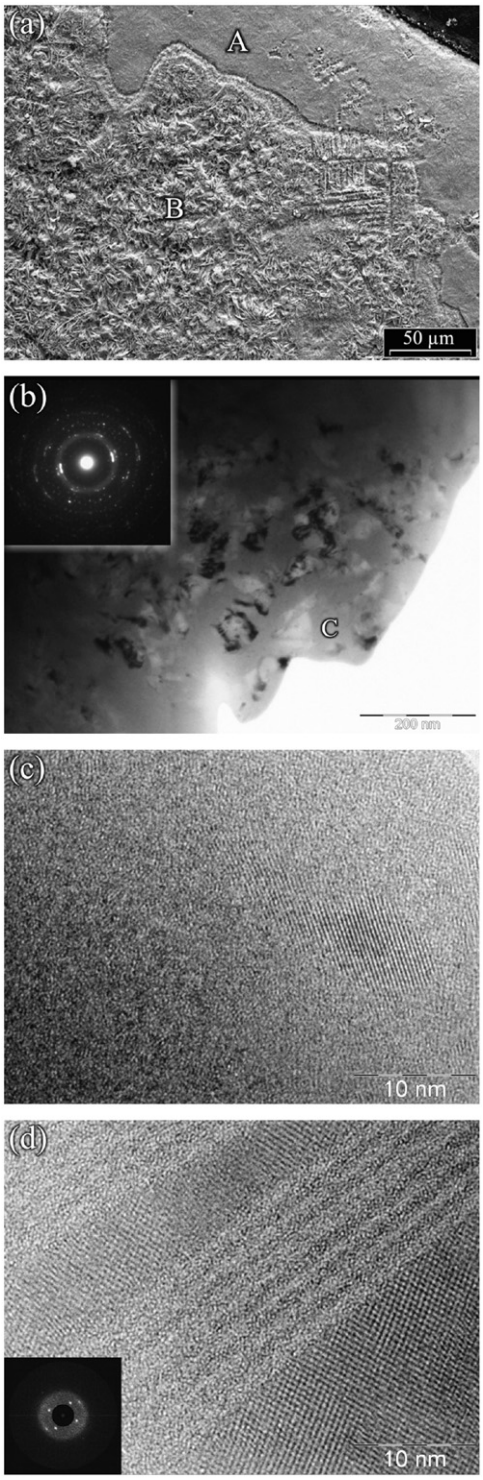

Fig. 5. The microstructure of sample C5 in the as cast condition. (a) SEM micrograph showing the two distinct regions: the peripheral one (A), with a uniform contrast and the central zone (B) with a eutectic-like contrast. (b) Bright field TEM image of zone B, showing crystalline Nd and δ-type plates surrounded by an apparent "amorphous" matrix C. (c) The "amorphous matrix" is actually a composite, with crystalline Nd-rich particles (pinning points) embedded in an amorphous phase. (d) The amorphous exhibits a band contrast of period 1.5 ± 0.1 nm.

Acknowledgment

The authors thank Dr. Alfredo Tolley for helping with TEM results.

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