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Research articles

Evidence of exchange coupling in τ-MnAlC/FeCo system

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ABSTRACT

The τ-MnAlC/FeCo system has potential to be applied as rare earth-free permanent magnet, due to exchange coupled between hard and soft magnetic phases as alternative for the development of high energy product permanent magnets. In this work the hard-magnetic phase $Mn_{53.3}Al_{45}C_{1.7}$ ($\mu_0 H_c = 0.37$ T of coercive force, $M_r = 23.52$ Am^2/kg of remanent magnetization, $M_s = 52.94$ Am^2/kg of saturation magnetization and $(BH)_{max} = 3.89$ kJ/m^3 of maximum energy product) was mixed with the soft magnetic phase $Fe_{65}Co_{35}$ ($\mu_0 H_c = 0.007$ T and $M_s = 221.33$ Am^2/kg) using a solid-state procedure. The magnetic materials were sintered using different ratios of hard and soft magnetic phases: 95:5, 90:10, 85:15 and 80:20; and different sintering temperatures (300, 400, 500 and 600 °C) in order to improve the magnetic properties. The magnetic exchange coupling between MnAlC and FeCo was proved by the hysteresis loop and its corresponding Thamm-Hesse analysis. The best result was obtained for MnAlC/FeCo (95/5 wt%) sintered at 500 °C during 30 min, for which the magnetic properties were $\mu_0 H_c = 0.277$ T, $M_s = 76.43$ Am^2/kg and $(BH)_{max} = 5.57$ kJ/m^3.

1. Introduction

Permanent magnetic materials with high performance are characterized by high magnetic anisotropy ($K_u = 1.7$ MJ/m^3), high Curie temperature ($T_c \sim 1000$ K) and a theoretical $(BH)_{max} \sim 110$ kJ/m^3 [1,2]. These class of materials are used for technological applications, consumer electronics, medical industry, transportation, alternative energy and others [2]. Due to this wide field of applications, hard magnetic materials have been receiving great scientific interest to improve their magnetic properties, specially focusing on rare earth (RE)-free magnets, due to the high prices of REs. Different processes have been implemented to obtain these new systems such as sintering, thermal treatments, refinement of grain size and others. These processes are the basis of the new exchange coupling model between hard and soft magnetic phases [3–12]. In this model, the magnetic properties are dependent on the intrinsic properties of both phases and it is proposed as an alternative solution to the issue of the high demand of RE free magnets.

The exchange coupling model developed, especially in magnetic films [13,14], suggests the preparation of nanocomposite magnets by coupling 85% of hard magnetic phase and 15% of soft magnetic phase. Recent work [15] proposes the τ-MnAl phase as a potential hard magnetic phase, because it has superior magnetic and mechanical properties than alnicos and hexaferrites permanent magnets [16]. The τ-MnAl is metastable phase with face centered tetragonal structure (fct), which is known in the literature as $L1_0$ [17,18]. The carbon addition helps to stabilize and increase the directional order along the [0 0 1] easy axis, which can lead to coercivity values between 2 and 3 kOe as already shown in Ref. [2]. Jian et al. [19] studied the microstructure and magnetic properties of alloys of $Mn_{53.3}Al_{45}C_{1.7}$ obtained by arc melting and ball milling, achieving stabilization of the ε-phase through annealing at 1373 K for 24 h followed by a low temperature annealing at 873 K for 30 min to obtain the τ-phase. The obtained phases were corroborated by XRD. By scanning electron microscopy (SEM), it was identified a continuous particle size reduction from 20 to 0.5 μm, and by vibrating sample magnetometry (VSM) it was seen a decrease in the saturation magnetization and an increase in the coercive field with the increase of the milling time.

For exchange coupling materials, the soft magnetic phase requires high magnetic permeability, high saturation magnetization and low coercivity [20]. The FeCo soft phase has recently been used for the exchange coupling with a hard-magnetic phase to increase the $(BH)_{max}$

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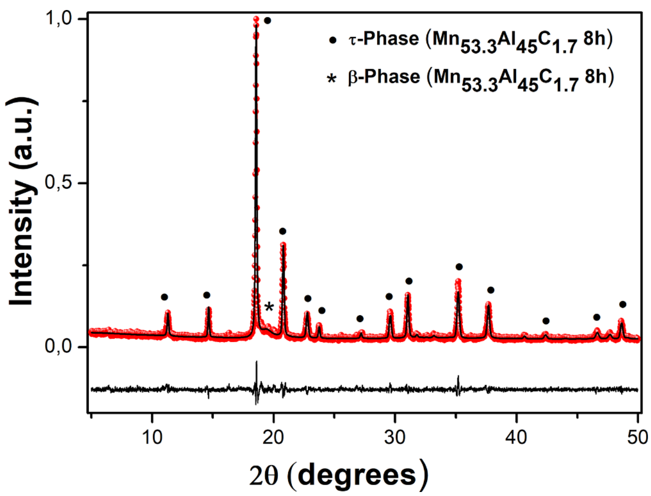

Fig. 1. X-ray pattern of the $Mn_{53.3}Al_{45}C_{1.7}$ sample milled for 8 h after annealed at 550 °C for 20 min.

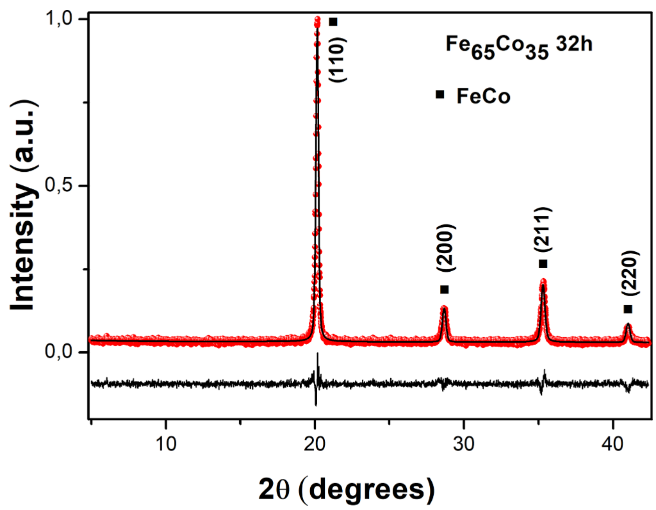

Fig. 2. X-ray pattern of $Fe_{65}Co_{35}$ milled for 32 h after annealed at 800 °C for 72 h.

in thin films. Dang et al. [21] studied the improvement of the $(BH)_{max}$ through the exchange coupling of thin films of MnAlC/FeCo, obtained by DC magnetron sputtering. They found an effective magnetic exchange coupling between MnAlC and FeCo thin films when the soft phase film thickness was less than 8 nm, and with this a significant improvement in the $(BH)_{max}$ was obtained. Recently, Trujillo et al. [22] studied the exchange coupling in nanocomposite magnets by milling melt-spun ribbon of $Mn_{54.3}Al_{44}C_{1.7}$ with α-Fe powders. They obtained the hard phase and optimized it after a heat treatment at 500 °C for 20 min. The mixture between τ-$Mn_{54.3}Al_{44}C_{1.7}$ and α-Fe phases showed, by XRD, a decrease in the τ-phase peaks. The nanocomposite sintering between 500 and 600 °C showed a decreasing tendency of the coercivity and the increase of the saturation magnetization. The evidence of the exchange coupling between the particles was studied by the Thamm-Hesse analysis [23] of the hysteresis loops.

Recent works have shown that the τ-MnAl hard magnetic phase optimization depends on the production method and thin films are the focus of recent works. Until now, researchers are working on the optimization of the τ-MnAl phase mixed with a soft phase through the exchange coupling in bulk samples, implementing mechanical alloying, sintering and other techniques. The main goal in this work is to obtain a magnetic exchange-coupling between hard magnetic (τ-MnAlC) and soft magnetic (FeCo) phases to improve the energy-product. For this reason, in this study, we propose to improve the magnetic properties of bulk nanocomposite magnets by optimizing the exchange coupling between the τ-$Mn_{53.3}Al_{45}C_{1.7}$ hard magnetic phase and the $Fe_{65}Co_{35}$ soft magnetic phase. The study by mechanical alloying and sintering, mixing 5 to 20% in mass of the soft phase, were performed to optimize the magnetic properties focused on RE-free permanent magnet, that can be used in the different applications mentioned above.

2. Materials and methods

$Mn_{53.3}Al_{45}C_{1.7}$ and $Fe_{65}Co_{35}$ alloys have been obtained by melt spinning and arc melting, respectively, from high purity elements. The FeCo alloy was annealed at 800 °C by 72 h and then quenched in water to homogenize and stabilize the α (A2) phase of FeCo which is disordered at that temperature according to its phase diagram. This phase presents a soft magnetic behavior. After the heat treatment, mechanical alloying was carried out for 32 h assisted with oleic acid to reduce the particle size and improve its soft magnetic behavior. MnAlC alloy was obtained by melt spinning. 3 wt% of Mn in excess was added to compensate its evaporation during the melting process. The ribbons presented only hexagonal ε-MnAl phase, in accordance with previous reports [22]. After that, the ribbons were annealed at 550 °C for 20 min to stabilize the τ-MnAl tetragonal phase; finally, the sample was ball milled for 8 h at 150 rpm to reduce the particle size and increase the coercivity value. Finally, the soft and hard phases were mixed at mass percentages of 5, 10, 15 and 20% of FeCo. Then the mixtures were homogenized for 1 h by mechanical alloying at low energy (150 RPM). Further, they were compacted to 75 kN of pressure and sintered at 300, 400, 500 and 600 °C for 30 min.

The samples were characterized by X-Ray Diffraction (XRD) carried out on a Stoe Stadi P diffractometer with Mo $K_{\alpha 1}$ radiation, in transmission geometry, in the 2θ range between 5 and 50°; Vibrating sample magnetometry (VSM) with an applied external field of 2 and 3 T for the soft and hard phases, respectively. Demagnetization correction was made for the magnetic measurements. The Thamm-Hesse method was used to study the type of predominant interactions between particles. In order to evaluate the magnetic interaction, we use a simple relation, which is called the ΔM-plot, $\Delta M = M_{init} - (1/2) \times (M_{up} + M_{down})$, where the M_{init}, M_{up}, and M_{down} are the magnetization values over the initial magnetization curve, upper, and lower part of the hysteresis loop, respectively, as described in Ref. [23]. Scanning Electron

Table 1
XRD parameters of $Mn_{53.3}Al_{45}C_{1.7}$ and $Fe_{65}Co_{35}$ samples.

Sample	Phase	Lattice parameter [Å] ± 0.001	Crystallite size		Weight fraction	Density (g/cm^3)
			$\Phi_{\parallel}$ [nm] ± 0.05	$\Phi_{\perp}$ [nm] ± 0.05		
$Mn_{53.3}Al_{45}C_{1.7}$	τ	a = 3.921 c = 3.586	347.68	627.05	85	5.27
	β	a = 6.906	233.56	123.11	15	5.53
$Fe_{65}Co_{35}$	$\alpha(A_2)$	a = 2.860	184.58	431.01	100	8.85