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*> ~ 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> ~ 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 magnetcrystalline 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/cm³, 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 nanograined YCo_5 exhibiting high coercive field such as $H_c \sim 10$ kOe and grain size ~ 30 nm. Later, Sánchez *et al* [7] produced YCo_5 nanoparticles with <*D*>~ 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 mechanichal 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 YCo_5 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 YCo_5 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 (t_a = 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 YCo_5 powders annealed at 820 °C for t_a = 2.5, 3.0, 3.5 and 4.5 min, respectively. The main phase of all samples is YCo_5 phase; however XRD patterns shows also additional small lines (in Fig. 1 these lines are indicaed by *) corresponding to Y_2Co_{17} phase decomposed from YCo_5 phase. All peaks of YCo_5

phase correspond to hexagonal $CaCu_5$-type structure (PDF #17-078) and those of Y_2Co_{17} phase can be indexed with the rhombohedral Th_2Zn_{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_2Co_{17} phase [4].

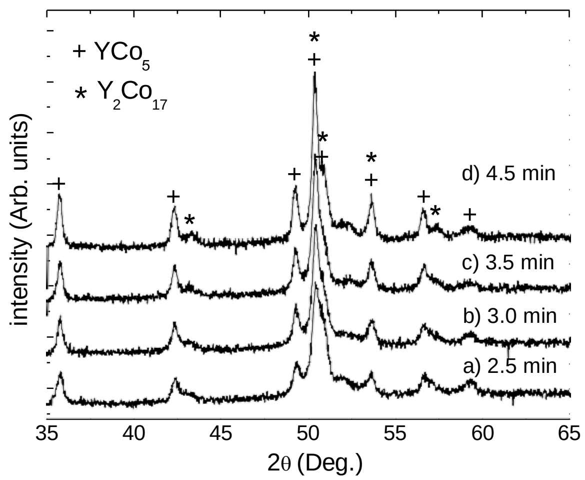

Fig. 1. Powder X-ray diffraction patterns of mechanical milled YCo_5 nanostructured powders as a function of annealing time t_a: a) 2.5; b) 3.0; c) 3.5; d) 4.5 min.

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 θ 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 σ values were determined by fitting the experimental data to the linear $(\delta 2\theta/\tan\theta)^2$ *vs*. δ2θ/(tanθsinθ) plot [9]. The determined <*D*> and σ 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 σ magnitude. This result is expected because, generally, <*D*> increment is accompanied with a strain diminution [4].

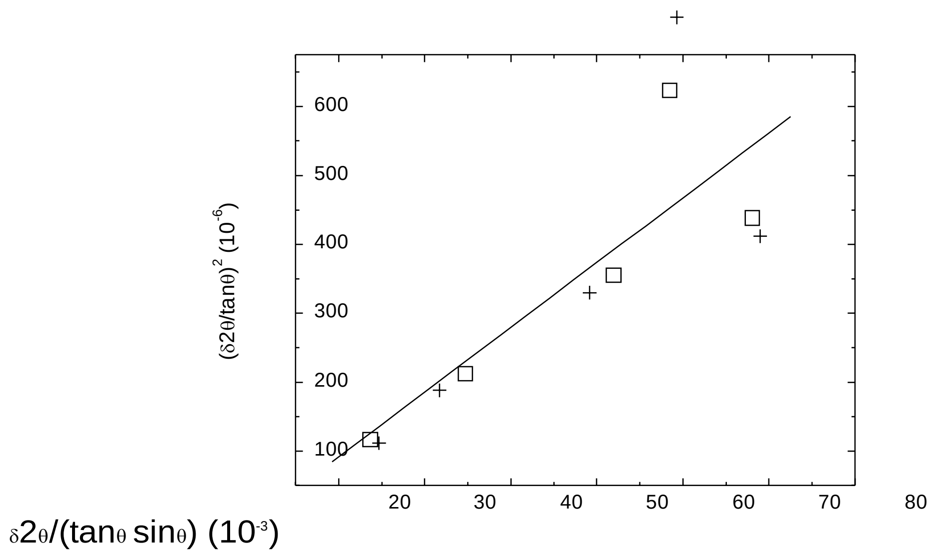

Fig. 2. Plot of $(\delta 2\theta/\tan\theta)^2$ vs (δ2θ/tanθsinθ) for YCo_5 powders obtained after mechanical milling for 4 h and subsequently annealed at 820 °C for 2.5 min.

Fig. 3 shows a characteristic dark field mode micrograph of nanostructured YCo_5 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.

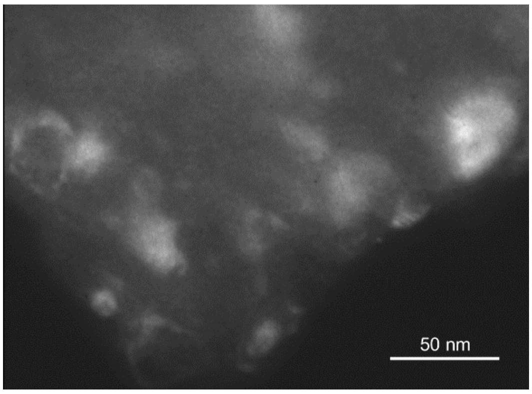

Fig. 3. TEM dark field image of the microstructure of YCo_5 annealed at 820 °C for 3.5 min.

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_2Co_{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*>

~ 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

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].

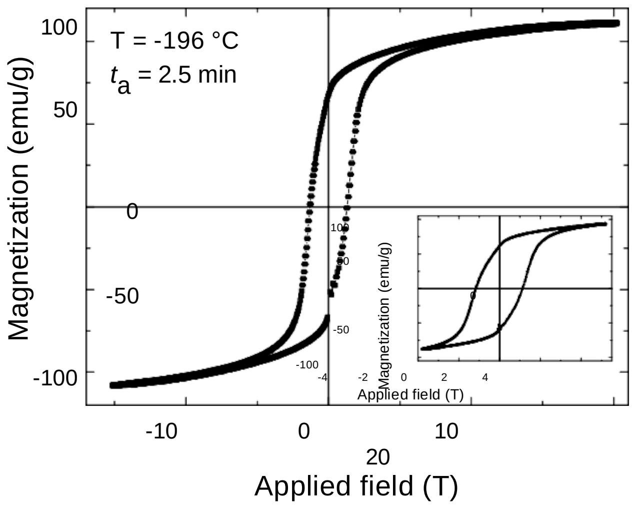

Fig. 4. Hysteresis loops of YCo_5 powders milled for 4 h annealed at 820 °C for 2.5 min measured with maximum field of 20 T at temperature of -196 °C. The inset shows the loop obtained at -196 °C with maximum applied field of 5 T.

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.

t_a [min]	σ [10^{-3}]	<D> [nm]	$H_{c, RT}$ [kOe] 5 T	$H_{c, -196°C}$ [kOe] 5 T	$H_{c, -196°C}$ [kOe] 20 T	$M_{s, -196°C}$ [emu/g] 20 T	$M_{r, -196°C}$ [emu/g] 20 T	M_s/M_r 20 T
2.5	2.5	17	8.8	11.5	13.0	110	68	0.62
3.0	2.3	19	9.0	11.8	13.1	108	67	0.62
3.5	1.9	32	8.8	11.6	13.0	107	66	0.62
4.5	1.8	39	6.9	10.9	12.8	110	64	0.5

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 ≤ 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*> ~ 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.

Acknowledgments

The author J.T. Elizalde Galindo wants to thank to CIMAV and Vienna University of Technology for the opportunity the work on its installations. Besides, all authors want to acknowledge to ALFA Programme with contract no AML/B7-311/97/0666/II-0147-FI for the support to this research.

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