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 powers. 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-metalurgy method by Kono in 1958 [1]. The alloys are known to be obtained by two methods. The one method is quenching form the high temperature $\varepsilon$-phase (hcp structure [2]) followed by heating at around 770 K. The other method is cooling from the high temperature $\varepsilon$-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, mechanically 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 μm), Al (53-106 μm) and C (75 μm) 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- (55-0.5x) 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 CuKα 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.

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 α-Mn structure and transform to β-Mn with Al addition. Both α-Mn and β-Mn are cubic and the XRD spectra are similar. Almost all peaks appear at the nearly-same angles except for α-Mn(422) and β-Mn(310). Since CuKα target is used, a peak of β-Mn(310) with an intensity of 62% is expected at 2θ=45.4 deg. However, no peak at the angle is observed: we conclude that the milled powders have supersaturated α-Mn structure. This analysis is different from the previous reports of β-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 in 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 μm of pure Al to 150 μm which depends on the composition, and then decrease to 10 μm 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 $\varepsilon$-phase. The $x=6$ alloy is almost $\varepsilon$-phase except for a small amount of Mn$_3$AlC intermetallic compound. Mn$_3$AlC is paramagnetic at room temperature having ferromagnetism at low temperature and Curie temperature of 15 °C [11]. Therefore, we find that the $\varepsilon$-phase has the magnetization at 16 kOe ($\sigma_{16}$) of 5.5 emu/g. It should be noted that $\varepsilon$-phase has ferromagnetism. This is contrasted to the previous report [1]. A typical hysteresis loop of the $\varepsilon$-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.

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 $\gamma_2$, $\varepsilon$, and $\beta$-
Mn are observed. The milling time is only 10 h and homogenising is 1150°C. By carbon addition, intermetallic Mn₃AlC (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, $\sigma_s$ 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 $\varepsilon$-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 $\varepsilon$-phase after the homogenizing heat treatment, the following transition to $\tau$-phase does not sufficiently occur by the second heating due to residual stress.

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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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