



Ferromagnetic α -Mn-type Mn–Al alloys produced by mechanical alloying

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Abstract

Using the mechanical alloying technique, we have produced ferromagnetic α -Mn-type alloys from Mn–45,70,85at.%Al mixed powders. During milling, Al atoms are partially solubilized in the α -Mn phase and the magnetic properties of the milled powders change from paramagnetic to ferromagnetic. The saturation magnetization is about 10 e.m.u. g^{-1} for the as-milled Mn–70at.%Al powder.

Keywords: Mechanical alloying; Ferromagnetism

1. Introduction

Pure α -Mn has a b.c.c. structure with two clusters of 20 atoms per unit cell [1] and is stable up to 973 K. Mn atoms are distributed over four crystallographically non-equivalent sites: site 1 with two atoms, site 2 with eight atoms, site 3 with 24 atoms and site 4 with 24 atoms. Neutron diffraction studies [1–3] have shown that antiferromagnetism occurs below 95 K (T_N) and the magnetic moments are different at the four crystallographic sites. Kasper and Roberts [2] emphasized the importance of two factors in determining the magnetic structure: (1) the effect of interatomic distance on the exchange interaction and hence the mode of spin alignment and (2) the geometry of the atomic arrangement. Distinct magnetic coupling between Mn atoms may not be induced for short interatomic distances (2.37 Å or less). It becomes antiferromagnetic for intermediate distances (2.49–2.82 Å) and ferromagnetic for long distances (2.96 Å or more).

In the Mn–Al phase diagram [4] Al is slightly soluble in the α -Mn phase. Using the mechanical alloying process, which is one of the most suitable methods for making a supersaturated solid solution, we have tried to produce Mn–Al alloys. This paper deals with the structural changes and magnetic properties of mechanically alloyed Mn–Al powders.

2. Experimental details

Pure α -Mn and Al powders were mixed in a glove-box to give compositions of Mn–45,70,85at.%Al. They

were then sealed in a cylindrical SUS 304 vial (100 mm diameter \times 200 mm length) together with SUS 304 rods (10 mm diameter \times 190 mm length) and placed in a glove-box filled with pure Ar gas. The powder-to-rod weight ratio was about 1:23. Mechanical alloying (MA) of the as-mixed powders was carried out at a rotation speed of 100 rev min^{-1} under a vacuum of 2×10^{-4} Torr. The milled specimens were characterized by X-ray diffraction (XRD) measurements. Their magnetic properties were studied using a vibrating sample magnetometer (VSM) in the temperature range between 78 and 1073 K. The chemical compositions of the specimens were determined by induction-coupled plasma (ICP) analyses and He carrier fusion-thermal conductivity methods.

3. Results and discussion

Fig. 1 shows the XRD patterns of mechanically alloyed Mn–45at.%Al powders after various milling times. During the initial stage of MA, Al atoms diffuse rapidly into the α -Mn matrix and the Al peaks disappear after 300 h of MA.

Fig. 2(a) shows the saturation magnetization σ_s and the coercive force H_c for variously milled specimens. After 100 h of MA, σ_s increases rapidly from 0 to 4 e.m.u. g^{-1} and then becomes constant, even though the α -Mn phase does not transform to another phase. H_c also increases rapidly up to 130 Oe after 100 h, probably owing to the increase in stored strain and Al

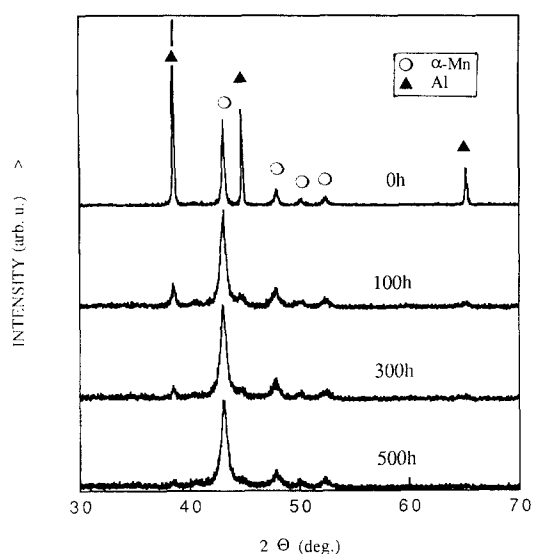


Fig. 1. X-Ray diffraction patterns of Mn-45at.%Al powders after various milling times.

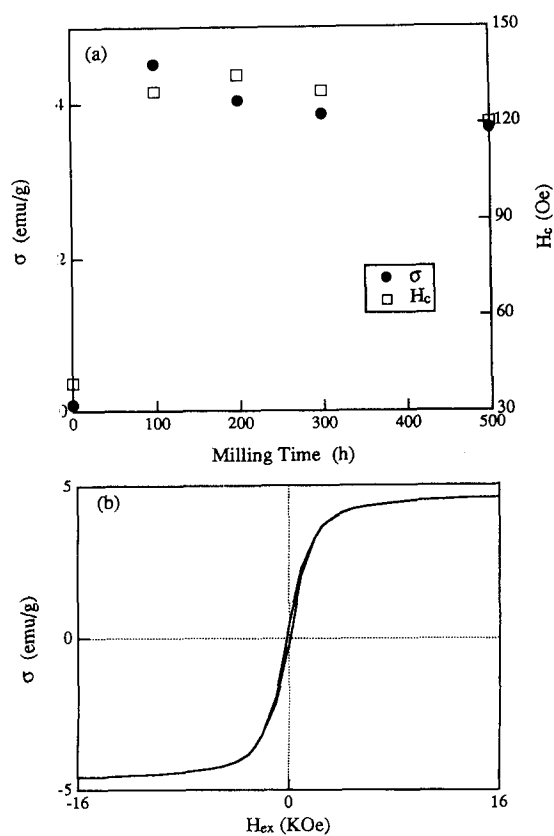


Fig. 2. (a) Saturation magnetization σ_s and coercive force H_c of Mn-45at.%Al powders as a function of milling time. (b) Hysteresis curve of 100 h milled Mn-45at.%Al powder.

solution. As seen in Fig. 2(b), the hysteresis curve of the 100 h milled specimen shows a ferromagnetic characteristic: σ_s is saturated above 3 kOe. The Fe contamination content of the milled Mn-45at.%Al powders is less than 1 at.% after 100 h of MA, as seen in Table 1.

Table 1

Chemical analysis of Mn-45at.%Al powders after selected milling times. The results for Mn, Al, Cr and Fe have been obtained by ICP analyses and those for O by the He carrier fusion method

Milling time (h)	Chemical composition (at.%)			
	Mn	Al	Fe	O
0	49.2	50.2	<0.1 (max.)	0.6
100	49.5	48.5	0.6	1.2
500	47.5	46.1	3.5	2.3

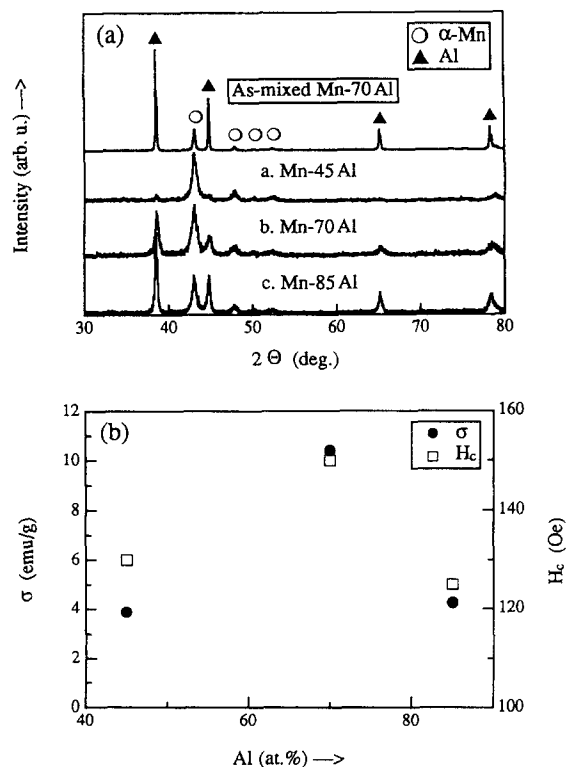


Fig. 3. (a) X-Ray diffraction patterns and (b) saturation magnetization and coercive force (σ_s and H_c) of 300 h milled Mn-45,70,85at.%Al powders.

Fig. 3(a) shows the X-ray diffraction patterns of 300 h milled Mn-45,70,85at.%Al powders. Above 70 at.% Al the intensities of the Al peaks are larger than those of the Mn peaks, indicating that Al atoms are partially solubilized. In Fig. 3(b) it is seen that σ_s increases with increasing Al composition, with a maximum value of 11 e.m.u. g^{-1} around 70 at.% Al. H_c shows a similar tendency to σ_s [5].

Figs. 4(a) and 4(b) show the thermomagnetic curves for 300 h milled Mn-70,85at.%Al powders under a magnetic field of 16 kOe during a heating and cooling cycle. Upon heating from 78 to 1000 K, σ_s decreases gradually up to 600 and 700 K and very rapidly at around 680 and 710 K for the Mn-70 and 85at.%Al powders respectively. The differential scanning calorimetry (DSC) trace and corresponding XRD pattern

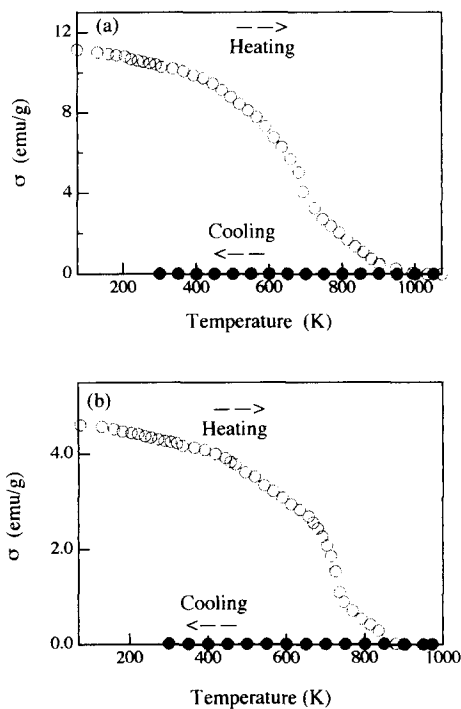


Fig. 4. Thermomagnetic curves of as-milled Mn–Al powders measured under 16 kOe of external magnetic field during heating and cooling cycle: (a) Mn–70at.%Al; (b) Mn–85at.%Al.

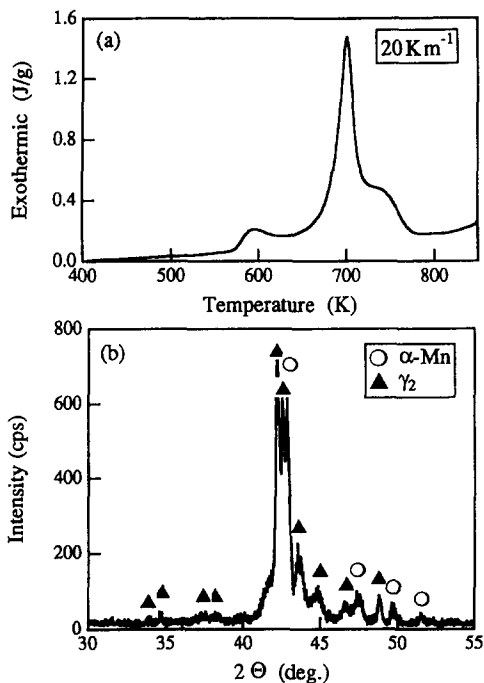


Fig. 5. (a) DSC trace of as-milled Mn–70at.%Al powder heated at a rate of 20 K min⁻¹. (b) Corresponding XRD pattern after heating to 800 K.

of the as-milled Mn–70at.%Al powder shown in Fig. 5 indicate that the temperature of 680 K corresponds to a phase transformation from α to γ_2 , while those of the as-milled Mn–85at.%Al powder shown in Fig. 6 indicate that the temperature of 710 K corresponds

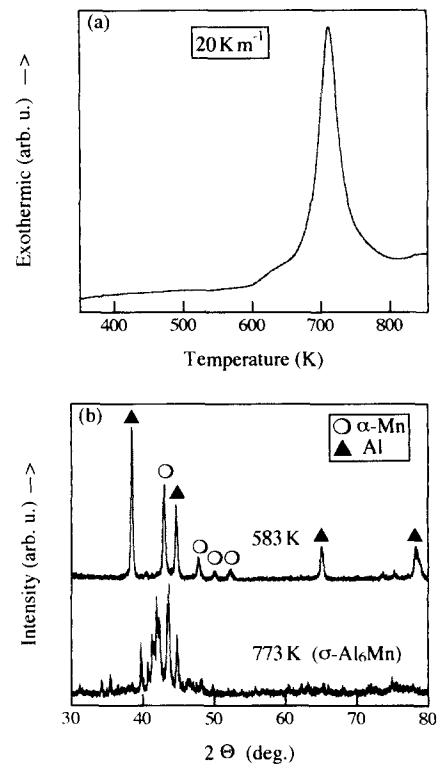


Fig. 6. (a) DSC trace of as-milled Mn–85at.%Al powder heated at a rate of 20 K min⁻¹. (b) Corresponding XRD pattern after heating to 800 K.

to a phase transformation from α to σ -Al₆Mn. After the appearance of these equilibrium phases, σ_s becomes negligibly small during the cooling stage of these alloys. The occurrence of these phase transformations prior to the magnetic transformations makes it difficult to estimate the Curie temperature T_c of the as-milled Mn–Al powders.

Mechanically alloyed Mn_{1-x}Al_x ($x = 45, 70, 85$ at.%) powders display a ferromagnetic characteristic up to about 700 K, merely owing to Al solution in the α -Mn phase. The appearance of the ferromagnetism in the α -Mn-type alloyed powders is not yet understood. At this moment we suggest the following factors.

(1) The substitution of Al atoms in the α -Mn matrix partially destroys the antiferromagnetic arrangement and forms ferromagnetic clusters. The number of such ferromagnetic clusters increases with increasing Al substitution. However, they may decrease above about 70 at.% Al owing to the decrease in Mn atoms.

(2) In the XRD patterns of Fig. 1 the α -Mn diffraction peaks do not shift markedly after milling. However, a microscopic displacement may be generated by Al substitution into the α -Mn phase. If the negative and positive distortions are counterbalanced in the present alloys, a ferromagnetism may be induced in the expanded regions, as Kasper and Roberts [2] have predicted.

(3) A local environment effect [6,7] is also a plausible origin of the ferromagnetism. If the magnetic moments

of Mn atoms are influenced by the number of Al atoms at their nearest neighbour sites, a ferrimagnetic state such as ϵ -Mn₄N [8,9] can be realized.

In order to understand the origin of the ferromagnetism in the present α -Mn-type Mn-Al alloys, we plan to measure the microscopic displacement and the change in the magnetic moments of Mn atoms by neutron diffraction and nuclear magnetic resonance measurements.

4. Conclusions

In the milled Mn-45,70,85at.%Al alloyed powders, only the crystallite sizes become nanometre scale. Al atoms are partially solubilized in the α -Mn phase, but the XRD peak positions of the α -Mn phase do not change markedly. The saturation magnetization σ_s increases rapidly during the initial stage of milling owing to the solution of Al atoms in the α -Mn phase, with a maximum value of 11 e.m.u. g⁻¹ for the as-milled Mn-70at.%Al powder. During heating, the ferromagnetic α -Mn-type phase is stable up to about 600 K and becomes paramagnetic above 700 K owing to the phase transformation from α to γ_2 or σ . In the cooling stage these equilibrium alloys carry no magnetization. These results clearly demonstrate the formation of α -Mn-type ferromagnetic Mn-Al alloys by MA.

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