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Study of phases evolution in high-coercive MnAl powders obtained through short milling time of gas-atomized particles

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ABSTRACT

Gas-atomized $Mn_{54}Al_{46}$ particles constituted nominally of only ε- and γ_2-phases, i.e. no content of the ferromagnetic $L1_0$-type τ-phase, have been used to study the evolution of phases during short time of high-energy milling and subsequent annealing. Milling for 3 min is sufficient to begin formation of the τ-MnAl phase. A large coercivity of 4.9 kOe has been obtained in milled powder after annealing at 355 °C for 10 min. The large increase in coercivity, by comparison with the lower value of 1.8 kOe obtained for the starting material after the same annealing conditions, is attributed to the combined formation of the τ-MnAl and β-Mn phases and the creation of a very fine microstructure with grain sizes on the order of 20 nm. Correlation between morphology, microstructure and magnetic properties of the rapidly milled MnAl powders constitutes a technological advance to prepare highly coercive MnAl powders.

1. Introduction

The increasing demand of permanent magnet-based technological applications as well as global scarcity issues of rare-earth (RE) resources are significant drivers that demonstrate the need for alternatives to conventional RE-based permanent magnets in many applications. Opening of new and previously closed mines has mitigated the supply risk of light REs (Nd, Pr) but this risk remains for heavy REs (Dy, Tb). Dysprosium (Dy) is needed to provide high coercive and maintain magnetic properties in NdFeB-based magnets. Independent of the lasting criticality of Dy, Nd remains a strategical material with a well-localized geographical distribution. This situation has prompted a widespread search for RE-free permanent magnet alternatives. Among these alternatives, materials with economical raw material cost are identified as the established ferrites (oxides), Alnico magnets as well as Mn-based magnetic materials [1–3]. Mn-based permanent magnets have been regarded as promising to fill the performance gap between traditional ferrite and Alnico permanent magnets (energy product $(BH)_{max}$<10 MGOe) and the RE-based magnets ($(BH)_{max}$ = 20–30 MGOe) [1]. High magnetization and appreciable magnetic anisotropy are reported for binary Mn-based alloy systems, such as MnGa [4,5], MnBi [6,7] and MnAl [8,9], — with the abundant global distribution of Mn and Al resources in the Earth's crust — have highlighted MnAl alloys as a promising choice among RE-free permanent magnets. This current work focuses on the coercivity development in MnAl powder obtained through milling and annealing by starting from $Mn_{54}Al_{46}$ alloy particles prepared by the gas-atomization technique.

The ferromagnetic τ-phase in the MnAl is metastable and forms from the non-magnetic and stable ε-phase. The mechanism of τ-phase transformation from the ε-phase is controversial. Some studies explain the origin of this transformation through a two-step process consisting first in the formation of an intermediary ε′-phase followed by a displacive shear mechanism which transforms the ε′-phase to the τ-phase [10–12]. However, other studies refer to a "massive transformation" consisting of a compositionally invariant, diffusional nucleation and growth process [13–15]. There are also reports combining both routes to explain the ε-to-τ phase transformation [16]. The structure and magnetic properties of the MnAl

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system have been widely studied because the microstructural changes and defects introduced during the metastable τ-phase transformation highly influence its magnetic properties. Studies have reported various techniques to prepare MnAl-based alloys, including hot extrusion, melt spinning, mechanical alloying, mechanical milling (MM), cryomilling, and gas-atomization [8,9,17–23]. Ball milling is a well-known technique used for microstructure refinement and strain inducement, but also for promotion of metastable phase formation. Previous studies show that high coercivities (above 4 kOe) can be achieved in MnAl after milling for a typical time duration of several to dozen of hours [20,21,24,25]. A coercivity of 5.3 kOe has been recently reported by Lu et al. [26] in isotropic MnAl powders by starting with melt-spun ribbons, annealing at 410 °C for 30 min and subsequent milling for 23 h. McCurrie et al. [27] obtained a maximum coercivity of 5 kOe for 63–75 μm particles obtained from grinding and sieving a slow cooled down MnAl ingot. Wei et al. [28] achieved the same maximum value of coercivity in MnAl melt-spun ribbons after annealing at 450 °C for 45 min followed by grinding for a shorter time of 90 min, at the expense of decreasing dramatically magnetization with increasing grinding time. Zeng et al. [9] achieved a close maximum coercivity of 4.8 kOe in pre-alloyed powders after milling for 8 h and annealing at 400 °C. Additionally, it is noted that carbon additions to MnAl stabilizes the τ-phase. Recently, a short milling time of 1–1.5 h applied to ternary MnAl-C alloys was reported to donate powder coercivities of H_c = 4.1–4.6 kOe with τ-phase and ε-phase as starting materials, respectively [24].

In this current study, we use a rapid milling process that has been proven recently to be very efficient in tuning the microstructure for optimization of permanent magnet properties in cobalt ferrite ($CoFe_2O_4$) [29]. Here we report a significant advance in binary MnAl alloys by achieving a coercivity of 4.9 kOe upon only 3 min of milling of MnAl gas-atomized particles followed by annealing at 355 °C for a short time (10 min). This annealing temperature is lower than the typical range of 400–700 °C reported in the literature [18,26,28,30,31]. In contrast with previous studies, a side-by-side comparison is provided here of the evolution of morphological, microstructural and magnetic properties with annealing temperature of the powders in the as-atomized and as-milled forms, thereby allowing the effects of milling and of annealing to be identified.

2. Experimental

The starting material was gas-atomized powders of composition $Mn_{54}Al_{46}$ (±0.4 at.%). During the gas-atomization process, the molten alloy is atomized by inert gas jets into fine metal droplets which are quenched in the atomizing tower. Further details of these powders are published elsewhere [21]. Mechanical milling in a Planetary Fritsch-Pulverisette for 3 min at rotation speed of 900 rpm was performed with tungsten carbide vials and balls with oleic acid as the surfactant. The powder-to-oleic acid ratio was 5:1, and the balls-to-powders mass ratio was 40:1. The loading and sealing of the vials were performed in an Ar-controlled atmosphere glove box. Both as-received and milled powders were annealed in N_2 with a ramp rate of 10 K/min at temperatures ($T_{annealing}$) of 350–475 °C for 10 min. The samples were structurally and morphologically characterized using a Bruker D8 Advance A25 diffractometer with Cu Kα radiation and using a Zeiss-Evo scanning electron microscopy (SEM). Average crystallite sizes have been determined from application of the Scherrer formula to X-ray diffraction (XRD) patterns. Rietveld refinement of the XRD data was carried out to analyze the phase proportions and grain sizes of the starting and milled powders. The epsilon – tau structural transformations were studied using a Perkin–Elmer DSC-7 differential scanning calorimeter (DSC), with a temperature ramp rate of 20 K/min in flowing argon gas. Upon cooling to room temperature, the samples were reheated in the DSC using the same experimental conditions to acquire a baseline for subsequent analysis. A high-purity sapphire sample in an Al pan was used as a standard for the DSC calibration. Magnetic properties were measured at room temperature using a Lakeshore 7400 series vibrating sample magnetometer with a maximum applied field of 20 kOe.

3. Results and discussion

3.1. Morphology and microstructure

XRD data and SEM images of the gas-atomized MnAl starting particles and particles milled for 3 min (prior to annealing) are presented in Fig. 1. The XRD pattern of the starting material [Fig. 1(a)] shows Bragg reflection peaks of ε- and γ_2-phases without any traces of τ-MnAl phase, within the limitations of the characterization technique, in agreement with the results of previous studies [20]. A milling time as short as 3 min is sufficient to initiate the transformation of the ε-phase into the τ-MnAl phase, as shown in Fig. 1(b), where coexistence of the three phases (τ, ε and γ_2) is found. The increased Bragg peak widths indicate reduced grain size and structural disorder induced by mechanical milling, which is typically reported for conventional milled MnAl systems (MM for 8–20 h) [9,20,21]. Average crystallite sizes ~10 nm have been determined for both the remaining ε-phase and the newly formed τ-phase in the as-milled powders. This value contrasts with the mean crystallite size much larger than 100 nm determined for the ε-phase in the starting gas-atomized MnAl particles. Rietveld refinement of the XRD results reveals that 3 min of milling leads to the transformation of ε-to τ-phase (~20 wt % content). Microstructural modification induced by this short milling time becomes obvious from a direct comparison of the SEM images shown in Fig. 1(c) and (d), respectively. Approximately spherical particles with sizes of 10–40 μm are shown in Fig. 1(c) for the gas-atomized starting material. Milling for 3 min leads to a finer microstructure with flattened irregular-shaped morphologies with particle sizes ranging from hundreds of nanometers to 10 μm in lateral size and a thickness varying from hundreds of nanometers to 1.5 μm.

DSC curves of starting and as-milled samples are shown in Fig. 2. A prominent exothermic feature in the range 425 °C < T < 500 °C is observed for the starting gas-atomized sample, which corresponds to the ε→τ phase transformation. After a 3-min milling period, the DSC data indicates that the exothermic peak shifts to lower temperatures from a peak temperature of 472 °C for the starting sample down to 395 °C for the as-milled sample. In addition, an endothermic peak appears that is partially overlapped with the exothermic peak in the annealed sample, which is composed of various processes as indicated by the maxima found at 418 and 459 °C. Such endothermic processes were previously observed at the initial steps of milling for Fe-based alloys, ascribed to the decomposition (pseudo-melting) of metastable intermetallics [32].

Fig. 3 shows XRD patterns and Rietveld refinement results of the phase fractions existing after annealing at different temperatures (350–475 °C for 10 min) for the starting gas-atomized particles [Fig. 3(a) and (b), respectively] and for particles milled for 3 min [Fig. 3(c) and (d), respectively].

Rietveld refinement indicates that the phase fraction of the starting powder is ~80 wt % ε-phase and ~20 wt % γ_2-phase. A decrease in the ε-phase fraction and an increase of τ- and β-phase content is observed with increasing the annealing temperature (T_{anneal}) [Figs. 3(a) and (b)]. The amount of γ_2-phase does not vary significantly with annealing temperature. Annealing of the as-atomized particles at T < 365 °C [Fig. 3(a)] does not cause a

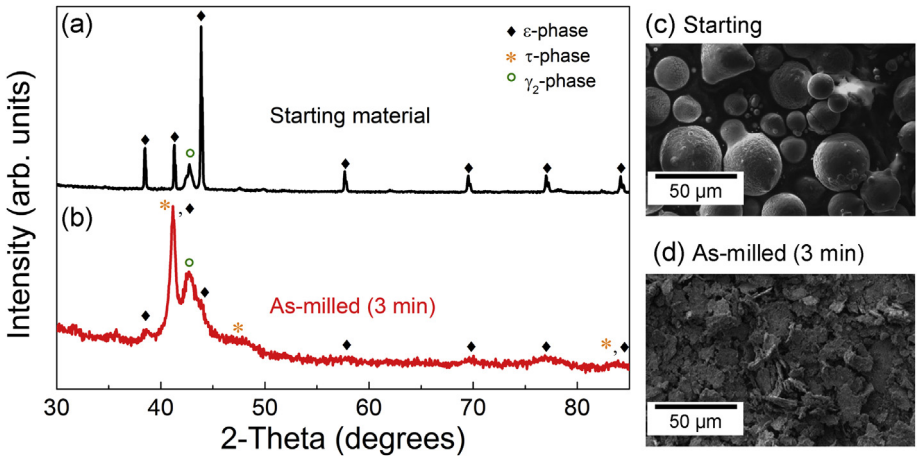

Fig. 1. XRD data of (a) starting gas-atomized MnAl particles and (b) powder after milling for 3 min. SEM images of (c) starting and (d) 3 min milled gas-atomized MnAl (scale bar: 50 μm).

significant change in the phase content of the powders, i.e., ε- and γ_2-phases [Fig. 1(a)]. However, annealing at T > 375 °C yields an increase of the content of τ-phase at the expense of the ε-phase, and is accompanied by an increase of the amount of β-phase. The intensity of the diffraction peaks corresponding to τ-MnAl phase strongly increases with increasing T_{anneal}, as shown in Fig. 3(a), signifying formation of additional τ-MnAl. The constitution of phases after annealing at the maximum temperature studied here (475 °C) is ~70 wt % τ-phase, 15 wt % β-phase and 15 wt % γ_2-phase, with no further detection by XRD of the ε-phase.

The distribution of phases is largely affected by the rapid milling procedure as a direct comparison of Fig. 3(b) and (d) indicates. As shown in Figs. 1(b) and 3(d), milling for 3 min is sufficient to begin formation of τ-phase. The general trend for the phase constitution of as-milled particles [Fig. 3(d)] is a decrease of ε- and γ_2-fraction phases with increasing T_{anneal}, which is accompanied by an increase of the β-phase fraction content and a progressive decrease of the τ-phase content (after an initial increase for T_{anneal} < 375 °C). This behavior contrasts with the phase evolution previously observed for the as-atomized material [Fig. 3(b)], with a continuous increase of the τ-phase fraction in the complete temperature range under study. These results are in agreement with the observed DSC results, which showed a shift to lower temperatures of the nucleation of τ-phase and indicate that the transformation rate of τ-phase from its parent ε-phase is dependent on the ε-phase grain size

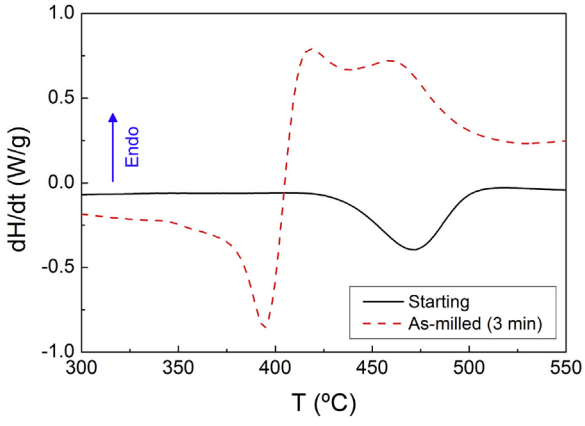

Fig. 2. DSC curves of starting (continuous line) and as-milled (dashed line) samples, measured at a heating rate of 20 K/min.

[9,21]. The rapid milling process reduces the average crystallite size from above 100 nm (starting as-atomized particles) to <10 nm, promoting the complete ε to τ transformation at T_{anneal} = 365 °C, which is below the transformation temperature of 475 °C in non-milled material and below the typical transformation temperature range of 400–700 °C reported in the literature [18,30,31]. The diffraction peaks of the β-phase shift to lower angles in comparison to a pure β-Mn phase, and the measured lattice parameter of the cubic β-phase (a = 0.6444 ± 0.003 nm) is closer to that of β-Mn_3Al_2 (a = 0.63245 nm, $P4_132$), which has been also reported for 10 h-milled MnAl-based systems [33,34]. This result might be an indication that milling followed by annealing allows the metastable τ-MnAl phase to transform into β-Mn(Al) phase, with a composition close to Mn_3Al_2. No β-Mn(Al) phase was observed prior to annealing in as-milled powders. Annealing at 375 °C for a short time of 10 min guarantees the total disappearance of the ε-phase present in the as-milled powder and results in ~30 wt% of τ-, ~50 wt % of β- and ~20 wt% of γ_2-phase fractions [Fig. 3(c)]. The rather low content of τ-MnAl phase is mainly due to the absence of 100 wt % (but 75 wt %) content of ε-phase in the starting gas-atomized MnAl particles.

3.2. Magnetic properties

Representative hysteresis curves of starting and as-milled powders prior to and after annealing are presented in Fig. 4. The starting gas-atomized MnAl powders (inset Fig. 4) are paramagnetic consistent with absence of ferromagnetic τ-MnAl in the XRD data (Fig. 3) and in accordance with previous results [20]. Ferromagnetism is detected after rapid milling of only 3 min without any post-annealing treatment, indicating the presence of the τ-MnAl phase, and consistent with the XRD results [Figs. 1 and 3(b)]. This direct transformation of ε-to τ-MnAl phase through milling with no need of annealing has been recently reported in cryomilled MnAl ribbons [12]. Mechanical milling at cryogenic temperatures suppresses the high temperatures (typically hundreds of degrees) locally achieved during conventional milling, demonstrating the possibility of direct ε-to τ-MnAl phase transformation in the process [12]. By contrast with that study, the starting material here used does not contain the τ-MnAl phase, but it is only formed after milling. The use of a very short milling time likely avoids large temperature excursions achieved when milling for long times (typically several hours). The refinement of the ε-phase through milling and the likely microstrain induced during

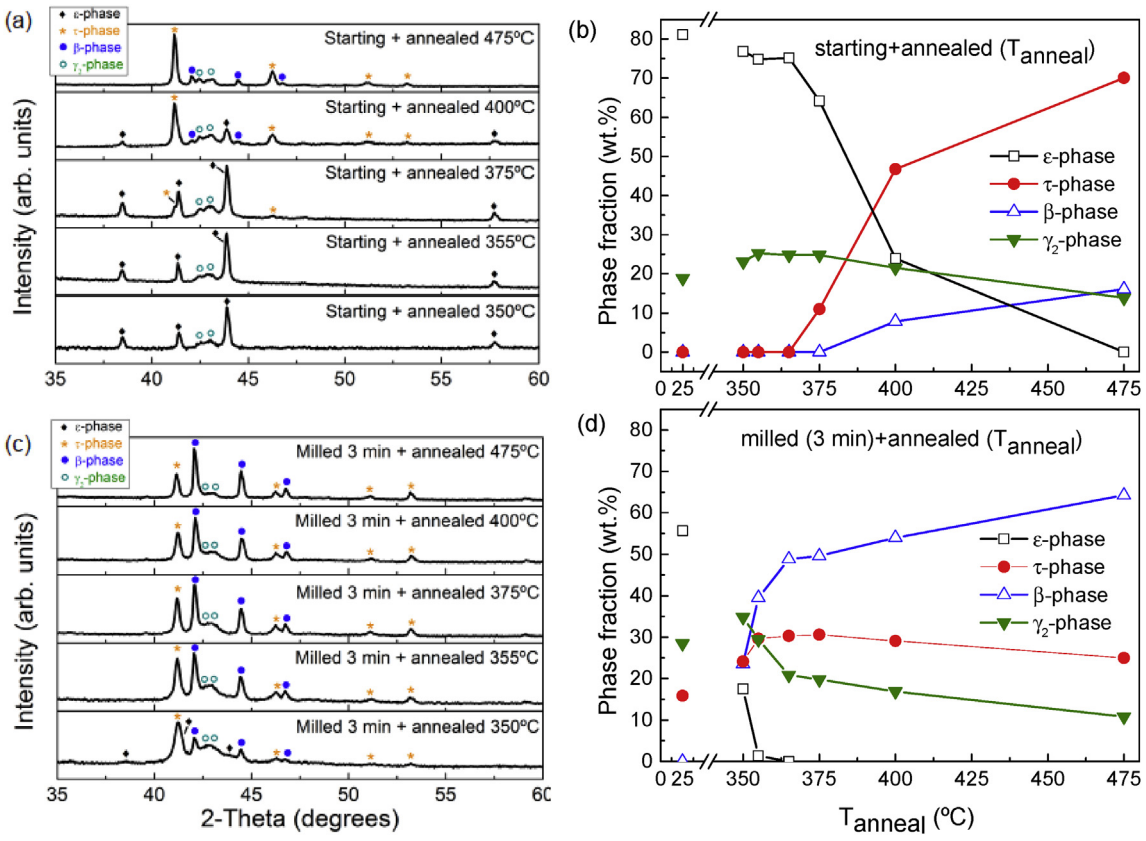

Fig. 3. XRD data of (a) starting gas-atomized MnAl material and (c) milled upon annealing. Rietveld refinement results of the existing phase fractions in (b) starting material and (d) milled samples, obtained from XRD results (a) and (c), respectively.

the process are concluded to be beneficial factors determining the ε-to τ-phase transformation during the milling process [Fig. 3(d)] [12,26]. These results are consistent with a strain induced ε-to-τ phase transformation in good agreement with the result obtained by Marshall et al. [12] by using cryomilling and, in a similar manner, with no need of annealing to ease the transformation. However, in the case of Ref. [12] the starting ribbons contained a certain amount of τ phase, which is not the case of the gas-atomized powders used in the current study.

Annealing affects very differently the shape of the hysteresis loops of the as-prepared and the as-milled powders, demonstrating the strong effect that the rapid milling procedure has on the morphology and microstructure of the gas-atomized MnAl particles (Fig. 4). Annealing of the milled powders at 355 °C results in improved magnetic properties (H_c = 4.9 kOe; M_r = 12.9 emu/g; M_s = 22.6 emu/g) relative to those measured for the gas-atomized particles after identical heat treatment (H_c = 1.8 kOe; M_r = 0.3 emu/g; M_s = 1.9 emu/g). This improvement is directly related to two factors: first, the beginning of crystallization of τ-MnAl phase in the as-milled powders, and second, to the enhanced ε-to τ-phase transformation produced by annealing the highly refined ε-phase (~5 nm grain size). Annealing at a higher temperature of 375 °C improves further the magnetic properties (Fig. 4) for both materials. This result is attributed to an increased τ-MnAl phase content (~10 and ~30 wt%τ-phase in powders milled and annealed at 375 °C and non-milled and annealed at 375 °C, respectively) as well as to microstructural changes introduced by the milling process, which directly influence coercivity. This latter aspect will be discussed in the following section.

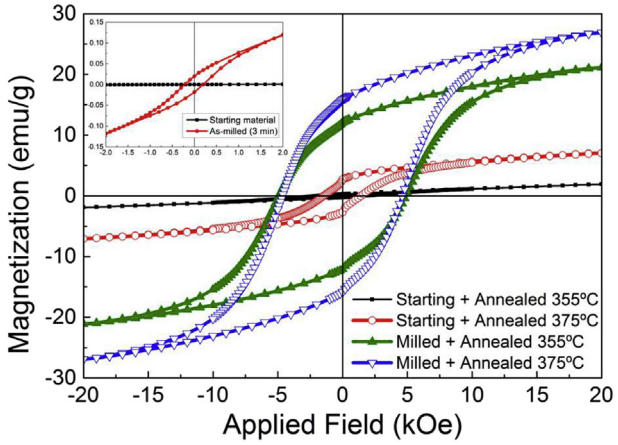

Fig. 4. Hysteresis loops of starting (gas-atomized MnAl particles) and as-milled samples annealed at selected temperatures. Inset: Hysteresis loops for starting material [square symbols] and milled (3 min) powders [circles].

Fig. 5(a) shows the evolution of coercivity with annealing temperature for the as-atomized material and the as-milled powder. The first observation is the attainment of milled and annealed powders with a coercivity that is approximately three times larger than those found in non-milled and annealed powders over the complete annealing temperature range of this study. This result indicates the effectiveness of the rapid (3 min) milling procedure to increase H_c of gas-atomized MnAl particles followed by annealing for a short time. In particular, annealing the as-milled powder at 350 °C for 10 min results in a large value of coercivity, H_c = 4.5 kOe. The largest coercivity of 4.9 kOe is obtained for the milled powders after annealing at 355 °C, while the as-atomized material shows

maximum H_c = 2.0 kOe after annealing at 365 °C. Relatively low remanence and magnetization measured at 20 kOe maximum field, M_{20kOe}, values of 7.7 and 16.4 emu/g [Fig. 5(b)], respectively, are attributed to the rather low content (about ~25 wt%) of τ-MnAl phase [Fig. 3(d)] in this stage of the processing. However, a maximum applied field of 20 kOe is not sufficient to fully saturate the samples under study, as shown in the hysteresis loops from Fig. 4. The main factors that contribute to the much larger coercivity obtained for the as-milled MnAl powders are the increased content of the hard ferromagnetic phase τ-MnAl and formation of the β-Mn phase, and the reduced grain size of the τ-MnAl phase resulting in an enlarged number of grain boundaries. The average crystallite size increased from ~20 nm (T_{anneal} = 350 °C) to ~80 nm (T_{anneal} > 350 °C) for the milled samples. Annealing at the maximum studied temperature of 475 °C yields even higher values. Annealing at 400 °C results in about ~50 and ~30 wt% content of τ-MnAl phase for the as-atomized and for the milled particles, respectively, i.e. a significantly larger fraction of τ-MnAl phase present in the former. However, the coercivity of the annealed as-atomized particles remains much lower (1.5 kOe) than that of the milled and annealed counterparts (4.6 kOe). Consequently, it is concluded that the formation of milling-induced defects may act as strong domain wall pinning centers in this system [8,12,30,31,35,36]. Based on the different phase fractions found in materials subjected to different annealing temperatures, [Fig. 3(b) and (d)], it is hypothesized that the non-magnetic β-Mn(Al) phase plays a determinant role pinning domain walls, as suggested in previous studies [8,9,23,37–40].

Magnetic remanence follows the same trend with annealing temperature as the M_{20kOe} for both starting and as-milled particles [Fig. 5(b)]. The stepped increased of M_{20kOe} and M_r with increasing

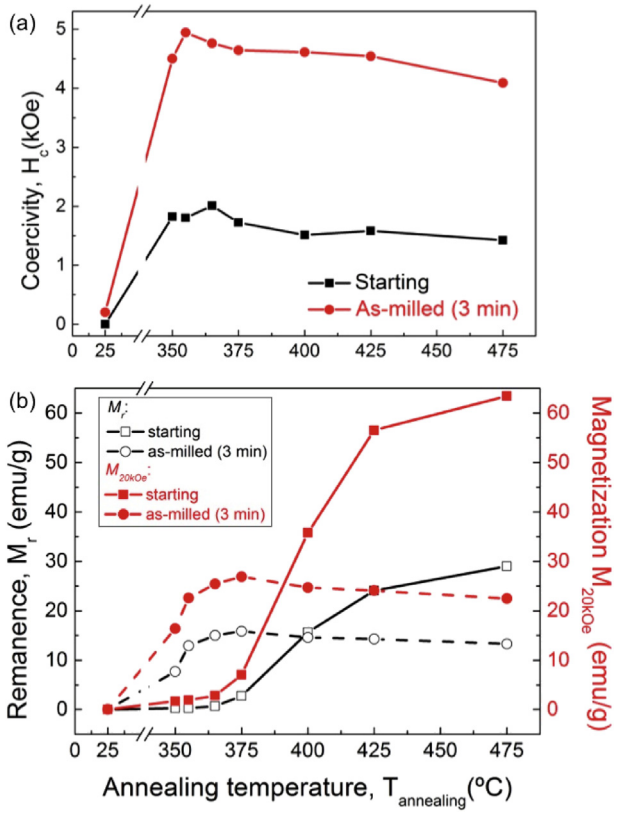

Fig. 5. Influence of annealing temperature on (a) coercivity, H_c, and (b) remanence, M_r, and magnetization measured with a maximum applied field of 20 kOe, M_{20kOe}, for non-milled and milled gas-atomized MnAl samples.

T_{anneal} measured for the starting material in the complete temperature range under study (350–475 °C), is a consequence of the enhanced content in the ferromagnetic τ-MnAl phase with annealing temperature shown in Fig. 3(b). However, for the as-milled powders, the evolution of magnetization with T_{anneal} does not follow the same evolution of τ-MnAl phase content. The magnetization values M_{20kOe} and M_r increase in the temperature range 350–375 °C while, by looking at the evolutions of the phase fractions in Fig. 3(d), the τ-MnAl phase content remains approximately constant in the range 350–375 °C. This increase in magnetization could be attributed to an enhanced order of the τ-MnAl phase in the as-milled powders achieved through annealing [23,41,42].

It is hypothesized that the highly energetic rapid milling procedure promotes the formation of τ-MnAl phase through a combination of local heating and the creation of dislocations in the starting material to promote the ε-to τ-MnAl phase transformation. However, the level of ordering of the created τ-MnAl phase has been shown to be also of importance to explain the evolution of the magnetization [9,12,20,21]. Disorder induced during milling might result in Mn atoms occupying Al sites and, consequently, decreasing the ferromagnetism due to the antiferromagnetic coupling between Mn atoms on A and B sites in the lattice, i.e. reducing the magnetization. In fact, the superlattice (100) diffraction maximum of the τ-phase is absent for as-milled powder but is detected after annealing. Subsequent annealing further promotes the ordering process and therefore increases magnetization. However, annealing above 375 °C leads to the decomposition of the τ-MnAl phase into the β-phase [Fig. 3(d)] resulting in the observed decrease in magnetization [Fig. 5(b)].

4. Conclusions

Gas-atomized MnAl particles constituted nominally by ε- and γ_2-phases have been milled for a short time of 3 min in Ar using oleic acid as a surfactant. This rapid milling procedure results in the formation of the ferromagnetic τ-MnAl phase from transformation of the initial paramagnetic ε-phase. A large coercivity of 4.9 kOe has been attained after annealing the 3-min milled powder at 355 °C for 10 min. This coercivity value demonstrates a 2.5-fold enhancement compared to the largest coercivity of its unmilled counterparts (2.0 kOe). Magnetization remains however rather low due to the reduced content (below 30 wt%) of the τ-MnAl phase obtained after milling and annealing. The large coercivity achieved in milled and annealed powders is demonstrated to result from refinement of the microstructure and to the combined effect of the transformation of ε-to τ-MnAl phase and the formation of the non-magnetic β-phase. Formation of the β-phase is promoted with increased annealing temperature and it is concluded that the β-phase plays a role in enhancing the coercivity, most likely through a domain wall pinning mechanism. This work demonstrates the possibility of achieving highly coercive isotropic MnAl powders - among the largest coercivities reported-for binary MnAl alloys- with a remarkably short milling processing time. A study recently published [43] by authors of this work details the evolution of the magnetic properties for the gas-atomized MnAl particles when varying the milling time (30-270 s).

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