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## Magnetic properties of mechanically alloyed Mn-Al-C powders

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**Abstract.** We have prepared supersaturated-solution Mn-Al-C alloy powders by mechanical alloying using a planetary high-energy mill. The starting materials were pure Mn, Al and C powders. The mechanically-alloyed powders were subjected to a two-step heating. Although starting particles are Al and Mn with additive C, the Al peak disappears with MA time. With increasing MA time, transition from  $\alpha$ -Mn to  $\beta$ -Mn does not occur; the  $\alpha$ -Mn structure maintains. At 100 h, a single phase of supersaturated-solution  $\alpha$ -Mn is obtained. The lattice constant of  $\alpha$ -Mn decreases with increasing MA time. From the Scherrer formula, the crystallite size at 500 h is obtained as 200Å, which does not mean amorphous state. By two-step heating, high magnetization (66 emu/g) was obtained from short-time-milled powders ( $t=10$  h). The precursor of the as-milled powder is not a single phase  $\alpha$ -Mn but contains small amount of fcc Al. After two-step heating, the powder changes to  $\tau$ -phase. Although the saturation magnetization increases, the value is less than that by conventional bulk MnAl (88 emu/g). Meanwhile, long-time-milled powder of single  $\alpha$ -Mn phase results in low magnetization (5.2 emu/g) after two-step heating.

### 1. Introduction

Hard magnetic Mn-Al alloys were first obtained using conventional powder-metallurgy method by Kono in 1958 [1]. The alloys are known to be obtained by two methods. The one method is quenching from the high temperature  $\epsilon$ -phase (hcp structure [2]) followed by heating at around 770 K. The other method is cooling from the high temperature  $\epsilon$ -phase at a controlled cooling rate. The obtained hard-magnetic alloys have  $\tau$ -phase (CuAu structure). Typical properties are saturation magnetization ( $\sigma_s$ ) of 88-96 emu/g [1,3] and coercive force of 1.5 kOe [4]. The coercive force is increased by additional cold working: coercive force of 4.6 kOe is obtained [3]. Furthermore, carbon addition is effective to cold working [5].

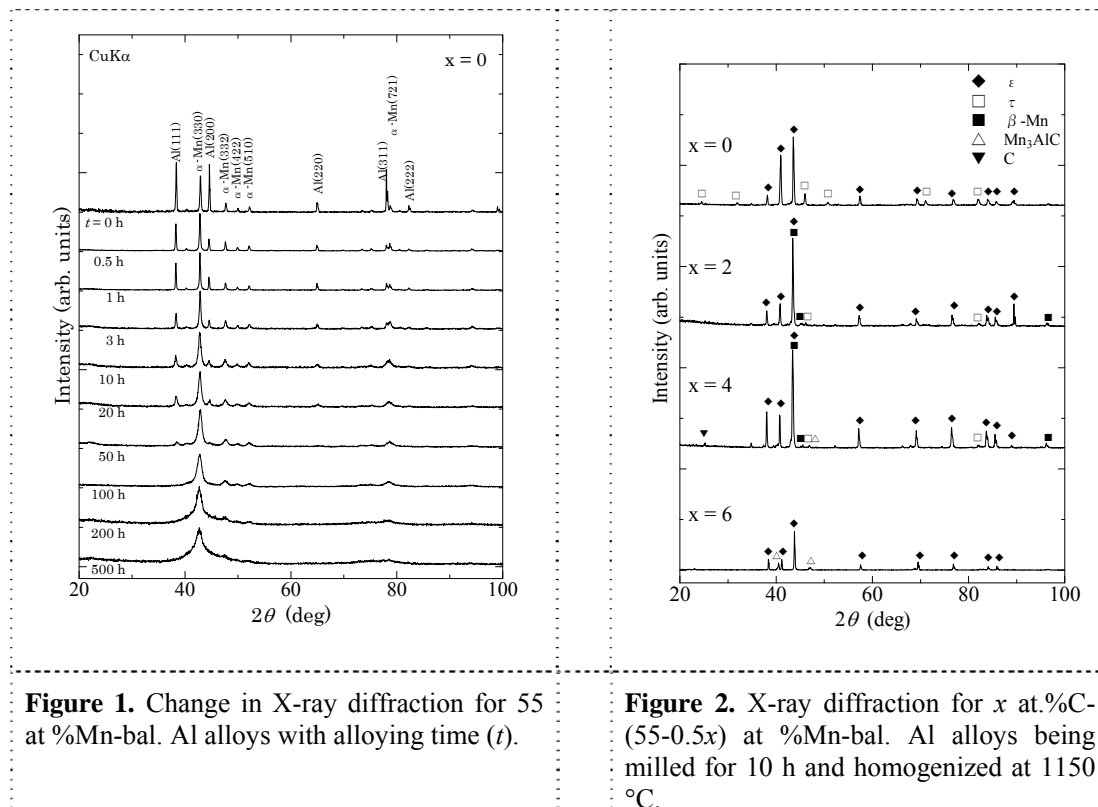
On the other hand, mechanical alloying (MA) has been applied to this alloy system [6-9]. As-milled alloys does not show  $\tau$ -phase: it is not clear whether the phase of the milled alloys is  $\alpha$ -Mn or  $\beta$ -Mn structure. Furthermore, the as-milled alloys have low saturation magnetization and low coercivity. By heating, high coercivity is obtained.

In this study, we prepare Mn-Al-C powders by mechanical alloying. The alloys were followed by two-step heating to obtain high saturation magnetization as well as high coercivity. Main parameters for comparing magnetic properties of the two-step-heated alloys are C addition (0-6 at %), milling time (10 h, 200 h) and second-step heating temperature (500-700°C).

## 2. Experimental

MA was carried out in a planetary high-energy ball mill (Fritsch Pulverisette P-5) starting from pure element powders of Mn (75  $\mu\text{m}$ ), Al (53-106  $\mu\text{m}$ ) and C (75  $\mu\text{m}$ ) with 99.9 % purity. All the alloys studied were prepared from mixtures of Mn, Al and C. The nominal compositions are two series: (1) 60, 55, 50 at %Mn-bal. Al and (2)  $x$  at %C- (55-0.5 $x$ ) at %Mn-bal. Al ( $x=0, 2, 4, 6$ ). The powder samples were loaded into a cylindrical stainless-steel vial together with balls of the same material in a nitrogen atmosphere [10]. The ball-to-powder weight ratio was 12:1. The milling process was performed at a speed of 150 r.p.m. (revolutions per minute) up to 500 h. The mechanically-alloyed powders were subjected to a two-step heating. The homogenization is done at 1050°C for 3 hours, and the heating is done at 500-700 °C for 10 to 60 min.

The characterization was carried out by X-ray diffraction (XRD) using CuK $\alpha$  radiation, by thermal analysis with differential thermal analyzer (DTA) under an argon atmosphere at a heating rate of 0.33 K/s, magnetic measurements obtained from a vibrating-sample magnetometer (VSM). Also, the mean particle sizes were measured by laser diffraction particle size analyzer.



**Figure 1.** Change in X-ray diffraction for 55 at %Mn-bal. Al alloys with alloying time ( $t$ ).

**Figure 2.** X-ray diffraction for  $x$  at %C- (55-0.5 $x$ ) at %Mn-bal. Al alloys being milled for 10 h and homogenized at 1150 °C.

## 3. Results and discussion

### 3.1 As-milled alloy

Figure 1 shows change in X-ray diffractions for Mn-Al alloys with alloying time ( $t$ ). At  $t=0$  h, strong Al (111) peak is seen and is decreases with milling time. In equilibrium Mn-rich Mn-Al system, pure Mn is  $\alpha\text{-Mn}$  structure and transform to  $\beta\text{-Mn}$  with Al addition. Both  $\alpha\text{-Mn}$  and  $\beta\text{-Mn}$  are cubic and the XRD spectra are similar. Almost all peaks appear at the nearly-same angles except for  $\alpha\text{-Mn}(422)$  and  $\beta\text{-Mn}(310)$ . Since CuK $\alpha$  target is used, a peak of  $\beta\text{-Mn}(310)$  with an intensity of 62% is expected at  $2\theta=45.4$  deg. However, no peak at the angle is observed: we conclude that the milled powders have supersaturated  $\alpha\text{-Mn}$  structure. This analysis is different from the previous reports of  $\beta\text{-Mn}$  [6, 9].

Since the XRD data is not shown [6,9], the changing process from  $\alpha$ -Mn to  $\beta$ -Mn in the structure is not clear. In the equilibrium state, the solubility of Al into  $\alpha$ -Mn is only 2 at % at room temperature [1]. Replacement of more than 2 at% results in transition to  $\beta$ -Mn and the  $\beta$ -Mn keeps up to 40 % Al. At  $t=500$  h, all the fcc-Al peaks disappear and only  $\alpha$ -Mn(330) and  $\alpha$ -Mn(721) peaks remain as shown in Fig. 1. The lattice constant of  $\alpha$ -Mn solution decreases with MA time, i.e. Al inclusion. This is partly due to included stress in the alloys. We confirmed a decrease in lattice constant of pure  $\alpha$ -Mn by mechanical grinding. The crystallite size is calculated using Sherrer formula neglecting included stress. The crystallite size obtained from the  $\alpha$ -Mn(330) decreases from 800 Å to 150-200 Å at  $t=500$  h. The apparent mean-particle sizes observed by laser diffraction particle size analyzer increase once from 40  $\mu\text{m}$  of pure Al to 150  $\mu\text{m}$  which depends on the composition, and then decrease to 10  $\mu\text{m}$  at 100-h milling. The size keeps constant after 100 h. Effect of C addition on the crystallographic change is not observed in XRD spectra.

The supersaturated-solution  $\alpha$ -Mn is ferromagnetic with a low saturation magnetization ( $\sigma_s$ ) of 0.8 emu/g and the maximum coercivity ( $H_c$ ) of 0.3 kOe. This is due to imbalance in the number of anti-ferromagnetic Mn atom.

### 3.2 Homogenized alloys

Figure 2 shows change in XRD spectrum with C content ( $x=0-6$ ) for the alloys with  $x$  at %C-(55-0.5 $x$ ) at %Mn-bal. Al after 1150°C heating. The milling time is only 10 h; therefore the precursor is a mixture of main phase  $\alpha$ -Mn with a small amount of fcc-Al (see Fig. 1).

By the homogenizing heating, both saturation magnetization and coercivity increase. The  $x=0$  alloy includes small amount of  $\tau$ -phase and have higher saturation magnetization of 25 emu/g. Meanwhile, C-containing alloys ( $x=2-6$ ) has almost single  $\epsilon$ -phase. The  $x=6$  alloy is almost  $\epsilon$ -phase except for a small amount of  $\text{Mn}_3\text{AlC}$  intermetallic compound.  $\text{Mn}_3\text{AlC}$  is paramagnetic at room temperature having ferromagnetism at low temperature and Curie temperature of 15 °C [11]. Therefore, we find that the  $\epsilon$ -phase has the magnetization at 16 kOe ( $\sigma_{16}$ ) of 5.5 emu/g. It should be noted that  $\epsilon$ -phase has ferromagnetism. This is contrasted to the previous report [1]. A typical hysteresis loop of the  $\epsilon$ -phase alloy ( $x=6$ ) is shown in Fig. 3. From the XRD, the alloy has a single phase (see Fig. 2). This shows the C-addition stabilizes as reported by Zeng *et al.* [12]. The change in  $H_c$  with C-addition is slightly different from  $\sigma_s$ : the largest  $H_c$  is for  $x=0$  alloy and decreases with C-addition.

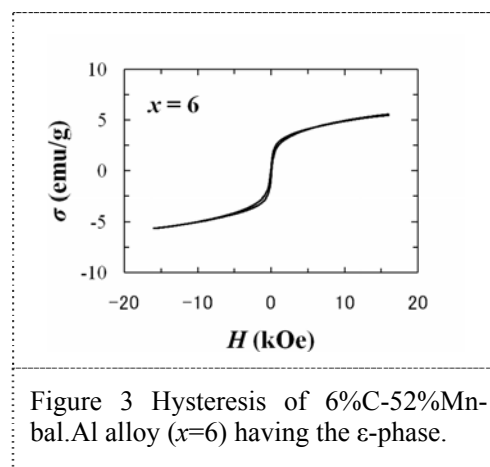
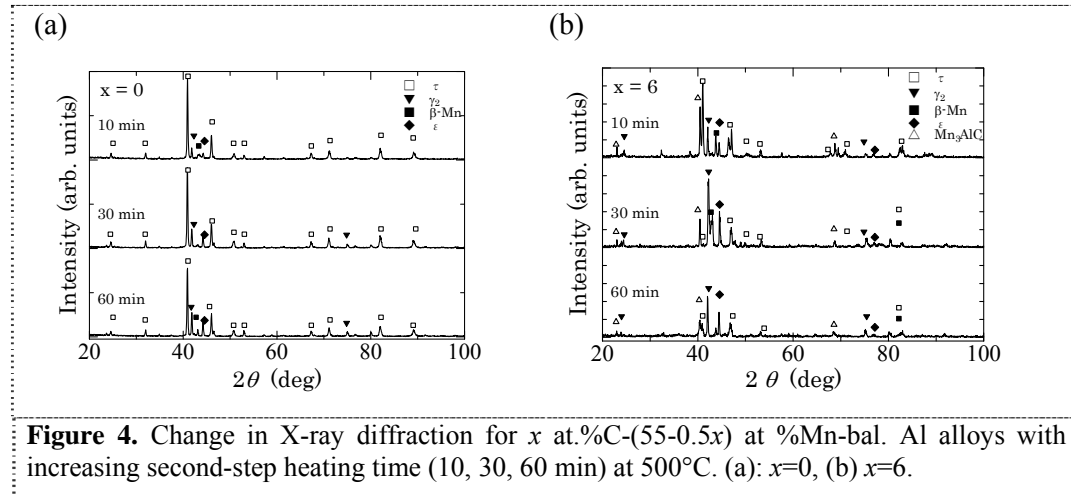


Figure 3 Hysteresis of 6%C-52%Mn-bal.Al alloy ( $x=6$ ) having the  $\epsilon$ -phase.

### 3.3 Second-step heated alloys

After the second-step heating, main phase of the alloys is changed to  $\tau$ -phase. XRD spectra for  $x$  at %C-(55-0.5 $x$ ) at %Mn-bal. Al ( $x=0, 6$ ) is shown in Fig. 4. However, small amount of  $\gamma_2$ ,  $\epsilon$ , and  $\beta$ -

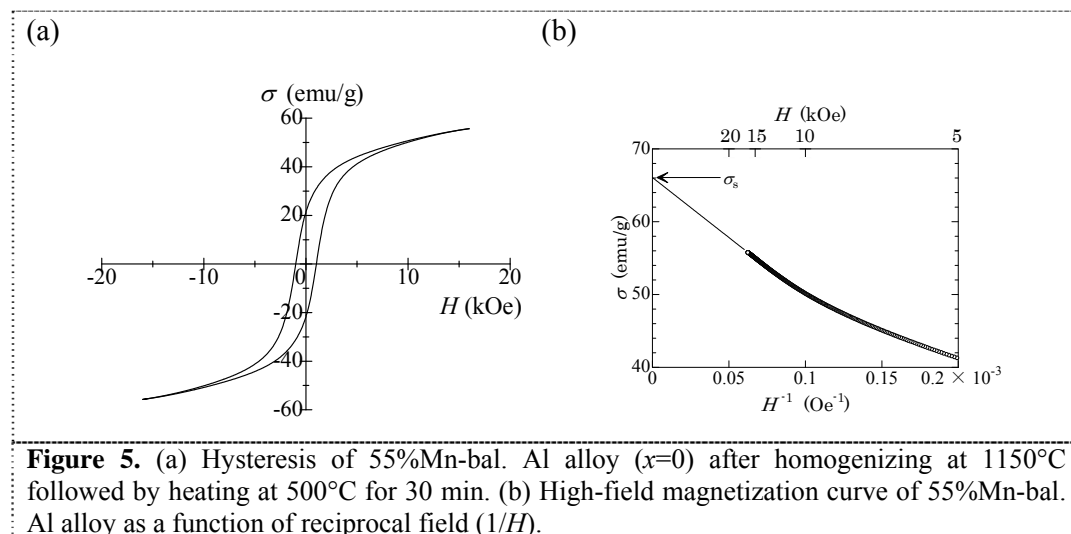


**Figure 4.** Change in X-ray diffraction for  $x$  at.%C-(55-0.5 $x$ ) at %Mn-bal. Al alloys with increasing second-step heating time (10, 30, 60 min) at 500°C. (a):  $x=0$ , (b)  $x=6$ .

Mn are observed. The milling time is only 10 h and homogenising is 1150°C. By carbon addition, intermetallic  $\text{Mn}_3\text{AlC}$  (perovskite structure) is observed.

The largest  $\sigma_s$  is obtained for C-free alloys. However,  $H_c$  is as low as 1 kOe. The hysteresis loop is shown in Fig. 5(a). Since the magnetization is not saturated at 16 kOe, saturation magnetization ( $\sigma_s$ ) is obtained by extrapolation to  $1/H=0$  using  $H^{-1}$  law as shown in Fig. 5 (b). In an exact calculation, we must consider an  $H^2$  term [13], however, we used only a main  $H^{-1}$  term. A  $\sigma_s$  value of 66 emu/g is obtained. High  $H_c$  of 2.6 kOe is obtained for  $x=4$  alloy, however,  $\sigma_{16}$  is decreased to 40 emu/g and  $\sigma_s$  is 52 emu/g.

These magnetic and crystallographic properties for the short-time milled alloys ( $t=10$  h) are contrasted to long-time milled powder ( $t=200$  h). After homogenization, the main phase of 200 h milled powder is  $\epsilon$ -phase. However, after second-step heating, the main phase of powder is  $\beta$ -Mn with small amount of  $\tau$ -phase, which has as small as 5.2 emu/g. The reason is thought as follows. After long time milling, a large amount of stress is stored in the supersaturated solution  $\alpha$ -Mn. Although the crystal structure is changed to  $\epsilon$ -phase after the homogenizing heat treatment, the following transition to  $\tau$ -phase does not sufficiently occur by the second heating due to residual stress.



**Figure 5.** (a) Hysteresis of 55%Mn-bal. Al alloy ( $x=0$ ) after homogenizing at 1150°C followed by heating at 500°C for 30 min. (b) High-field magnetization curve of 55%Mn-bal. Al alloy as a function of reciprocal field ( $1/H$ ).

#### 4. Conclusions

Supersaturated-solution  $\alpha$ -Mn (in the vicinity of 50%Mn-50%Al composition) is obtained after 100 h milling for Mn-Al and Mn-Al-C alloys. The lattice constant of supersaturated-solution  $\alpha$ -Mn decreases by Al inclusion. The almost single  $\epsilon$ -phase has ferromagnetism having saturation magnetization of 6.5 emu/g. The largest saturation magnetization ( $\sigma_s$ ) of 66 emu/g by the homogenization at 1150°C followed by heating at 500°C in this experiment. High  $H_c$  of 2.6 kOe is obtained for C-including alloys which have  $\sigma_s$  of 52 emu/g. To obtain  $\tau$ -phase alloys and consequently higher magnetization, short-time milling (10 h) is better than long-time milling (200 h).

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