

Towards rare-earth-free permanent magnetic materials – thermal evolution of magnetic and structural properties in nanostructured MnAl

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Introduction:

The high cost of strategic elements (*i.e.* rare-earth metals, REs) used in strong permanent magnetic materials (PMMs) employed in advanced applications has reinvigorated research into the development of alternative magnetic materials [1, 2]. Nanostructured magnetic systems consisting of ferromagnetic (FM) and antiferromagnetic (AF) phases hold promise as novel RE-free PMMs as a result of the potential for large resistance to demagnetization (or intrinsic coercivity, H_{ci}) and high magnetization. Exchange interactions between FM and AF phases can result in useful effects such as exchange bias (H_{ex} , the unidirectional shift of the magnetic hysteresis loop to stabilize H_{ci}) and remanence enhancement (increase of the magnetic remanence, M_r , to augment the magnetic flux, B) [3]. Understanding the magnetic and structural attributes responsible for these effects in FM/AF nanocomposites is anticipated to allow tailoring of the magnetic response. The present work focuses on elucidating the magnetic and structural properties of MnAl(C) alloys, synthesized by the non-equilibrium technique of rapid solidification via melt spinning to access and retain metastable nanostructured states.

Materials and Methods:

Ribbons of nominal composition Al₄₅Mn₅₅ were melt-spun under a He atmosphere at a wheel speed of 64 m/s, then isochronally annealed under vacuum (30 min intervals) at low temperatures (T) to induce progressive changes in the structural and magnetic properties. The volume-averaged chemical composition was determined using energy-dispersive x-ray spectroscopy (EDX). The crystal structure was examined by x-ray diffraction (XRD). The magnetic response was probed by superconducting quantum interference device (SQUID) magnetometry. The thermal character of all structural and corresponding magnetic transformations was evaluated using differential scanning calorimetry (DSC).

Results:

The compositional homogeneity of melt-spun Al₄₅Mn₅₅ is verified to within ± 1 at.% Mn on the microscale by EDX measurements. Structural data collected on the as-spun ribbons with XRD (Fig. 1) reveal two dominant hexagonal phases (*hcp-1* and *hcp-2*) with unit cell lattice parameters (a , c) and corresponding unit cell volumes (V) which evolve with annealing. Heat treatment at a slightly elevated $T_{\text{anneal}} \sim 345$ °C results in the formation of an additional face-centered-tetragonal (*fct*) phase (Fig. 1).

Magnetic data reveal two contributions to the field-cooled magnetization at 10 K (Fig. 2) – (i) *contribution-1* has a large rectangular shape and a sizeable exchange bias (H_{ex}) shift of ~ 13 kOe and (ii) *contribution-2* is evidenced by small bumps at low H with no H_{ex} shift – which both evolve with annealing. Heat treatment at low T_{anneal} causes a gradual decrease in the H_{ex} shift of *contribution-1* and causes the low- H fluctuations from *contribution-2* to slowly grow. Subsequent annealing at $T_{\text{anneal}} \sim 345$ °C results in both an abrupt order-of-magnitude rise in the saturation magnetization (M_s) of *contribution-2* and a simultaneous precipitous decline in the H_{ex} shift of *contribution-1*. Measurement of the thermal character by DSC demonstrates that an

exothermic transformation begins slowly around $T \sim 320$ °C and occurs only in the initial heating curve.

Discussion and Conclusions:

Preliminary interpretations of these data obtained from melt-spun $\text{Al}_{45}\text{Mn}_{55}$ suggest that nanoscopic fluctuations in the local Mn content cause a structural and corresponding magnetic phase separation into regions of Mn-rich and Mn-poor *hcp* phases with ferromagnetic (FM) and antiferromagnetic (AF) character, respectively [4]. Exchange interactions between these regions produce the large H_{ex} values observed in *contribution-1* at low T . The simultaneous increase in M_s of both contributions and decrease in the H_{ex} of *contribution-1* point to a decrease in AF character in *contribution-1* as a result of heat treatment at low T_{anneal} (Fig. 2). Magnetic and structural data indicate that further annealing at a slightly elevated $T_{\text{anneal}} \sim 345$ °C causes the rapid nucleation of a higher-magnetization FM phase (*i.e.* *contribution-2*) with a *fct* structure at the expense of the *hcp* phases, as the result of an irreversible exothermic transformation event.

Future Work:

Further investigations will be aimed toward augmenting the FM response by implanting nanostructured $\text{Al}_{45}\text{Mn}_{55}$ in a Fe matrix and developing correlations between the magnetic and structural behaviors in the new nanocomposites.

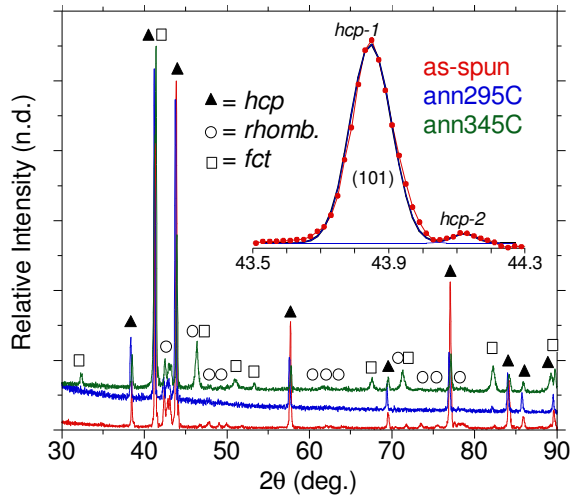


Fig. 1. Change in XRD patterns with heat treatment. Inset: *hcp* (101) peak.

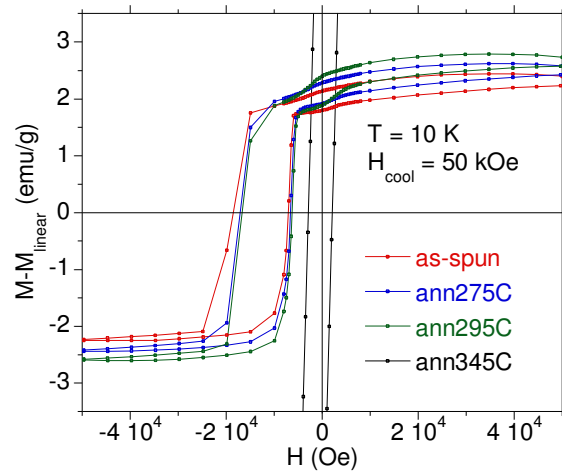


Fig. 2. $M_{\text{FC}}(H)$ @ 10 K as function of annealing temperature.

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References:

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