Nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys with enhanced magnetic properties

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Abstract

Nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ powders (*average crystal size d = 12 nm*) were produced by arc melting pure metals followed by mechanical milling and annealing. Different milling/annealing times and annealing temperatures were used to optimize the hard magnetic properties of these nanopowders. A noticeably enhanced coercivity and remanence (*coercivity of 2.1 MA/m, and σr/σmax = 0.7 respectively*) were observed in samples milled for 240 minutes and then annealed for 1 minute at Temperatures ~1200K. Such remarkable magnetic properties stem from the high magnetocrystalline anisotropy field and the homogeneous grain size of the $Sm_{0.5}Y_{0.}5Co_5$ nanocrystals.

Keywords: Permanent magnets; magnetic anisotropy; nanocrystalline materials; high coercivity materials.

Introduction

Since their discovery in the late 1960s, rare-earth cobalt-based permanent magnet materials have attracted considerable attention due to their high anisotropy fields , relatively high saturation magnetizations and high Curie temperatures [1]. More recently, it was demonstrated that synthesizing such materials in nanostructural form can further enhance their magnetic properties [1-3]. In particular, Y-Co based permanent magnets are of great interest for new applications where high operation temperatures (up to 573 K) are needed or a stable magnetic field in a variable

temperature environment is required [4]. In the present work nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ powders were synthesized by mechanical milling followed by annealing and their hard magnetic properties have been investigated.

Experimental details

$Sm_{0.5}Y_{0.5}Co_5$ alloys were prepared by arc-melting pure elements in argon atmosphere. The as-cast ingots were then crushed and mechanically milled. The milling process was carried out under argon atmosphere by using a high-energy Spex 8000 mixer/mill with a powder-to-ball ratio of 1:8. Different milling times up to 480 minutes were employed. The as-milled powders were subsequently annealed for 1 to 5 minutes at temperatures ranging from 850 to 1200 K in order to optimize their microstructure and coercivity. Structural analysis was carried out from X-ray diffraction (XRD) data collected on a Siemens D5000 diffractometer. Differential scanning calorimetry measurements were performed using a TA Instruments DSC-2920 and magnetic properties were measured on a LDJ 9600 vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 1.3 MA/m, a Quantum Design Physical Properties Measurement System (PPMS) with a maximum applied magnetic field of 2.4 MA/m, and with a pulsed field magnetometer (PFM) with a maximum applied magnetic field of 6.4 MA/m.

Results and discussion

Figure 1 shows powder XRD data from $Sm_{0.5}Y_{0.5}Co_5$ alloys in the following stages of the synthesis process: a) as cast sample, b) sample mechanically milled for 240 minutes, and c) sample annealed at 1173K for 1 minute. All peaks observed in the

as-cast alloy can be indexed to a hexagonal $Sm_{0.5}Y_{0.5}Co_5$ phase with the same unit cell as in the known YCo_5 structure (PDF #17-078). No impurity phases or extra peaks are observed. Therefore, the as-cast sample represents an appropriate precursor for processing by mechanical milling. After 240 minutes of mechanical milling the amorphous state of $Sm_{0.5}Y_{0.5}Co_5$ is reached. This is demonstrated by the XRD data which show only one weak-intensity broad maximum corresponding to the strongest reflection from the abovementioned crystalline phase. Further processing by annealing at Temperature > 850K for 1 to 5 minutes leads to the formation of nanometric-size crystalline powders. Indeed, the XRD pattern from the sample annealed at 1173K for 1 minute (Fig 1. c) can be indexed to the same hexagonal $Sm_{0.5}Y_{0.5}Co_5$ phase as the one in the as-cast alloy, and Scherrer analysis of the broad diffraction peaks yields an average crystallite size *d* =12 nm [5].

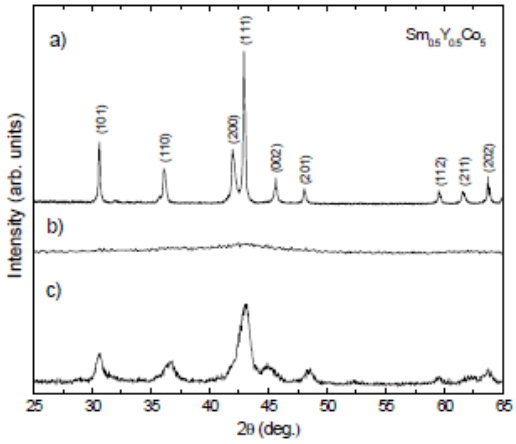

Fig. 1 Powder X-ray diffraction patterns in different stages of the synthesis process a) as cast alloy, b) alloy mechanically milled for 240 minutes, c) alloy annealed at 1173K for 1 minute.

The annealing temperatures required to re-crystallize the amorphous $Sm_{0.5}Y_{0.5}Co_5$ alloys were determined from differential scanning calorimetry (DSC) measurements carried out on as-milled samples. The DSC curve from amorphous $Sm_{0.5}Y_{0.5}Co_5$ milled for 240 minutes, shown in Fig. 2, reveals two exothermic peaks: one centered at 623 K and other at 773 K. The former corresponds to relaxation processes, while the latter indicates the crystallization of the amorphous sample. Consequently, the annealing temperatures necessary to crystallize as-milled $Sm_{0.5}Y_{0.5}Co_5$ nanopowders have to be higher than 800 K. We used 850 K< temperatures <1200 K in our present study.

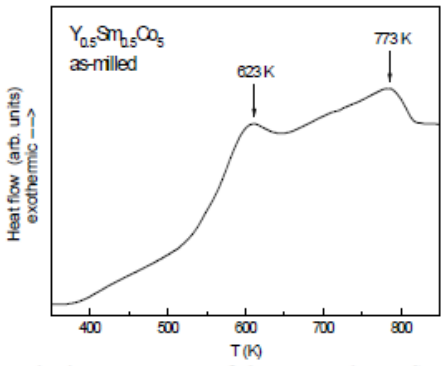

Fig. 2 Differential scanning calorimetry curve of the amorphous $Sm_{0.5}Y_{0.5}Co_5$ alloy mechanically milled for 240 minutes.

To investigate the evolution of the magnetic properties of the $Sm_{0.5}Y_{0.5}Co_5$ alloy with the milling time, the coercivity, and the maximum specific magnetization, σ_{max}, were measured for the as-cast alloy and for samples milled for different times, t_m , using a maximum applied magnetic field of 1.3 MA/m (It is worth to notice that the samples magnetization do not reach saturation for the applied magnetic fields). Fig. 3 shows the *coercivity vs. milling time* (solid circles) and σ_{max} vs t_m (solid triangles) dependencies for milling times ranging from 0 to 480 minutes. Initially the coercivity increases from its low

value in the as-cast alloy to a maximum value that is reached for tm ≈15 minutes. Upon further increasing the milling time, the coercivity, continuously decreases up a lower value that is reached for t_m = 480 minutes. The maximum magnetization σ_{max} show a different t_m -dependence: upon increasing the milling time, the σ_{max} initially *decreases* and it reaches a minimum value for the same time (t_m ≈15 minutes) when the coercivity reached its maximum value. Afterwards, the maximum magnetization σ_{max} continuously increases up to a value significantly greater than that in the as-cast alloy, while the coercivity decreases up to a value near to the as-cast alloy value. The initial steep increase of the coercivity , and the corresponding diminution of σ_{max}, are due to the combination of a rapid grain size refinement with a progressive accumulation of defects induced by milling. On the other hand, the further diminution of the coercivity and the corresponding increase of σ_{max}, can be attributed to the progressive destruction of the magnetocrystalline anisotropy that occurs as the sample reach the amorphous state [6,7].

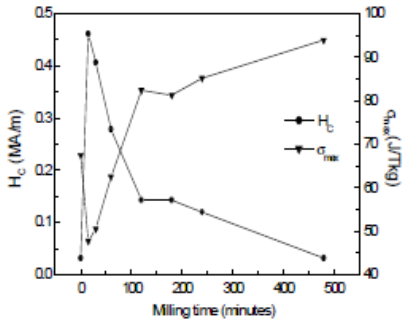

Fig. 3 Evolution of the coercivity and maximum specific magnetization σ_{max} with the milling time for the as milled $Sm_{0.5}Y_{0.5}Co_5$ alloy .

The amorphous alloys were annealed to produce a nanocrystalline structure with an increased magnetic anisotropy. A higher magnetic anisotropy, due to the nanoscale structure, should lead to better hard magnetic properties (e.g. higher coercivity and remanence). The alloy milled for 240 minutes was annealed at temperatures between 850 and 1200K for 1 to 5 minutes. For each annealed sample the virgin magnetization curve and the corresponding hysteresis loop were measured using both DC and pulsed magnetic fields. The shape of the virgin magnetization curve can give information on the mechanism of magnetization, and from the hysteresis loop the coercive field, and remanent magnetization ratio, σ_r/σ_{max}, can be determined. Fig. 4 shows virgin magnetization curve and hysteresis loop of the nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ sample annealed at 1173K for 1 minute measured in a DC magnetic field (with a maximum applied magnetic field 2.4 MA/m). *In figure 4 the vertical scale is expressed in units of magnetic moment.*

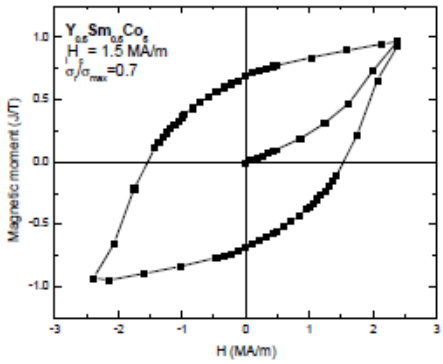

Fig. 4 Virgin magnetization curve and hysteresis loop measured in DC magnetic field for the $Y_{0.5}Sm_{0.5}Co_5$ alloy annealed at 1173 K for 1 minute

This sample exhibits high values of the coercive field, and remanent magnetization ratio, σ_r/σ_{max}. The shape of the virgin magnetization curve indicates a

pinning-type magnetization mechanism similar to the one reported for the isostructural compound $Pr_{0.5}Y_{0.5}Co_5$ [8]. At the same time, the smooth hysteresis loop suggests a very fine and uniform crystallite size [9]. This sample has enhanced values of coercivity and remanent magnetization ratio: coercive field of 1.57 MA/m and σ_r/σ_{max} = 0.7 respectively. The observed coercive field is most likely due to the pinning of domain walls by magnetic inhomogenities [8], while the high σ_r/σ_{max} ratio can be attributed to strong magnetic exchange interactions between fine magnetic crystallites [10]. Fig. 5 shows a threequadrant hysteresis curve for the same nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloy, measured in a pulsed magnetic field. Despite the high value of the maximum applied magnetic field, the sample does not reach the saturation state, a characteristic property of many magnetic nanoparticle systems [3].

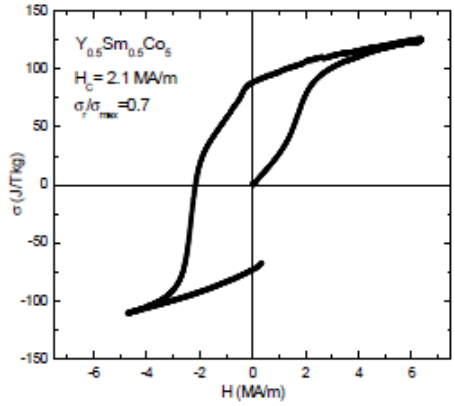

Fig. 5 Virgin magnetization curve and three-quadrant hysteresis loop measured in a pulsed magnetic field for the $Sm_{0.5}Y_{0.5}Co_5$ alloy annealed at 1173 K for 1 minute.

With pulsed magnetic fields a remanent magnetization ratio σ_r/σ_{max} of 0.7, was determined, which is near to the value obtained by using DC applied magnetic fields. The coercivity exhibits a value of 2.1 MA/m, which is remarkably higher than that value

obtained by DC measurements due to the higher values of the magnetic fields applied in pulsed field magnetometry.

Conclusion

Highly anisotropic nanostructured $Sm_{0.5}Y_{0.5}Co_5$ powders were synthesized by arc-melting, mechanical milling for 240 minutes, and annealing at 1173 K for 1 minute. As indicated by Scherrer analysis of X-ray diffraction data, the average grain size was 12 nm. A high coercivity ,2.1 MA/m and an enhanced remanence $\sigma_r/\sigma_{max} = 0.7$ were observed. The former is attributed to the high anisotropy field of the $Sm_{0.5}Y_{0.5}Co_5$ alloy and to the uniform nanostructure induced by mechanical milling. The latter stems from strong exchange interactions between nanocrystallites.

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