High coercivity nanocrystalline YCo_5 powders produced by mechanical milling

J. L. Sánchez Ll, J. T. Elizalde-Galindo, J. A. Matutes-Aquino

Abstract

High coercivity nanostructured YCo_5 powders were successfully prepared by mechanical milling of as-cast alloys and subsequent vacuum annealing. Almost single phase YCo_5 alloys, obtained by arc melting, were processed by high energy mechanical milling using a SPEX 8000 mill. After 4 h of milling, powders become nearly amorphous. DSC scans revealed the existence of an irreversible broad exothermic transition with a maximum at 516 °C associated with the crystallization process. Annealing in high vacuum at 800 °C during 2.5 min led to the formation of YCo_5 nanoparticles with an average particle size of 12 nm. A high intrinsic coercivity of 7.23 kOe together with a σ_r/σ_s ratio of 0.75 were obtained.

Keywords: A. Intermetallic compounds; A. Nanocrystalline materials; A. High coercivity materials; D. Permanent magnets.

The discovery in 1966 of high uniaxial anisotropy field of YCo_5 opened a new era in the field of permanent magnetic materials [1]. This intermetallic compound crystallizes in the hexagonal $CaCu_5$-type crystal structure (space group P6/*mmm*). Because of the non-magnetic character of Y^{+3} its relevant intrinsic magnetic properties such as magnetocrystalline anisotropy, Curie temperature and saturation magnetization are determined by Co-sublattices. This phase combines a saturation induction and Curie point similar to those of $SmCo_5$ with a high enough anisotropy field value for practical

coercivity development [2]. Thus, it can be considered amongst the suitable candidates for the preparation of high energy permanent magnets. To date most of the work done on RCo_5-type magnets have been focused on $SmCo_5$ alloys [3] (R = rare earth). The huge uniaxial anisotropy field value of this compound strongly facilitates the coercivity development when it is processed into a high density fine particle textured polycrystal by powder metallurgy and sintering.

In the last few years, nanostructured magnets based on rare earths and transition metal compounds have attracted considerable attention due to their interesting magnetic and technological properties [4–6]. More recently, a renewed interest has risen on R–Co compounds due to their potential as precursors for high temperature magnets. The most common processing routes employed nowadays to fabricate these materials are rapid quenching by melt spinning and mechanical alloying [7,8]. More recently mechanical milling, has been also successfully used to produce high coercivity nanocrystalline powders [8]. Powders processed by this method commonly show better magnetic properties than those produced by mechanical alloying [9]. By using this technique high coercivity nonocrystalline R–Co compounds, such as $PrCo_5$ [10], Sm_2Co_{17} [11] and $Pr(Co,Zr)_7$ [12], have been successfully obtained. In this paper we report on the synthesis by mechanical milling of highly coercive nanocrystalline YCo_5 powders.

Raw materials were used in the form of powders with purity of 99.9% for Y (Alfa Aesar; average particle size, -40 mesh) and 99.8% for Co (Alfa Aesar; particle size, 150 mesh). They were adequately mixed in a mortar and then pressed into tablets at 2.4

Ton/cm^2. Small buttons with nominal composition YCo_5 were produced by arc melting under a high purity Ar atmosphere. The as-cast alloys were coarsely pulverized and sieved with a 177 mm pore size sieve. The powders were mechanical milled (MM) in argon atmosphere by using a SPEX 8000 ball mill for a time period ranging from 15 min to 8 h. The as-milled amorphous powders were wrapped in tantalum foils and annealed in high vacuum at 800 8C during 2.5 min in closed vycor ampoules. Annealing was followed by quenching in water. X-ray diffraction (XRD) analysis was performed on finely ground powders with an automated Siemens model D5000 diffractometer. A graphite monochromator was used to select the Cu Kα-doublet (λ = 1.542Å), Scanning was carried out in the interval 20< 2θ < 70° with a step increment of 0.050°. Differential scanning calorimetry (DSC) curves were measured on a as-cast and as-milled powders in a T A Instruments model 2920 DSC calorimeter. The curves were recorded from room temperature up to 600 °C under an argon high purity flow; the heating rate employed was 5 8C/min. Microstructural studies of annealed powders were carried out using a Philips CM200 transmission electron microscope. Magnetic measurements were done in a vibrating sample magnetometer LDJ Model 9600. Hysteresis loops were recorded with a maximum field of H_{max} = 16 and 25 kOe.

The experimental powder XRD pattern of the arc-melted YCo_5 alloy is plotted in Fig. 1a. All the reflections were identified in the pattern (marked by open circles in the figure); they belong to the hexagonal 1:5 phase ($CaCu_5$-type crystal structure). This is consistent with the microstructure observation by scanning electron microscopy (not shown here). From this analysis it is concluded that the hexagonal YCo_5 compound is

the major phase in the as-cast alloy, therefore we have an appropriate precursor for the processing by mechanical milling. Fig. 1b and c shows the evolution of XRD patterns with the milling time. As it is observed, for a milling time as short as 30 min, the XRD lines become broader and their intensities decrease as a result of the fast reduction in the grain size of the YCo_5 phase. This is a direct consequence of the effect of the high energy collisions between the powders and balls during milling on grain size. Further increase in the time of milling leads to the progressive destruction of the 1:5 structure. After 4 h of milling a nearly amorphous phase precursor has been formed (Fig. 1c). It should be noted that just at $2\theta = 44.8°$ a weak, but detectable, reflection is observed (marked by an arrow in the figure). This is close to the position of the most intense reflection of a-Fe. It is well known that powder contamination with the steel grinding medium (balls and vial) is an unavoidable drawback of high energy milling techniques [13]. The amount of Fe added as estimated by EDAX was 1.3% wt.

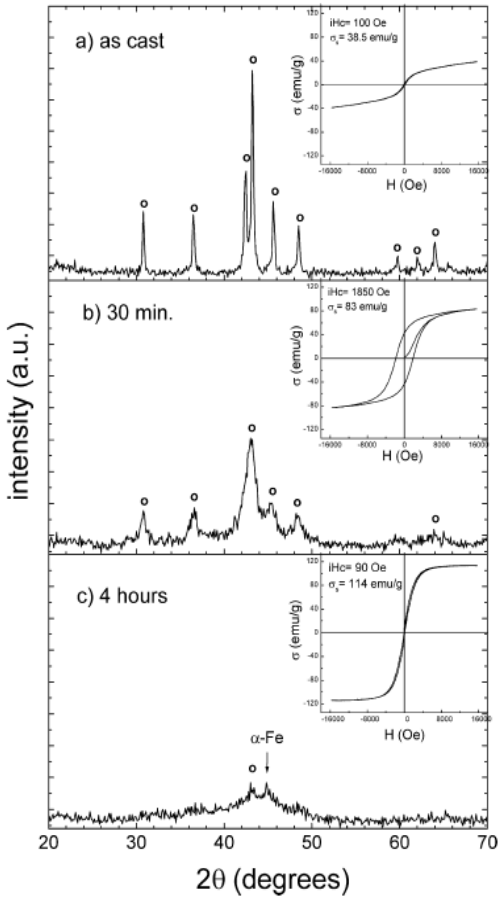

Fig. 1. Powder XRD patterns of YCo_5 alloys: (a) as-cast sample; (b) MM for 30 min; (c) MM for 4 h. The open circles indicate reflections that correspond to the 1:5 phase, while the most intense reflection of α-Fe is marked by an arrow. In the inserts the corresponding hysteresis loops are shown.

The dependence of intrinsic coercivity, ${}_iH_C$; and spontaneous saturation magnetization, σ_s; on milling time for as-milled YCo_5 powders is shown in Fig. 2. In the first 30 min, a very sharp increase in the coercivity is observed. However, a moderate coercivity value is attained. This behavior should result from a combination of a fast grain size refinement together with a progressive accumulation of defects. Further increase in the time of milling leads to the continuous and rapid decrease in ${}_iH_C$; above 2 h very low coercivities are obtained. The progressive accumulation of structural

defects, as a consequence of the intensive milling, should have a strong influence on this physical quantity. This also leads to the rapid magnetic softening of the material as it is revealed by the hysteresis loops shown in the insert of Fig. 1b and c. σ_s shows a rapid increase for short times of milling, the value reached for amorphous powders is close to the one exhibited by crystalline YCo_5 intermetallic phase [1,2].

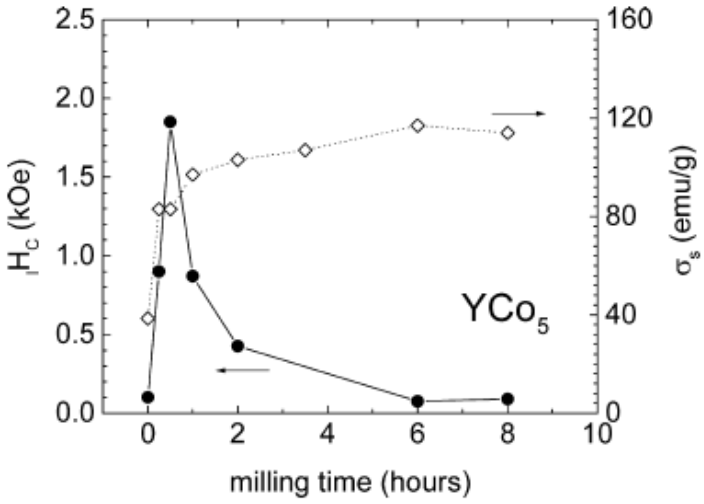

Fig. 2. Coercive field and saturation magnetization as a function of the milling time for mechanical milled YCo_5 powders (measured at $H_{max} = 16$ kOe).

Fig. 3 shows the DSC curves recorded on heating for ascast and 4 h mechanical milled YCo_5 alloys. The as-cast sample does not exhibit thermal transitions in the temperature interval measured. On the contrary, for the powder milled during 4 h the curve shows a broad exothermic peak starting at 465 8C with a maximum at 516 8C. This transition is not observed in the on-cooling curve (not plotted in the figure), evidencing its irreversible character. Therefore, this is attributed by us to the crystallization process of the amorphous phase.

In order to determine the optimum thermal treatment, powders were annealed at different times intervals and temperatures between 600 and 800 °C. Better magnetic properties were obtained after annealing at 800 °C during 2.5 min. The XRD pattern of this sample is plotted in Fig. 4. All the reflections in the diffractogram were satisfactorily indexed; they correspond to the hexagonal compound YCo_5 showing that this is the main phase formed in the sample.

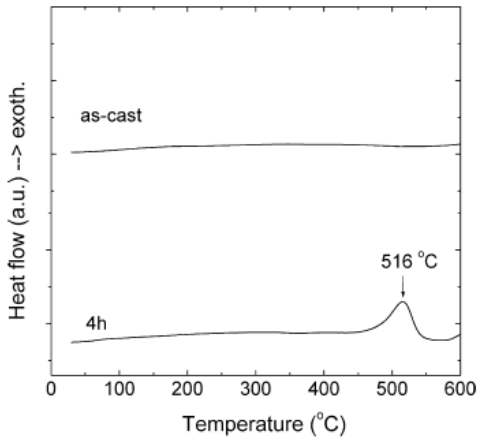

Fig. 3. DSC scans for as-cast and 4 h mechanical milled YCo_5 alloys.

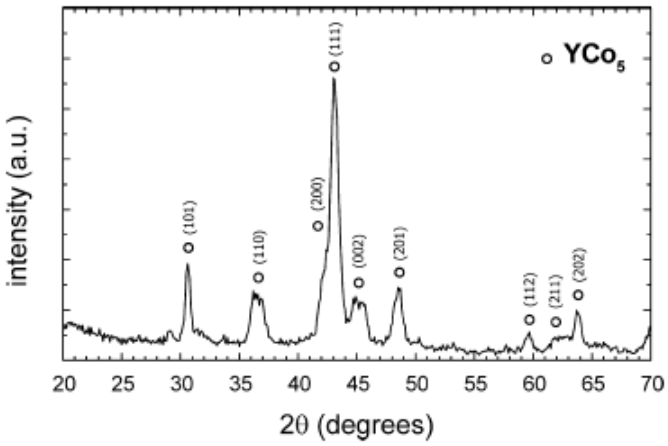

Fig. 4. Powder XRD pattern of YCo_5 powders annealed at 800 °C for 2.5 min.

The broadening of the lines suggests the formation of a fine particle microstructure. The TEM dark-field micrograph of annealed powders is shown in Fig. 5. Average size of particles is about 12 nm. The minor hysteresis loop of this sample is plotted in Fig. 6. It was recorded for a maximum external field of H_{max} = 25 kOe: A coercivity of ${}_{I}H_{C}$ = 7.23 kOe has been measured. In spite of its isotropic character, the sample shows an σ_s=σ_r ratio of 0.75. This substantial remanence enhancement reflects the exchange coupling between nanoparticles.

In summary, present investigation has established that nanostructured YCo_5 powders can be prepared by mechanical milling and subsequent short annealing in high vacuum. An amorphous precursor was obtained from coarsely grounded YCo_5 are melted alloys after 4 h of milling in a SPEX 8000 type ball mill. The on-set of the crystallization stars around 465 °C. However, as in many other systems optimum magnetic properties are obtained after annealing at well higher temperatures, in this case at 800 °C.

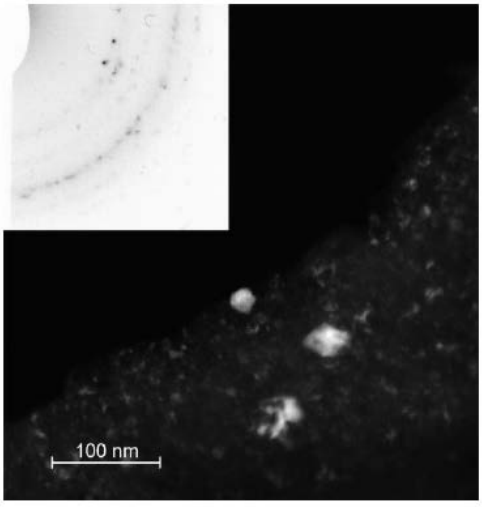

Fig. 5. TEM dark-field micrograph of YCo_5 powders annealed at 800 °C for 2.5 min.

The magnetic hardening of the powder results from the formation of YCo_5 nanograins with an average particle size of 12 nm. The powder exhibited an intrinsic coercivity of 7.23 kOe measured for a minor hysteresis loop at H_{max} = 25 kOe: The remanence enhancement observed should be associated with the exchange coupling between nanograins.

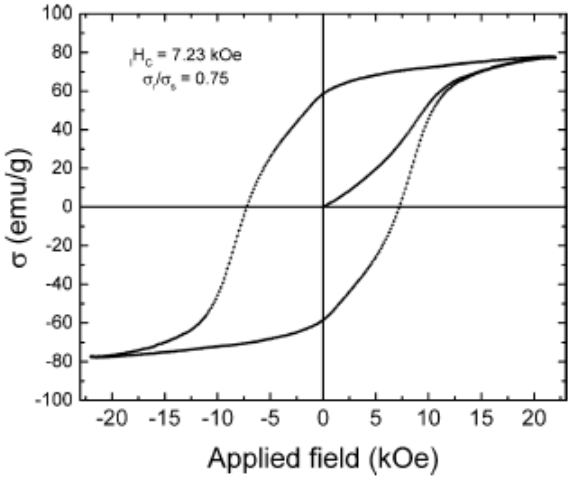

Fig. 6. Hysteresis loop of YCo_5 powders annealed at 800 °C for 2.5 min.

Acknowledgments

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