Nanocrystalline $PrCo_5$ alloy obtained by mechanical milling

F. J. Rivera-Gómez, J.T. Elizalde-Galindo, J.A. Matutes-Aquino

Abstract

Nanostructured $PrCo_5$ powderswere obtained by mechanical milling, annealing in high vacuum in sealed ampoules and subsequent quenching in water. The highest intrinsic coercivity value ($_iH_C$ = 1.385MA/m) and magnetization ratio (σ_r/σ_{max} = 0.66) were determined in powders milled for 240 min and annealed at 1073K for 1 min. The enhanced remanence (σ_r/σ_{max} > 0.5) suggests strong exchange interactions between the adjacent crystallites. This is in good agreement with the small average crystallite size, <D> = 15 nm. The high magnetic properties observed in these nanostructured PrCo5 intermetallic alloys have their origin in its relatively high uniaxial magnetocrystalline anisotropy field, and in the homogeneous nanostructure developed by mechanical milling process and subsequent annealing.

Keywords: Permanent magnets, Nanostructured materials, Rare earth alloys and compounds, Microstructure.

Introduction

Permanent magnets are fabricated with magnetic materials that show strong resistance to invert its magnetization, they maintain the magnetization large and stable when subjected to their own demagnetizing fields, and to opposing external fields, and to a range of temperature changes. The properties that define this behavior are intrinsic coercivity, $_iH_c$, and remanent magnetization, σ_r. They determine the maximum energy product value, $(BH)_{max}$, that is the figure of merit that assess the global quality for permanent magnets [1]. The magnetic materials with the best properties for developing permanent magnets are intermetallic alloys based in rare earths (RE) and transition metals (TM). RCo_5 alloys (R = Sm, Y and Pr) are the most attractive alloys due to its good intrinsic magnetic properties [2,3]. Such alloys have enhanced magnetic properties in nanostructured state [4,5]. Recently nanocrystalline $RECo_5$ compounds have been obtained by different processing routes, like melt spinning [6,7], mechanical alloying [8], and mechanical milling [9,10]. From these works, it can be observed that $PrCo_5$ is a material with good intrinsic magnetic properties for use in high energy permanent magnets. In this work we discuss the structural and magnetic properties of $PrCo_5$ powders produced by mechanical milling.

Experimental

Rawmaterials were used in the form of ingots with purities of 99.9% for Pr (Alfa Aesar) and 99.8% for Co (Alfa Aesar). Small ingots of near stoichiometric composition $PrCo_5$ were produced by arc-melting the raw materials under a high purity Ar atmosphere. The samples were prepared by using 0.985 g of Pr and 2.029 g of Co, where a 5% excess of Pr was used to compensate its evaporation. The ingots were turned over and re-melted four times to improve homogeneity. The as-cast ingots were then coarsely pulverized in agate mortar and sifted using a mesh number 80. Then, powders were mechanical-milled for periods ranging from 30 to 240 min. The milling was carried out under argon atmosphere using a SPEX 8000 ball-mill with a powder to ball weight ratio of 1:10. The as-milled amorphous powders were annealed at temperatures between 1023 and 1123K in high vacuum closed vycor ampoules (5×10^{-5} Torr) followed by quenching in water. For that, the ampoules were placed into the furnace which had been preheated to the desired temperature and held for the desired time, and finally quenched in water. Annealing times between 0.5 and 5.5 min were used. X-ray diffraction (XRD) patterns of finely ground powders were measured with an automated Siemens model D5000 diffractometer with graphite monochromator (Cu-Kα radiation). Microstructural studies were carried out using a Philips CM200 transmission electron microscope (TEM). Magnetic measurements were done at room temperature with a vibrating sample magnetometer LDJ Model 9600 (H_{max} = 1.273MA/m) and with an Oxford Instruments MAGLAB with superconductor coil (H_{max} = 7.162 MA/m). Differential scanning calorimetry (DSC) curves, were measured on as-cast and as-milled powders in a TA Instruments model 2920 DSC calorimeter. The curves were recorded from room temperature up to 873K under an argon flow; the heating rate employed was 5 K/min.

Results and discussion

Fig. 1 shows the XRD pattern series of as-cast and mechanically milled alloys. In Fig. 1a all reflections observed for $PrCo_5$ phase were identified with those of hexagonal $CaCu_5$-type phase (PDF #17-906) [11]. There are also a couple of reflections with Miller index (4 0 0) and (4 1 1) identified with the phase Pr_2O_3 (ICSD #96203). The amount of this phase calculated by using Rietveld refinement method was about 0.5 wt%. Therefore, this sample is an appropriate precursor for the processing by mechanical milling.

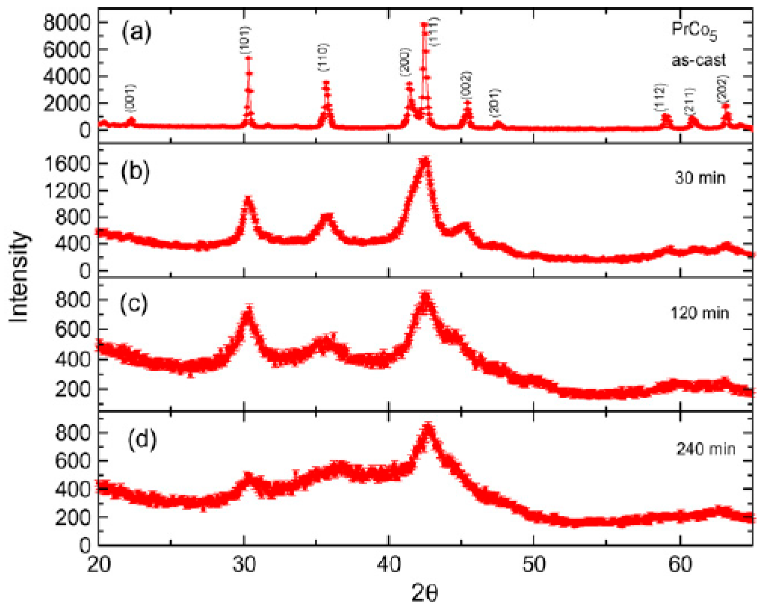

Fig. 1. X-ray diffraction patterns of as-cast and mechanical milling alloys.

Fig. 1b–d shows the evolution of XRD patterns during the milling process. As observed for milling times as short as 30min (Fig. 1b), the XRD lines become broader and their intensities decreased as a result of the fast reduction of the crystal size of the $PrCo_5$ phase. This is a direct consequence of the high energy collisions between the powders and balls during milling. Further increases in milling time leads to progressive destruction of $PrCo_5$ crystal structure (Fig. 1c); and finally, after 240 min of milling, a nearly amorphous phase was obtained with a small amount of residual 1:5 phase indicated by their (2 0 0) and (1 1 1) small intensity peaks (Fig. 1d). The amorphous state is confirmed by the DSC curve (Fig. 2) which shows an exothermic peak during heating due to the amorphous to crystalline transition but the inverse transition during cooling does not occur.

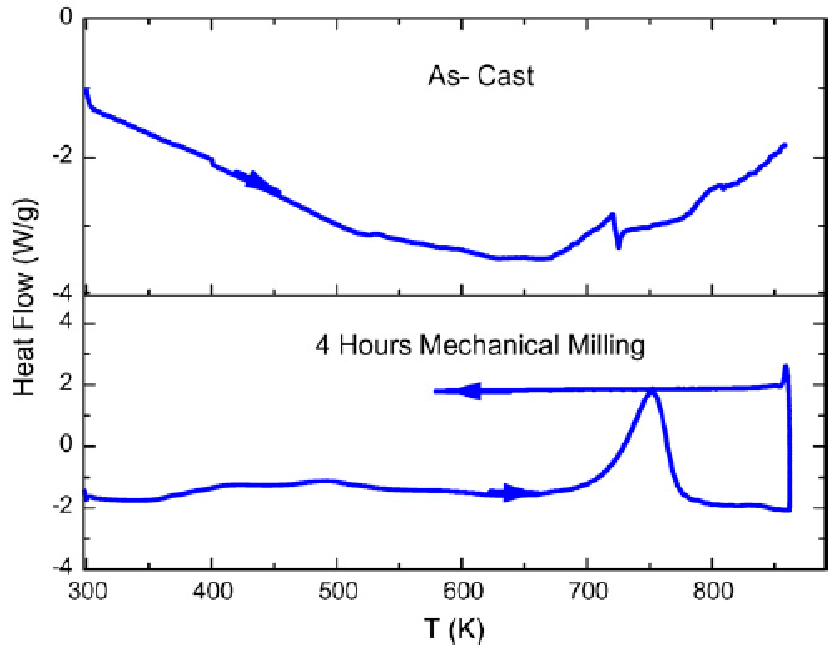

Fig. 2. DSC scan for as-cast and 240 min mechanical-milled $PrCo_5$ alloys.

Fig. 3 shows the effect of mechanical milling time on magnetic properties. The maximum magnetization, σ_{max}, increased in the first 30min to 80% of its biggest value and with further increasing of the milling time, it reached its maximum value of 0.000125 $Tm^3\ kg^{-1}$. Besides that, the coercivity, ${}_iH_c$, reached its maximum value after 30min of milling, due to reduction in the grain size and for higher milling times ${}_iH_c$ decreased until it reached aminimum value of 6.923 kA/m at 240min of milling. This was due to destruction of long-range order in crystallites and subsequent diminution of magneto crystalline anisotropy [4]. The XRD pattern series show that the near amorphous state is reached at 240 min of milling, which is in good agreement with other studies on this kind of intermetallic alloys [8,12].

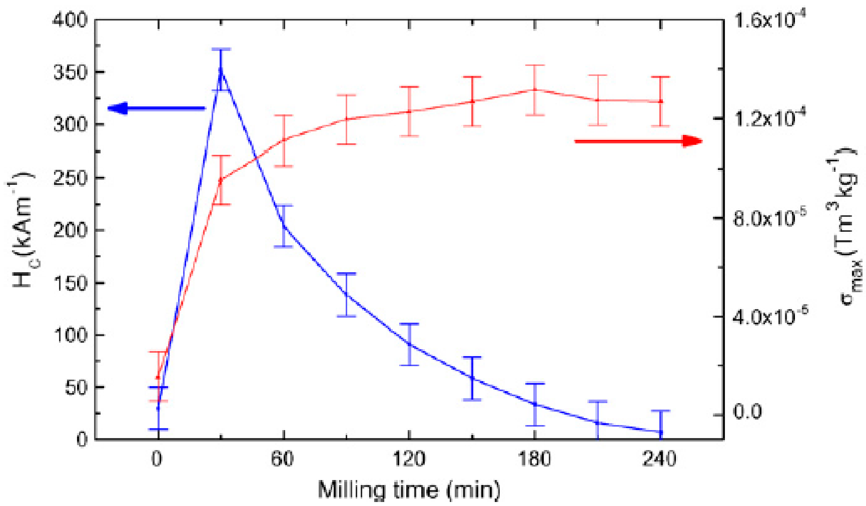

Fig. 3. Effect of mechanical milling on magnetic properties.

The amorphous powders obtained after mechanical milling were annealed under different conditions in order to optimize the nanometric average grain size <D> and their associated high magnetic properties. The best magnetic properties were reached after a treatment at 1073K for 1min with subsequent quenching in water.

Fig. 4 shows the XRD pattern of $PrCo_5$ alloy annealed at 1073K for 1 min. The main peaks could be indexed with the hexagonal $CaCu_5$-type structure with lattice parameters: a = 5.01±0.01Å and c = 3.98±0.01Å. These values are in good agreement with those reported for stoichiometric $PrCo_5$ [8]. The asymmetry in the (1 1 0) and (0 0 2) peaks suggest a small quantity of 2:17 secondary phase. The amount of this phase calculated by using the Rietveld refinement method was about 6.5 wt%, which confirms that 1:5 phase with hexagonal structure represents the overwhelming majority phase in the annealed powders of the sample. All peaks are broad indicating small crystallite sizes, which agree with the average grain size value, <D> = 15 nm, calculated by using Rietveld method implemented in fullprof program [13].

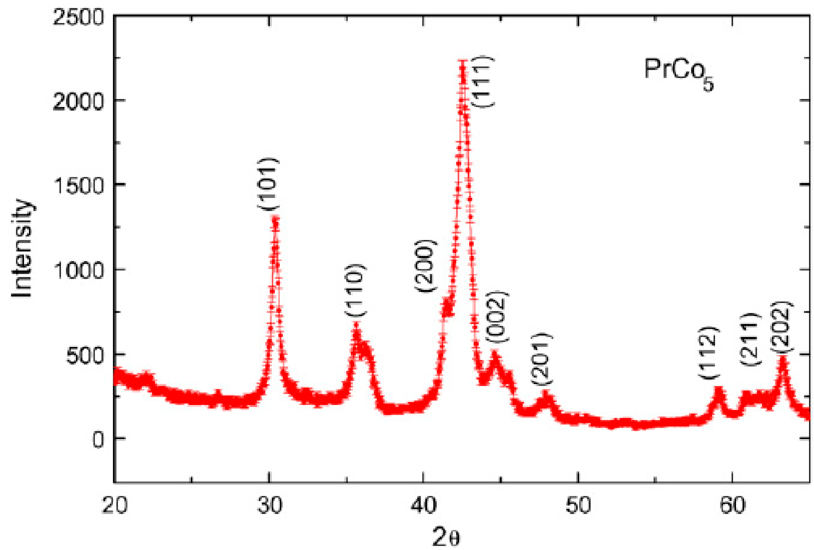

Fig. 4. X-ray diffraction patterns of $PrCo_5$ alloy annealed at 1073 K during 1 min.

Fig. 5 shows the hysteresis loop for $PrCo_5$ after 240 min of mechanical milling and annealing at 1073K for 1min. The shape of the initial magnetization curve suggests a pinning-type magnetization process [14], in good agreement with that proposed for the isostructural YCo_5 intermetallic alloy [15]. The demagnetization curve observed in this hysteresis loop is smooth, indicating a fine and uniform grain size in the sample [16]. The maximum intrinsic coercivity value was 1.385 MA/m, for a maximum applied field of 5.570MA/m at room temperature. Enhanced remanence ratio $\sigma r/\sigma_{max}$ = 0.66, suggests magnetic exchange interactions between adjacent crystallites in these nanostructured powder.

The average grain size of 20nm observed by TEM is slightly larger than the average grain size obtained by the Rietveld refinement method but still below the monodomain critical size d_{crit} for this intermetallic compound (~1μm) [9]. This reduced average grain size is in accordance with the enhanced remanence observed at the hysteresis loop shown in Fig. 5. The difference in the size values obtained from XRD and TEM can be attributed to the fact with TEM it is possible to observe only a small quantity of particles while with XRD it is possible to measure with more accuracy [17].

Conclusions

In summary, $PrCo_5$ alloy powders with good magnetic properties for applications as permanent magnet, were obtained with the mechanical milling technique, subsequent heat treatment, and quenching in water. Enhanced magnetic properties of σ_{max} =0.000117Tm^3 kg^{-1}, σ_r = 0.0000777 Tm^3 kg^{-1}, σ_r/σ_{max} = 0.66, $_iH_c$ = 1.385 MA/m, and $(BH)_{max}$ = 77.43 kJ/m^3 have been obtained in stoichiometric $PrCo_5$ powders, milled for 240min and annealed at 1073K for 1 min. Single-domain grains with a mean grain size of 15nm were developed by mechanical milling and subsequent annealing. The high values of magnetic properties are ascribed to high intrinsic properties of the PrCo5 alloys and to the nanometric microstructure developed.

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