Journal of Magnetism and Magnetic Materials 115 (1992) 183–186
North-Holland

Fabrication and magnetic properties of manganese–aluminium permanent magnets *

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The magnetic properties of Mn–Al alloys depend on their chemical compositions, grain size, sintering temperature and additives, and are process sensitive. Effects of the sintering temperature, and the carbon addition on the magnetic properties of sintering Mn–Al magnets have been investigated. The electrical resistivity and magnetization of Mn–Al alloys have been studied between 4 and 1200 K. Large differences have been observed between the τ-phase and other non-magnetic phases. The best magnetic properties for the isotropic sintered samples in this study are $B_r = 2800$ G, ${}_bH_c = 1500$ Oe, and $(BH)_{max} = 1.2$ MG Oe.

1. Introduction

The existence of a ferromagnetic phase in the Mn–Al system containing about 71 wt% (or 55 at%) Mn is due to the metastable τ-phase whose structure and magnetic properties, etc., have been investigated extensively [1–7]. This phase, which has a CuAuI type structure and exhibits interesting permanent-magnet properties, has been produced in several ways, e.g. either by quenching the hcp high-temperature phase followed by an anneal near 800 K, or by cooling the hcp phase at rates of the order of 10^3 K/min. Because the magnetic properties of Mn–Al alloys are process sensitive, many techniques have been used to fabricate the Mn–Al permanent magnets, e.g. by casting [1], by warm extrusion [8], by powder method [9] and by rapidly quenching [10], etc. However, the sintering technique, as far as we know, has not been reported as a means of studying the permanent-magnet properties of Mn–Al alloys. Therefore, we have studied the magnetic properties of the sintered Mn–Al alloys. In this paper, we report the experimental results of the electrical resistivity and magnetization studies of cast Mn–Al samples and the permanent-magnet properties of the sintered Mn–Al samples. Effects of carbon on the magnetic properties of sintered Mn–Al magnets have also been investigated.

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* Presented at ICM '91, 2–6 September 1991, Edinburgh, Scotland.

2. Experimental

The MnAl and MnAlC alloys containing Mn between 70 and 72 wt% were prepared by melting proper amount of high-purity Mn, Al and C in an induction melter under a positive pressure of argon, and casting into 15 mm diameter molds. After the ingots were solutionized at 1373 K for 1 h they were oil-quenched to room temperature. These cast ingots have a B19 (ε′) structure. For τ-phase samples, it is necessary to anneal further at 800 K for 30 min and oil-quench. The cast $Mn_{55}Al_{45}$ samples were used to study the electrical resistivity and magnetization behavior between 4 and 1200 K.

0304-8853/92/$05.00

For preparing the isotropic sintered MnAl and MnAlC permanent magnet, these cast ingots had to be crushed into small pieces, and then pulverized in hammer and ball millers; the final particle size graded by sieving was roughly between 40 and 80 μm. The powders were pressed into cylindrical pellets under a hydrostatic pressure of 1 ton/cm^2. The sintering temperature has been varied between 1395 and 1523 K in argon atmosphere for roughly 15 min to produce liquid phases, then the samples were sintered at 1373 K for 1 h; these pellets were quenched and tempered at about 800 K for 40 min, and finally oil-quenched to room temperature.

A four-point ac method was used to measure electrical resistivity from 4 to 1200 K, and the heating and cooling rates were controlled at approximately 5 K/min. A vibrating-sample magnetometer and *B–H* tracer were used for the magnetic studies.

3. Results and discussion

The electrical and magnetic properties of $Mn_{55}Al_{45}$ alloys are very sensitive to its structure or heat treatment. Many mechanisms have been proposed for these structure variations. The usually accepted mechanism is that the high-temperature non-magnetic ε-phase (hcp) transforms into room-temperature non-magnetic ε′-phase (orthorhombic) by an ordering reaction and roughly at 800 K, it transforms into a metastable ferromagnetic τ-phase (fct) in a martensitic mode. Figure 1 shows the electrical resistivity of a cast ε′-phase $Mn_{55}Al_{45}$ sample as a function of temperature between 4 and 1200 K. The sequence of the experimental runs is indicated by arrows in the figures. The resistivity drops slowly from 4 to roughly 350 K and then stays almost temperature independent below roughly 800 K. Between 800 and 900 K, the resistivity decreases with increasing temperature, which is related to the formation of τ-phase [4]. The resistivity increases with increasing temperature between about 900 and 1050 K, a variation which is related to the formation of the stable β and 'Cr_5Al_8' type phases, according to van den Broek et al. [4]. Above

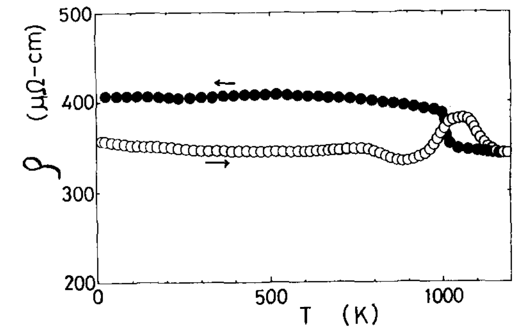

Fig. 1. Variation of electrical resistivity ρ with temperature for ε′-phase $Mn_{55}Al_{45}$.

~ 1050 K, the resistivity decreases again, which is related to the formation of ordered 'Cr_5Al_8' type and β phases. For slow cooling (~ 5 K/min), the resistivity shows an abrupt increase near 1000 K; this indicates that the high-temperature ordered structure changes back to the stable β and 'Cr_5Al_8' type structure. Because this is a stable structure, the resistivity data show no more structure variations below 1000 K on cooling.

The electrical resistivity of a cast τ-phase $Mn_{55}Al_{45}$ sample as a function of temperature between 4 and 1200 K is plotted in fig. 2. The resistivity monotonically increases with temperature below ~ 1050 K for the heating run. It is clear that the resistivity undergoes an abrupt slope change near 635 K which results from a ferromagnetic–paramagnetic phase transition for the

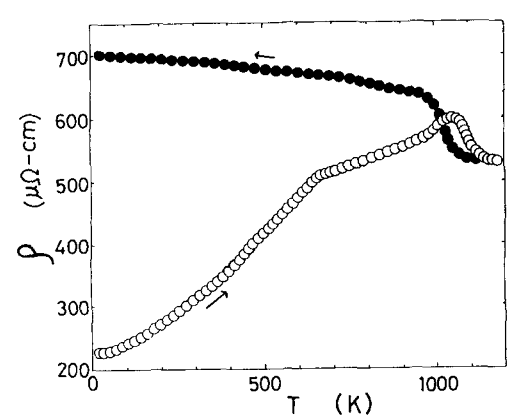

Fig. 2. Variation of electrical resistivity ρ with temperature for τ-phase $Mn_{55}Al_{45}$.

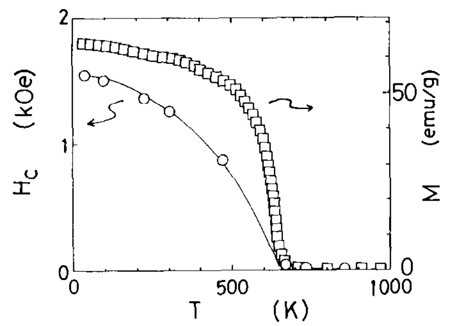

Fig. 3. Coercive force H_c and magnetization M at 0.8 T varied with temperature for τ-phase $Mn_{55}Al_{45}$.

τ-phase structure. Between 900 and 1050 K, the abrupt increase of the resistivity is due to the structure variation from τ-phase to a mixed β and 'Cr_5Al_8' phase. The explanation for the remaining runs in fig. 2 is similar to that of fig. 1. Figure 3 presents the magnetization M at 0.8 T and the coercive force H_c obtained from M vs. H curves between 4 and 1000 K for the cast τ-phase $Mn_{55}Al_{45}$ sample. It is again observed that the Curie temperature for τ-phase $Mn_{55}Al_{45}$ alloy is near 635 K. We have shown that (i) the resistivity and magnetization measurements are very sensitive to either magnetic or structural variations in the Mn–Al system, and (ii) large differences have been observed between the τ-phase and other non-magnetic phases.

For permanent-magnet studies of the sintered isotropic Mn–Al alloys, we have performed a long step-by-step sintering treatment on six Mn–Al samples with Mn concentration fixed at 70.5 wt% and varying both Al and C concentration, such that it contains 0, 0.5, 0.8, 1.0, 1.5 and 2.0 wt% C, respectively. We have found that under the same processing conditions, samples with carbon have better permanent-magnet properties than samples without carbon, and it shows that the best permanent-magnet properties occur for samples containing 0.8 wt% C, as shown in fig. 4. By varying the sintering temperature but keeping the remaining processes unchanged, the coercive force H_c (from B vs. H), remanence B_r and energy product $(BH)_{max}$ changes with different sintering temperature. As an example, fig. 5 shows these variations for the $Mn_{70.5}Al_{28.7}C_{0.8}$ (in wt%)

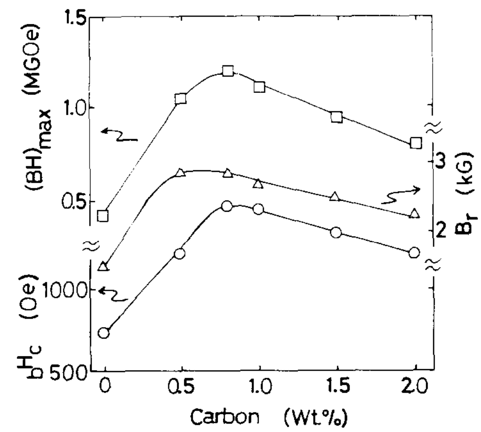

Fig. 4. Variation of $(BH)_{max}$, B_r and $_bH_c$ with carbon contents for sintered MnAlC samples with the Mn concentration fixed at 70.5 wt% and the tempering condition at 800 K for 40 min.

samples. It shows that the proper sintering condition for this system to yield a high $(BH)_{max}$ value is at 1503 K in Ar atmosphere for 15 min.

The best permanent-magnet characteristics achieved so far in this study for the sintered isotropic MnAlC alloys are $B_r = 2800$ G, $_bH_c = 1500$ Oe and $(BH)_{max} = 1.2$ MG Oe. These values are lower than those for the anisotropic MnAlC magnets produced by warm extrusion technique [8]. However, we believe that we have not yet achieved the optimum conditions. We will try to improve this promising isotropic permanent magnet in the near future.

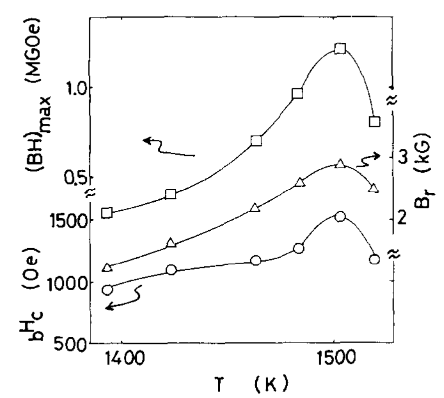

Fig. 5. Variation of $(BH)_{max}$, B_r and $_bH_c$ with sintering temperature for $Mn_{70.5}Al_{28.7}C_{0.8}$ (in wt%) samples.

Acknowledgement

The authors are grateful to the National Science Council of Taiwan for the financial support of this research work under grant No. NSC 80-0208-M001-63.

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