Annealing effect on microstructure and coercivity of YCo$_5$ nanoparticles obtained by mechanical milling

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Abstract

Nanocrystalline YCo$_5$ powders with high coercivity were prepared by mechanical milling and subsequent heat treatment at 820 °C for different annealing times, $t_a = 2.5, 3.0, 3.5$ and 4.5 min, obtaining average crystallite sizes of $<D> \sim 17, 19, 32$ and 39 nm., respectively. The coercivity values were determined from the hysteresis loops measured at maxima fields of $H_m = 5$ and 20 T. The highest coercivity was obtained for the sample exhibiting $<D> \sim 19$ nm, where at room temperature and $H_m = 5$ T, the coercivity value is of 9.0 kOe. At 77 K and $H_m = 5$ T, the coercivity increase to 11.8 kOe and for $H_m = 20$ T, a higher value such as 13.1 kOe was found. The $M_s/M_r$ ratio is enhanced to 0.62 indicating the occurrence of exchange interaction among nanocrystalline magnets.

Introduction

Nanocrystalline materials have an important role in the area of new soft- and hard- magnetic materials. They exhibit improved magnetic properties, which are interesting both from a basic understanding of magnetism as well as from a commercial point of view [1-4]. One aspect has been considered that the basic to understand magnetic properties is the relation between the microstructure (average crystallite size) and the coercivity [5]. It is well known that crystallite size is the fundamental extrinsic property that controls the coercivity, and generally can reach a high value for materials that exhibit high magnetocrystalline anisotropy [2,3]. This is
very interesting subject to study nanostructured hard magnet systems such as YCo$_5$ that exhibits high magnetocrystalline anisotropy $K_1 \sim 5.5 \times 10^7$ erg/cm$^3$, high crystal anisotropy field $H_A \sim 130$ kOe and moderate strength magnetization $4\pi M_s = 10.6$ kG [5]. Recently, Tang et al. [6] synthesized nanograin YCo$_5$ exhibiting high coercive field such as $H_c \sim 10$ kOe and grain size $\sim 30$ nm. Later, Sánchez et al. [7] produced YCo$_5$ nanoparticles with $<D>\sim 12$ nm with $H_c \sim 7.23$ kOe. However, in these previous works, the maximum applied field to obtain the coercive field was 5 T, much below the anisotropy field. In this work, we produced YCo$_5$ nanoparticles by mechanical milling of as-cast alloys and subsequently heat treatments at different annealing temperatures to investigate magnetic properties on these annealed samples measuring hysteresis loops applying magnetic field up to 20 T. The microstructure of nanostructured powders was investigated by means of X-ray diffraction and transmission electron microscopy.
Experimental procedure

Alloys with composition YCo₅ were prepared by arc melting pure elements in an Ar atmosphere; a 4% of Yttrium's weight was added to compensate losses during melting. The starting materials were Y and Co ingots with purity of 99.9% and 99.8%, respectively. The materials were re-melted 4 times to ensure homogeneity. The as-cast YCo₅ ingots were then coarsely pulverized and the obtained powders were mechanical milled by 4 h. The milling was carried out under argon atmosphere using a SPEX 8000 ball mill with a ratio of powders to ball of 1:8, obtaining amorphous powders. To obtain different average crystallite sizes, <D>, the as-milled amorphous powder were annealed at 820 °C for different annealing times (tₐ = 2.5, 3.0, 3.5 and 4.5 min) in high vacuum vycor tube followed by quenching in water. For the microstructure investigations, X-ray diffraction (XRD) patterns were recorded using an automated Philips diffractometer with Co radiation (λ = 1.789 Å), and microstructure images were carried out with a Philips CM200 transmission electron microscopy in dark field mode. Magnetic hysteresis loops were measured at room temperature and - 196 °C by using a pulsed field magnetometer applying a magnetic field up to 20 T.

Results and Discussion

Fig. 1(a), 1(b), 1(c) and 1(d) shows the X-ray diffraction patterns obtained for mechanical milled YCo₅ powders annealed at 820 °C for tₐ = 2.5, 3.0, 3.5 and 4.5 min, respectively. The main phase of all samples is YCo₅ phase; however XRD patterns shows also additional small lines (in Fig. 1 these lines are indicated by *) corresponding to Y₂Co₁₇ phase decomposed from YCo₅ phase. All peaks of YCo₅
phase correspond to hexagonal CaCu$_5$-type structure (PDF #17-078) and those of Y$_2$Co$_{17}$ phase can be indexed with the rhombohedral Th$_2$Zn$_{17}$-type structure (PDF #18-434). The broadening of the peaks indicates that the samples are constituted by fine particles. It is worth to note that the YCo$_5$ as-produced by mechanical milled is in amorphous phase at room temperature [7] and nanocrystalline powder is formed by subsequently annealing. Like all other RCo$_5$ compounds, during the annealing YCo$_5$ can decompose into to Y$_2$Co$_{17}$ phase [4].

Fig. 1. Powder X-ray diffraction patterns of mechanical milled YCo$_5$ nanostructured powders as a function of annealing time $t_a$: a) 2.5; b) 3.0; c) 3.5; d) 4.5 min.

XRD lines broadening analysis was performed using the Williamson-Hall plot. Different from the Scherrer’s formula [8], the Williamson-Hall method allows separating the contribution of the strain from the grain size [6]. Fig. 2 shows the Williamson-Hall plot, $(\delta 2\theta/\tan \theta)^2$ vs $\delta 2\theta/(\tan \theta \sin \theta)$ plot, where $\delta 2\theta$ is the full width half maximum and $\theta$ is the Bragg angle for the peak, obtained for YCo$_5$ ($t_a = 2.5$ min.) sample. An almost linear behavior was found, which behavior is also
observed for other three samples. The $<D>$ and micro-strains $\sigma$ values were determined by fitting the experimental data to the linear \((\delta \theta / \tan \theta)^2\) vs. \(\delta \theta / (\tan \theta \sin \theta)\) plot [9]. The determined $<D>$ and $\sigma$ values are shown in Table 1. As can be seen, $<D>$ increases from 17 up to 39 nm when the annealing time increases from 2.5 up to 4.5 min while a contrary effect is observed for $\sigma$ magnitude. This result is expected because, generally, $<D>$ increment is accompanied with a strain diminution [4].

Fig. 2. Plot of \((\delta \theta / \tan \theta)^2\) vs \(\delta \theta / (\tan \theta \sin \theta)\) for YCo5 powders obtained after mechanical milling for 4 h and subsequently annealed at 820 °C for 2.5 min.

Fig. 3 shows a characteristic dark field mode micrograph of nanostructured YCo5 powder annealed at 820 °C for 3.5 min. From this technique an average grain size of 32 nm was determined, which value is in excellent agreement with $<D>$ value determined from Williamson-Hall Plot.
The hysteresis loop of YCo$_5$ powders milled for 4 h and subsequently annealed at 820 °C for $t_a = 2.5$ min is shown in fig. 4. The magnetization as function of the applied field was measured at -196 °C with a maximum field, $H_m$, of 20 T. The inset shows the loop obtained at -196 °C with field up to 5 T. Similar loops were found for room temperature measurements. The shape of this loop is the typical hysteresis loops found in this work, showing a slight deformation from the square demagnetization curve due to presence of Y$_2$Co$_{17}$. As can be seen, the samples were not magnetically saturated at field of 5 T. The $H_c$ and maximum magnetization, $M_m$, continue increasing with increase of the applied field showing then the difficulty to align the sample magnetic moment in a field due to these particles exhibit very high anisotropy field. At -196 °C, the sample with $<D> \sim 19$ nm has a saturation magnetization ($M_s$) of 110 emu/g, a remanence ($M_r$) of 67 emu/g, a $M_r/M_s$
A ratio of 0.62, a coercivity of 13.1 kOe. These values are very high for YCo$_5$ magnets. At room temperature, our results are very similar to those reported in [6]. The $M_r/M_s$ ratio shows an enhancement indicating the existence of intergrain exchange interactions among these fine particles [1,2].

Fig. 4. Hysteresis loops of YCo$_5$ powders milled for 4 h annealed at 820 °C for 2.5 min measured with maximum field of 20 T at temperature of -196 °C. The inset shows the loop obtained at -196 °C with maximum applied field of 5 T.

The coercivity $H_c$, the magnetization at $H_m$, the remanence and $M_r/M_s$ ratio obtained at -196 °C are listed in Table 1. The coercivity found at room temperature is also included. Although the magnetic properties of first three samples are very similar, it seems that the most improved values happen for powders exhibiting an average crystallite size of about 19 nm. The significant deterioration of coercivity is found only for the latest sample, which its average crystallite size is of 39 nm and, additionally, the exchange interaction among grains is not observed ($M_r/M_s \sim 0.5$).
Table 1. Values of annealing time, strain, average crystallite size, coercivity obtained at room temperature and -196 °C with maximum applied field of 5 T and the values of coercivity, saturation magnetization, remanence and $M_r/M_s$ ratio found from the loops measurements with maximum field of 20 T.

<table>
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<th>$t_a$ [min]</th>
<th>$\sigma$ [$10^{-3}$]</th>
<th>$&lt;D&gt;$ [nm]</th>
<th>$H_{c, RT}$ [kOe]</th>
<th>$H_{c, -196^\circ C}$ [kOe]</th>
<th>$H_{c, -196^\circ C}$ [kOe]</th>
<th>$M_{s, -196^\circ C}$ [emu/g]</th>
<th>$M_{r, -196^\circ C}$ [emu/g]</th>
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Conclusion

Our results demonstrated that nanocrystalline YCo$_5$ powders prepared by mechanical milling and subsequent annealing at 820 °C for 2.5 min. $t_a \leq 4.5$ min obtaining $<D>$ between 19 and 39 nm exhibit a high coercivity values. At room temperature, the maximum coercivity value of 9.0 kOe was found for sample with $<D> \sim 19$ nm. For this sample, at -196 °C, the values of the coercivity, saturation magnetization and $M_r/M_s$ ratio were 13.1 kOe, 110 emu/g and 0.62, respectively. The enhanced $M_r/M_s$ ratio indicates the occurrence of exchange interactions among fine particles.

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References


