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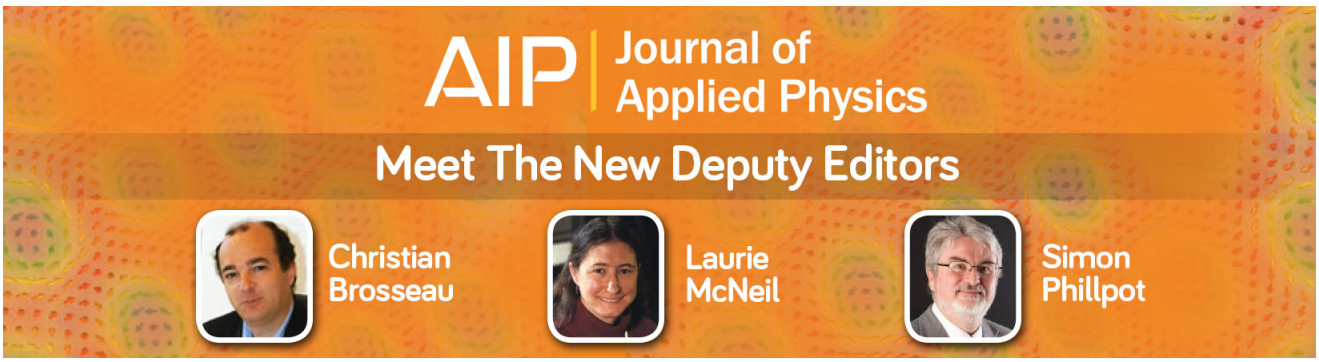

Nanostructured Mn–Al permanent magnets produced by mechanical milling

Qi Zeng[a] and Ian Baker
Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire 03755-8000

Zhi-cheng Yan
Department of Physics and Astronomy, University of Delaware, Delaware 19716

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Prealloyed powders of $Mn_{54}Al_{46}$ were mechanically milled, and the as-milled powders subsequently annealed at temperatures from 350 to 600 °C to produce the ferromagnetic $L1_0$-structured τ phase. It was found that the magnetic properties are strongly dependent on both the fraction of τ phase and the grain size. Due to the nanostructure, a large coercivity, up to 4.8 kOe, was obtained for $Mn_{54}Al_{46}$ powders annealed at 400 °C for 10 min. Both remanence curves and δM plots showed no exchange coupling between the τ-phase nanograins. The mechanism for the magnetization process was determined to be domain-wall pinning type. © *2006 American Institute of Physics*.
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I. INTRODUCTION

The ferromagnetic τ phase in the MnAl system, first reported by Kono[1] and Koch *et al.*,[2] continues to attract attention as a potentially important material for a range of technological applications requiring properties superior to conventional hard ferrites, Alnicos, and Fe–Cr–Co alloys but not as good as the rare-earth magnets. The low costs and availability of the Mn and Al, as well as the superior corrosion resistance, make these permanent magnets particularly attractive. The τ phase is metastable, and is usually produced by a rapid quench of the high temperature ε phase followed by isothermal annealing from 400 to 700 °C. Prolonged annealing results in decomposition of the τ phase to the equilibrium γ_2 and β phases.

Both mechanical alloying (MA) and mechanical milling (MM) have been used to synthesize a number of rare-earth permanent magnet alloys, including $Nd_2Fe_{14}B$,[3] $Nd(Fe,Mo)_{12}N_x$,[4] and $SmCo_5$.[5] These processing techniques can be used to produce a nanocrystalline microstructure, and they can have beneficial effects upon the magnetic properties. So far, only three studies have looked at the magnetic behavior of MA MnAl.[6–8] In one of these studies,[6] the MA powder was first consolidated, annealed at 1050 °C and then quenched, after which the material was no longer nanocrystalline. In another study,[7] a relatively high coercivity (H_C) of 3.3 kOe was obtained, but the maximum saturation magnetization (M_S) was only 20 emu/g. In the third study,[8] no hard magnetic properties could be obtained. In this paper we report that both a high H_C and a high M_S can be obtained by MM of MnAl alloys.

II. EXPERIMENT

The $Mn_{54}Al_{46}$ alloy was prepared by arc melting under an argon atmosphere. The ingots were subsequently heated to and held at 1150 °C for 20 h followed by water quenching to retain the ε phase. The crushed ingots were milled for 8 h in a hardened steel vial using a SPEX 8000 mill using hardened steels balls with a ball-to-charge weight ratio of 10:1. The vials were sealed under argon to limit oxidation. Both the as-milled powders and the quenched bulk samples were annealed at temperatures from 350 to 600 °C for 10 min to produce the ferromagnetic $L1_0$ τ phase.

The magnetic properties were measured at room temperature using a LakeShore 7300 vibrating-sample magnetometer (VSM) under an external magnetic induction field of 15 kOe. Some samples were also measured with an Oxford superconducting quantum interference device magnetometer (SQUID) under a field of 50 kOe. Microstructural characterization was performed using a Siemens D5000 diffractometer with a Cu x-ray tube and a KeVex solid-state detector set to record only Cu $K\alpha$ x rays.

III. RESULTS AND DISCUSSION

X-ray-diffraction pattern for the as-milled alloy showed peaks corresponding to hcp ε phase of the MnAl system. As shown in Fig. 1(a) the diffraction peaks were broad and of low intensity, indicative of a nanocrystalline grain structure. The grain size calculated from the (111) x-ray peak using the Scherrer formula is 8 nm. Annealing the as-milled sample of $Mn_{54}Al_{46}$ at 400 °C for 30 min caused the ε phase to transform to the fct τ phase [Fig. 1(b)]. The calculated τ-phase grain size was ~27 nm, which is much smaller than that produced by conventional casting, grinding, or extruding.[9,10] This is a result of the τ phase forming from the ε phase with a nanocrystalline grain structure. Increasing the annealing temperatures causes decomposition of the τ phase to the equilibrium nonmagnetic phase(s) [Fig. 1(c)]. Annealing at 600 °C for 30 min resulted in little of the τ phase [Fig. 1(d)].

Measurements showed that all the materials produced in this work were magnetically isotropic. Figure 2 shows the dependence of M_S and H_C on annealing temperatures for both MM and bulk $Mn_{54}Al_{46}$. The M_S for MM $Mn_{54}Al_{46}$ increases from 350 to 400 °C, then decreases with increasing annealing temperature from 400 to 600 °C. This is consistent with the x-ray-diffraction (XRD) data that the volume

[a]Electronic mail: qi.zeng@dartmouth.edu

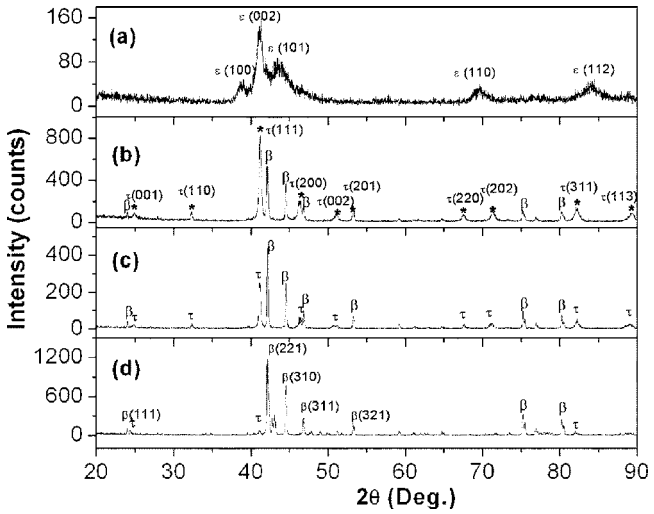

FIG. 1. XRD patterns of $Mn_{54}Al_{46}$ for (a) as-milled and annealed for 30 min at (b) 400 °C, (c) 500 °C, and (d) 600 °C

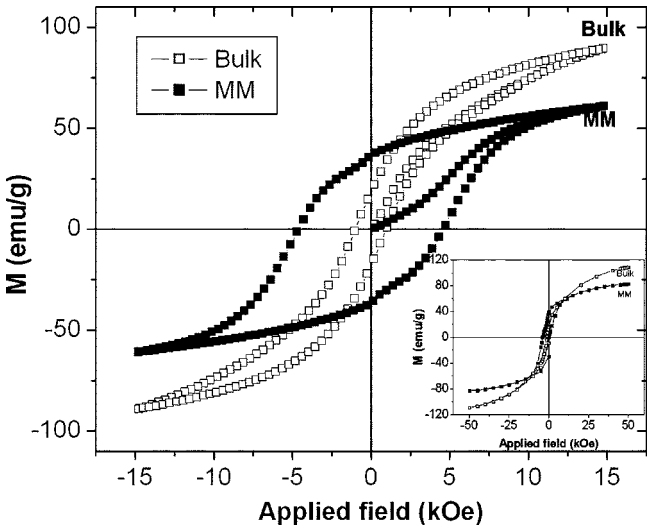

FIG. 3. Hysteresis loops for bulk and MM $Mn_{54}Al_{46}$ powders annealed at 400 °C for 10 min (inset contains the same loops measured at 50 kOe).

fraction of the magnetic τ phase decreases with annealing temperatures above 400 °C. For bulk samples, the M_S tends to increase with increasing annealing temperature from 300 to 500 °C. The H_C changes a little from 350 to 500 °C for MM samples. The optimal magnetic properties for MM samples, H_C=4.8 kOe and M_S=87 emu/g, were obtained for $Mn_{54}Al_{46}$ powders annealed at 400 °C for 10 min. These values are the highest reported for Mn–Al–C magnetically isotropic powders. In general, the M_S obtained in annealed MM samples was lower than that obtained in bulk samples, while the H_C was higher, due to the small τ-phase grain size. Figure 3 shows the hysteresis loops for both MM and bulk $Mn_{54}Al_{46}$ samples annealed at 400 °C for 10 min. For the MM sample, the remanence ratio M_r/M_S is 0.63 when the applied field is 15 kOe, which seems to be the characteristic of nanostructured exchange-coupled materials. However, the loop is far away from saturation, M_r/M_S tended towards 0.5 when the applied field increased to 50 kOe (see inset of Fig. 3). It is worth noting that the samples were still unsaturated under a field of 50 kOe. This is a characteristic of MnAl ferromagnetic alloys.[11]

Remanence curves and δM plots[12–14] were used to study the interaction between the τ-phase grains. The dc demagnetizing (DCD) curve charts the progress of the irreversible changes in magnetization. The isothermal remanence (IRM) curve contains contributions from both reversible and irreversible magnetization processes. δM is defined as $M_d(H) - [M_r(H_{sat}) - 2M_r(H)]$. A plot of δM against H therefore gives a curve characteristic of the interactions present. Figure 4 shows the δM curves for both MM and bulk samples annealed at 400 °C for 10 min. The overall negative and small δM for MM sample indicate that most of the τ-phase nanograins are isolated with only a small amount of dipolar interactions between them. No exchange coupling existed in this nanostructured material which explains why the remanence ratio is close to 0.5.

Figure 5 shows the dependence of the coercive force of both the MM and bulk samples on the magnetic-field strengths. It can be seen that the MM curve rises gradually at low fields until the field strength approaches H_C (5 kOe), when it rises quickly to saturation. This behavior indicates that the applied field gradually removes the domain walls from their pinning sites. This suggests that the mechanism for the magnetization process of the MM material is controlled by domain-wall pinning. The nonmagnetic phase(s) present could act as the pinning sites.

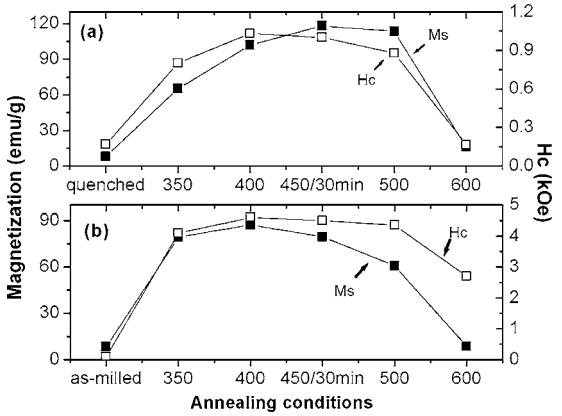

FIG. 2. Dependence of the M_S and H_C on the annealing temperatures for (a) bulk, and (b) MM $Mn_{54}Al_{46}$ annealed for 30 min.

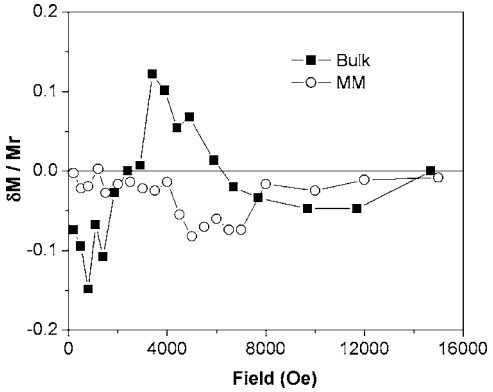

FIG. 4. δM curve for both MM and bulk samples annealed at 400 °C for 10 min.

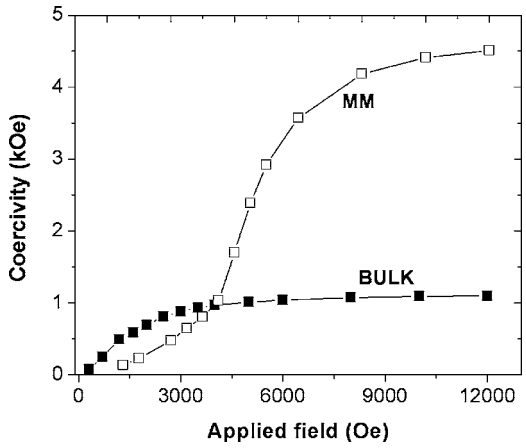

FIG. 5. The dependence of the H_C on the magnetic-field strength.

IV. CONCLUSIONS

The $L1_0$-structured τ phase in the Mn–Al system was produced by mechanical milling and subsequent annealing. The optimal magnetic properties, H_c=4.8 kOe and M_S =87 emu/g, were obtained for $Mn_{54}Al_{46}$ powders annealed at 400 °C for 10 min. These values are the highest reported for Mn–Al–C magnetically isotropic materials. The small grain size resulted in very high coercivity. Remanence curves and δM plots showed no exchange coupling in this nanostructured material. Measurements of the dependence of the coercivity on the magnetic-field strength suggested that magnetization reversal was domain nucleation controlled, and that the nonmagnetic phase(s) present could act as the pinning sites.

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