Abstract

Mn-based alloys are generally thought to be the potential rare earth free permanent magnets with acceptable magnetic properties due to its available high magnetization and anisotropy field. In this work, MnAl and MnGa based alloys have been investigated regarding to their processing, structures and magnetic properties. MnAl based alloys with various C additions and/or trace rare earth doping were prepared by melt spinning. The phase transitions during rapid quenching and post annealing were investigated. The composition and annealing process dependent magnetic properties were obtained. The anisotropic MnAlC flakes with improved magnetic properties were also fabricated by surfactant assisted ball milling using alloy ingot as the precursor. The effects of ball milling and post annealing processes on the phase structure and magnetic properties were discussed. As for Mn-Ga alloy, Mn$_7$Ga$_3$ binary alloy were prepared by melt spinning followed by post heat treatment. The preliminary results show relatively high coercivity. In addition, the prospect of MnAl and MnGa based alloys for permanent magnet applications were discussed in this paper.

Keywords: Permanent magnet; Mn-Al based alloys; Mn-Ga alloy; Melt spinning; Surfactant assisted ball milling.

Introduction

As is well known, rare earth (RE) resource has become a major concern in the international community. Developing strong permanent magnets without RE elements is urgently in need. Current interests towards RE free magnets have been aimed at Mn based compounds [1]. The fundamental behind this is that Mn atom has large atomic magnetic moment. For the alloys with only one magnetic element of Mn, the magnetic moment strongly depends on the atomic distance [2]. Currently, three types of Mn-based alloys, MnAl, MnBi and MnGa, are suggested to be good hard magnets with acceptable properties. They all have high magnetic anisotropy, typically higher than 1×10$^6$ erg/cc, at room temperature. For MnBi alloys, high coercivity ($H_c$) value (>10 kOe) can be obtained at even 150°C. MnAl compound is characterized with relatively high saturation magnetization $M_s$ (7200emu/cc) and relatively high Curie temperature $T_C$ (380°C). For MnGa compound, the exchange interactions of ferrimagnetism or ferromagnetism can be modified by adjusting the Mn content, and good hard magnetic properties were also reported. Most importantly, these RE-free magnets can be produced by cost-effective and sustainable manufacturing processes [1,2].

Mn-Bi alloys have been extensively studied due to their low temperature hard magnetic phase, and their magnetic properties increase with increasing temperature in a certain range. They can be prepared by various processes including melt spinning, ball milling, etc. Excellent magnetic properties have been obtained [3]. For Mn-Al alloys, the existing results [1] show that the alloys slightly above the equi-atomic composition have superior mechanical strength, excellent machinability and reasonable magnetic properties. Their theoretical maximum energy product ($BH_{max}$), magnetocrystalline anisotropy field $H_A$ and $M_s$ are reported to be 101 kJ/m$^3$, 3024 kA/m and 0.96 T, respectively [4]. Its hard magnetic properties derived from the formation of a L1$_0$ intermetallic phase (tetragonal τ-MnAl) with strong uniaxial magnetocrystalline anisotropy [5-7]. Unfortunately, the L1$_0$ (or τ) phase is a metastable one forming from a quenched-in high-temperature antiferromagnetic hexagonal disordered ε-phase (Neel temperature $T_N = 97K$) by annealing at ~550°C [8]. The addition of a small amount of carbon was found to stabilize the τ phase and prevents the decomposition of the alloy into the stable but nonmagnetic γ (Al,Mn) and β (Mn) phases. Some investigations showed that the alloy with 1.7 at.% C have the best hard magnetic properties since the uniformly dispersed fine MnAlC phases in τ phases can pin the domain wall and improve the coercivity [4,9-11]. The best magnetic properties with ($BH_{max}$) up to 64.4 kJ/m$^3$ were reported in an anisotropic Mn-Al-C alloy obtained by high-temperature extrusion [12,13]. Despite above progress, Mn-Al-based alloys have not been fully studied and explored, possibly due to the existing of the RE magnets with extremely high magnetic properties. There are not many publications on Mn-Al alloys since early this century except some work on Mn-Al thin films [14,15]. In particular, except the work
by Fazakas et al. [16] and our recent work [17], synthesis of MnAl
based hard magnetic alloys by rapid quenching has received
almost no attention. The MnAl magnets with elemental addition
other than C have also seldom been reported. In addition, up to
now, MnAl-based hard magnetic alloys have not been prepared
by surfactant-assisted ball milling (SABM) technique yet. As is
well known, SABM has drawn great attention recently for the
fabrication of high performance anisotropic NdFeB [18,19] and
SmCo [20-22] hard magnetic nanoparticles and sub-micro-
flakes with controlled particles size and shape.

Another Mn based alloy, Mn-Ga, has also been reported to
possess large $H_C$ value due to the formation of ferromagnetic
MnGa phase or ferromagnetic Mn$_3$Ga phase [23]. Recent work
[12,22] has shown very good properties in Mn-Ga thin films,
but preparations of bulk Mn-Ga alloys or Mn-Ga powders with
expected hard magnetic properties have not been very successful
[24]. Investigations of Mn-Ga alloys fabricated by conventional
methods like melt spinning or ball milling are, therefore, of
significance.

In this paper, we report the composition and process dependent
properties of MnAl(C,RE) alloys prepared by melt spinning. Both
heavy RE element Dy and light RE element Pr were employed
to investigate the effect of RE on the magnetism of Mn based
alloy. The phase transformations and the effect of heat treatment
on MnAlC alloys prepared by SABM were also investigated. The
formation mechanism of submicron flakes has been discussed.

In addition, the preliminary work on Mn$_{55}$Ga$_{30}$ alloy prepared
by melt spinning is described here.

**Experimental**

Both melt spinning and ball milling processes were employed
to achieve expected structure and properties in MnAl based
alloys. For melt spun alloys, Mn-Al ingots with various nominal
compositions, including Mn$_{55}$Al$_{45}$C$_{3}$ and Mn$_{52.3}$Al$_{45}$C$_{1.7}$RE$_{1}$
(RE=Pr or Dy) were prepared by argon arc melting. Pr and Dy
were chosen as the doping RE elements since they represent the
typical light and heavy RE element, respectively, and may give
various magnetism. Special care has been paid to melting the
alloys due to the big differences in the melting point and saturated
vapor pressure for the raw materials of Mn, Al and C. The as-cast
ingots were used to fabricate ribbon samples by a single-roller
melt spinning technique under argon atmosphere at a wheel
speed of 50 m/s. Selected ribbons were annealed at 500~650°C
for 30 min to produce the ferromagnetic L1$_0$ $\tau$-phase.

As-milled powders were annealed at temperatures from 400
K to 650 K for 1 h.

The phase structure of the samples was examined by X-ray
diffraction (Philips, Cu Ka radiation). Differential scanning
calorimeter (Perkin-Elmer TGA7) was employed to study the
structural transformations in selected temperature range with
temperature increase rate of 20°C/min. The magnetic properties
at various temperatures were characterized by a PPMS (Quantum
Design Co.) equipped with a VSM using an applied field of 5
T. The alloys composition was characterized by X-ray energy
disperse spectrum (EDS). The microstructure was characterized
by scanning electronic microscopy (SEM).

**Results and Discussion**

MnAl based alloys produced by melt spinning

Mn-Al(C) and Mn-Al-C-Pr/Dy alloys with selected compositions
were prepared by melt spinning. The final compositions of the
ribbons have been confirmed very close to the nominal
compositions based on the statistical Energy-dispersive X-ray
spectroscopy (EDS) analysis on selected samples [17]. The XRD
patterns for as-spun ribbons are shown in Figure 1.

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**Figure 1:** XRD patterns for as-spun MnAl based alloys with various compositions

All alloys have a single phase structure consisting of pure $\varepsilon$ phase. The C, Pr and Dy additions have no significant effect on
the phase structure.

DSC analysis was carried out to investigate the phase transition
temperatures. As shown in Figure 2.

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**Figure 2:** DSC curves for melt spun alloys: (a) Mn$_{55}$Al$_{45}$ (b) Mn$_{54}$Al$_{45}$C (c) Mn$_{52.3}$Al$_{45}$C$_{1.7}$ (d) Mn$_{52.3}$Al$_{45}$C$_{1.7}$Pr (e) Mn$_{52.3}$Al$_{45}$C$_{1.7}$Dy

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All compositions exhibit at least two phase transitions on heating from room temperature to 900°C. For Mn$_{55}$Al$_{45}$ alloy, the sharp exothermal peak at 484.7°C corresponds to the structural transformation of the quenched-in ε-phase to the metastable magnetic τ-phase. The endothermic peak around 850°C corresponds to the transformation of the τ-phase back into the non-magnetic ε-phase. The endothermic peak around 875°C indicates the precipitations of β phase and γ phase [17]. For C added alloys, only two peaks appeared. The first peak at 500–550°C and the second peak around 800°C correspond to ε→τ and τ→ε transformations, respectively, as above. 1% C addition reduces the τ→ε transformation temperature from ~850 to < 800°C. C and RE additions change the ε→τ transformation temperature but have no significant effect on the τ→ε transition. C slightly increases the ε→τ transformation temperature and Pr or Dy also pushes this transformation to higher temperature. The results indicate that C can stabilize the τ-phase and prevent it decomposition into nano-magnetic phases.

Based on DSC results, all samples were annealed at 500~650°C to obtain hard magnetic τ phase. L10 phase has been formed for all samples. Table 1 also shows the $T_c$ of MnAlC alloys with various C contents annealed at various temperatures. Table 1 shows the values of Curie temperature $T_c$ determined from the inflection points of M–T curves, for MnAlC alloys with various C contents after annealing at optimized temperatures. It is found that $T_c$ is very sensitive to the C concentration. A linear decrease of $T_c$ with C concentration is demonstrated. Introducing 1, 1.7, and 2 at.% C to Mn$_{55}$Al$_{45}$ alloy reduce the $T_c$ from 346 to 292, 268 and 258°C, respectively. This large drop of $T_c$ caused by C doping possibly explains the large discrepancy between the previous results obtained by Zeng et al. [11] and Fazakas et al. [16]. Inevitable carbon loss likely occurred in Zeng’s samples. Table 1 also shows the $T_c$ of τ phase for MnAlC alloys.

![Figure 3: XRD patterns for the alloys annealed at 600 °C or 550°C](image)

The binary Mn-Al alloy consists of mixed $\gamma$, $\beta$ and τ phases. With increasing temperature from 550°C to 600°C, the contents of $\gamma$ and $\beta$ phases increase at the expense of τ phase. The results clearly show that τ phase decomposed into the stable $\gamma$ and $\beta$ phases in the binary alloy. A small amount of C addition indeed stabilizes the hexagonal metastable L10 phases and prevents the ε phase’s decomposition into $\gamma$ and $\beta$ phases [6,17]. Also, co-doping Pr or Dy with C did not change the phase structure of heat treated Mn-Al-C alloys.

The magnetic properties of Mn-Al-C alloys annealed at various temperatures are shown in Figure 4.

The binary Mn$_{55}$Al$_{45}$ alloy has relatively low magnetic properties due to the mixed phase structure of τ, $\beta$, and $\gamma$ phases. C addition improves the hard magnetic properties since it promotes the precipitation of τ phase and also stabilizes the τ phase, as discussed as above. High $H_C$ of τ phase increases the coercivity of the sample. It is indeed found that the MnAlC alloy with 1.7 at.% C has the best combined magnetic properties.

![Figure 4: Magnetic properties for MnAl(C) alloys with various C contents annealed at various temperatures](image)

Table 1: The Curie temperature $T_c$ for MnAl based alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mn$<em>{53}$Al$</em>{45}$</th>
<th>Mn$<em>{52}$Al$</em>{45}$C$_1$</th>
<th>Mn$<em>{53}$Al$</em>{45}$C$_{1.7}$</th>
<th>Mn$<em>{53}$Al$</em>{45}$C$_2$</th>
<th>Mn$<em>{53}$Al$</em>{45}$C$_{1.7}$Pr$_1$</th>
<th>Mn$<em>{53}$Al$</em>{45}$C$_{1.7}$Dy$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$, °C</td>
<td>346</td>
<td>292</td>
<td>268</td>
<td>258</td>
<td>264</td>
<td>267</td>
</tr>
</tbody>
</table>

Note: the estimated error is ±1 °C.

with 1.7 at.% C and 1% RE additions. $T_c$ slightly decreases from 268 to 264 or 267°C for Pr or Dy additions, respectively.

Figure 5 shows the demagnetization curves at 5K for C and/or RE doped alloys after optimized annealing. It clearly shows the differences in $I_s$, $J_s$ and $H_c$ for all alloys. C addition improves the hard magnetic properties of the binary alloys by promoting the formation of hard phase. Addition of Pr can slightly improve the $I_s$, $J_s$ and $(BH)_{max}$, but the effect of Dy on magnetization is not positive and it only slightly enhances the coercivity. The effects of RE on the MnAlC are possibly related to the magnetic moment of RE atoms and the exchange interaction between the Mn and RE atoms. Pr and Dy doping can enhance the anisotropy and increase the atomic distance between Mn atoms [25]. The best properties were obtained in C and Pr co-doped MnAl alloy.

MnAlC flakes prepared by surfactant assisted ball milling (SABM)

SABM has been newly developed for preparing hard magnetic anisotropic NdFeB and SmCo powders [18,20]. This method has been employed for MnAlC powders in this work. XRD patterns of the Mn$_{51}$Al$_{46}$C$_3$ ingot and SABMed powders in Figure 6 indicate pure $\varepsilon$-phase. The broaden peaks for SABMed powders indicate nanocrystalline structures. The powders also show a strong (001) crystal texture. With increasing milling time from 1 to 4 hours, an increasing structural anisotropy is evident. After milling for longer time, the intensity of XRD peaks decreases gradually, resulting from the partial amorphization of the powders.

Figure 5: Demagnetization curves at 5K for optimally heat treated alloys

Figure 6: XRD patterns of Mn$_{51}$Al$_{46}$C$_3$ for bulk and as-milled powders

Figure 7 shows the XRD patterns for Mn$_{51}$Al$_{46}$C$_3$ powders after 12 h milling and annealing at various temperatures for 30 min. Different from Mn$_{54}$Al$_{46}$ alloy [26,27] annealing the as-milled Mn$_{51}$Al$_{46}$C$_3$ caused the $\varepsilon$-phase to completely transform into $\tau$-phase, even for the milling time up to 12 h. It is confirmed again that C stabilizes the $\varepsilon$-phase. Annealing at 400~500°C transforms $\varepsilon$ phase into $\tau$-phase completely. However, elevating the annealing temperature to 550°C resulted in a decomposition of $\tau$-phase into the non-magnetic $\beta$+$\gamma$ phases. The decomposition becomes more serious with increasing temperature to 650°C.

Figure 7: XRD patterns of Mn$_{51}$Al$_{46}$C$_3$ powders annealed at 400~650°C for 30 min

Figure 8 shows the SEM images of as-milled and annealed Mn$_{51}$Al$_{46}$C$_3$ flakes. High-aspect ratios are obtained in the flakes after milling for different time. From the structural examination, crushed MnAlC ingots were mainly composed of microm-sized particles 1-400 μm in size. After milling for up to 1 h, the powders were mainly composed of micron-sized MnAlC flakes with a thickness of 10 μm and a length of 20-150 μm. After 4 h milling the powders were mainly composed of submicron-sized flakes with thickness of 280-840 nm and length of 1-110 μm. With increasing milling time from 4 to 8 h the thickness and average length of the nanoflakes decreased significantly. The average thickness and length of the Mn$_{51}$Al$_{46}$C$_3$ flakes decreased to 132 nm and 54 μm for 8 h milling, respectively. In addition, no obvious changes were detected from the average thickness and length of the flakes before and after annealing.

The formation of MnAlC micron/submicron flakes and their subsequent transformation to texture nanoflakes during the SABM is similar to that for NdFeB [18] or SmCo [21]. In brief, the structure evolution and texture formation for the MnAlC flakes consist of the following steps: First, the internal strain in the particles increased rapidly at the beginning of ball milling, and the starting powders break into tens of microns or micron sized irregular particles. Secondly, the micro-sized particles cleaved along the easy glide basal planes to form submicron flakes. Thirdly, continuation of the cleavage of the easy glide planes via layer by layer peeling or plane splitting leads to the formation of the texture flakes. The surfactant plays multiple roles in the milling process, including preventing cold welding of crushed particles, keeping dispersion of nanoparticles, and reducing contamination during milling. Surfactant covering a particle or flake can also lower the energies of freshly cleaved surfaces, enable long-range capillary forces and lower the energy required for crack propagation [28,29].

The demagnetization curves for SABMed MnAlC powders annealed at 500°C are shown in Figure 9.
The coercivity and remanence ratio $J_r/J_s$ of bulk materials without ball milling are 106 kA/m and 0.26, respectively. Whereas for the powders subjected to ball milling, the coercivity has been enhanced. In addition, $J_r/J_s$ has also been enhanced by ball milling. For example, the coercivity increased from 106 kA/m for the as-cast bulk sample to 148 kA/m for 1h milling. Between 1~4 hours milling, the coercivity did not change much, but it abruptly increased from 168 to 214 kA/m with further milling from 8 to 12 h. The variation in coercivity may be explained by the dependence of $H_c$ on the τ-phase microstructure and the particle size reduction [12,29]. For those with milling periods of 1–12 h, higher $H_c$ value originates from MnAlC powders with the fct structure. The enhancement of $J_r/J_s$ may be contributed from the exchange-coupling interaction between the nanoscale hard grains [29].

The magnetization is about 68.8% of the theoretical value of 0.96T. The highest $H_c$ of 243 kA/m was also obtained in Mn$_{51}$Al$_{46}$C$_3$ annealed at 450°C. These values are much higher than that for melt spun ribbons, as shown early.

**MnGa alloys prepared by melt spinning**

Mn–Ga system has exhibited complicated binary phase diagram, characterized by several magnetic phases: $\eta$, $\gamma_1$, $\gamma_2$, and $\tau$. It has been reported that MnGa and Mn$_3$Ga have potential for permanent magnets. Hyh et al [24], investigated the nanostructured Mn$_3$Ga ribbons with various concentrations prepared by melt-spinning and heat treatment. Their results show that the material with $y = 1.2$, 1.4, and 1.6 prefers the tetragonal L1$_0$ structure and that with $y = 1.9$ prefers the D0$_{22}$ structure. A $M_s$ of 621 emu/cm$^3$ was found in Mn$_{1.2}$Ga alloy. Both the L1$_0$- and D0$_{22}$-Mn$_y$Ga samples show a high $T_c$ well above room temperature. The observed magnetic properties of the Mn$_y$Ga ribbons are consistent with the competing ferromagnetic coupling between Mn moments in the regular L1$_0$-MnGa lattice sites and antiferromagnetic coupling with excess Mn moments occupying Ga sites. In the present work, our preliminary work focused on the Mn$_{70}$Ga$_{30}$ alloys with Mn$_3$Ga phase. Due to the low vaporization point of metal Mn (~1900°C) and low melting pint of Ga, it is a challenge to obtain Mn-Ga alloys with pre-designed nominal compositions. By the precious process control of argon melting, we are able to target the objective composition. Table 2 shows the DES result of the compositional analysis for melt spun Mn$_{70}$Ga$_{30}$ alloy, demonstrating that the actual composition of our alloy is very close to the target composition.

Table 2: Objective and actual compositions for melt spun Mn-Ga alloy analyzed by EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>Objective concentration (at.%)</th>
<th>EDS results (at.%)</th>
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<tbody>
<tr>
<td>Mn</td>
<td>70</td>
<td>69.49</td>
</tr>
<tr>
<td>Ga</td>
<td>30</td>
<td>30.51</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 11 shows the surface image of as spun Mn$_{70}$Ga$_{30}$ ribbon prepared at a wheel speed of 50 m/s. As spun alloy has uniform grain size around 1μm. It indicates that Mn–Ga alloys have relatively low glass formability and it is relatively difficult to achieve nanocrystalline structure and amorphous structures, which are different from NdFeB based hard magnetic alloys [30].

Figure 12 shows the XRD patterns for the as spun Mn-Ga alloy and the alloys after heat treatment at various temperatures. Mn$_3$Ga phase appears in all alloys. With increasing annealing temperature from 673 to 973K, the XRD peak intensity increases. Further increase of temperature to 1073K, the peak intensity decreases, possibly due to the start of an phase transition. The phase structure of the obtained Mn-Ga is D0$_{19}$-Mn$_3$Ga and no D0$_{22}$-Mn$_3$Ga phase was found. It was reported that the magnetic properties of D0$_{19}$-Mn$_3$Ga phase is much lower than that of D0$_{22}$-Mn$_3$Ga phase.

Relatively low $J_s$ and $J_r$ were obtained, resulting from the weak magnetism of this D0$_{19}$ phase. However, the $J_s$ and $H_c$ can be greatly improved by heat treatment. After heat treated at 873K for 1 h, the $H_c$ of 6.72 kOe and $J_s$ of 6.15 emu/g can be obtained. To explain the reason for the dependence of $H_c$ on the annealing temperature, thermal analysis of DSC was carried out for the as spin Mn$_{70}$Ga$_{30}$ alloy. Figure 13b shows no DSC peak below 1000 K, indicating no first order phase transition at this temperature range. A phase transition at just above 1000 K should be responsible for the reduced magnetic properties for the alloys heat treated at 973 and 1073K. It remains a challenge to well explain the improved magnetic properties by annealing.

Prospects for Mn based permanent magnets

The present results showed that the magnetic properties of melt spun Mn-Al based alloys obtained so far are much lower than that reported for MnAlC magnets prepared by hot extrusion of annealed gas-atomized powders [13]. Surfactant assisted ball milling technique can enhance the magnetic properties of MnAlC alloys. Therefore, the processing has an important effect on the microstructure and properties of this type of alloys. A proper preparation and treatment process have to be developed for making full use of this low cost permanent magnet.

For MnGa based alloys, melt spinning technique has difficulty in producing nanocrystalline alloys. Since Mn$_{70}$Ga$_{30}$ alloy has relatively low glass formability, the as spun ribbons are generally micro- or submicro- crystalline. To enhance the magnetic properties, except forming the L1$_0$ structure in the heat treated materials, refining the grain size may be a possible approach.
which may be realized also by either doping the secondary elements or employing post-process like ball milling.

In addition, to enhance the remanence of the Mn-based alloys, magnetic anisotropy has to be pursued by advanced processes. Two processes can be proposed, i.e. magnetic field aligning the anisotropic powders and forming anisotropic crystal texture in bulk materials by deformation. To enhance the magnetism of Mn based alloys, future investigations should aim to achieve hard magnetic properties in Mn-based compounds with adjusted atomic distance by forming alloys or introducing interstitial atoms and realizing anisotropic grain structures.

Since NdFeB and hard ferrites have been well developed as the high properties high cost hard magnets and low properties low cost hard magnets, respectively, future application of Mn-based magnets should aim at low cost magnets with intermediate magnetic properties, which will fill the property gap between the NdFeB and Sr-/Ba- ferrites. To achieve this goal, extensive work have to be carried out in this field.

Conclusion

The effects of composition and heat treatment on the phase transition and magnetic properties of MnAl based alloys prepared by melt spinning have been investigated. Addition of C is beneficial to the formation of τ phase. The Mn_{53.3}Al_{45}C_{1.7} ribbon after annealed at 650°C for 10 min has the best combined magnetic properties. C content also has a significant effect on the T_C of τ phase. Doping of rare earth element Pr can slightly improve the hard magnetic properties, but Dy does not have positive effect on magnetization. Anisotropic MnAlC flakes with various sizes and thicknesses were fabricated by SABM. The as prepared flakes consist of only the hcp structured ε-phase, which can completely transform to the metastable ferromagnetic τ-phase after annealing at a proper temperature. C addition cannot prevent the decomposition of the τ-phase into the equilibrium non-magnetic β+γ phases at the temperature above 500°C. The magnetic properties are strongly dependent on the fraction of the τ-phase and ball milled time. A high coercivity of 242.8 kA/m and a saturation magnetization of about 4.9 T were obtained in SABMed flakes, which are much higher than that for melt spun ribbon. In addition, preliminary results on melt spun Mn-Ga alloy have been obtained. Heat treatment can significantly improve the magnetic properties of as-spun Mn_{70}Ga_{30} alloy. High coercivity of 6.72 kOe has been obtained after heat treatment. The present results indicated that the properties of Mn-Al and Mn-Ga based alloys are very much dependent on the preparation method.

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