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Effect of Isothermal Aging on Martensitic Transformation in Ni – Mn – Ga Alloys

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Effect of isothermal aging on martensitic transformation behavior was investigated in Ni - Mn - Ga ferromagnetic shape memory alloys. By aging at 673 - 873 K for an hour, martensitic transformation temperature, M*, increased about 30 K. This was accompanied by the Curie temperature increase of about 20 K. Magnetization also increased by the aging. The observed changes in the transformation temperatures and magnetization can be attributed to an increase in a degree of $L2_1$ order.

Key words: shape memory alloys, twinning magnetostriction, the Heusler alloys, long range order

1. INTRODUCTION

Ni – Mn – Ga is one of the first alloys which was shown to exhibit a large magnetostriction by magnetically induced twinning/detwinning in martensite phase [1], hereafter referred to as twinning magnetostriction. Thus this alloy is a potential candidate for high power magnetic actuator materials. However, the stability range of martensite phase is limited to below room temperature. For application purposes, it is desired to increase martensitic transformation temperature as well as magnetization. In general, this can be attained either by modification of composition, or heat treatment of parent phase or martensite phase. There are several investigations on aging effects in other shape memory alloys. For example, martensitic transformation temperature in Cu – Zn – Al shape memory alloys is extremely sensitive to martenstie aging [2-4]. Also it was shown for Ni – Mn – Al alloys, aging in the parent B2 phase induces ordering to $L2_1$ structure, leading to a decrease in martensitic transformation temperature[5].

Present study was undertaken to investigate the effect of isothermal aging on transformation behavior of Ni - Mn - Ga alloys.

2. EXPERIMENTAL

Alloy ingots of Ni - 23.0 at% Mn - 25.6at% Ga and Ni - 21.0 at% Mn - 25.7 at% Ga were prepared by argon arc melting. They were homogenized at 1073 K for 48 - 72 hours in an Ar atmosphere, then quenched into water at room temperature. Compositions of the ingots were analyzed by EDX in JEOL JSM – 6300 SEM. Samples for various measurements were then cut out from the ingots, and final heat treatment of 1 hour at 1073 K or 1173 K was given, followed by quenching into water. Isothermal aging was done at 673 K - 873 K in an argon atmosphere. DSC measurements were conducted on RIGAKU 8230 L with a heating/cooling rate of 10 K/min to characterize martensitic and magnetic transformation behavior. Magnetic measurements were made on RIKEN BHV-55 VSM with the maximum field of 1.5 T at room temperature. TEM observations were also made at room temperature on Hitachi H-800 operated at 200 kV.

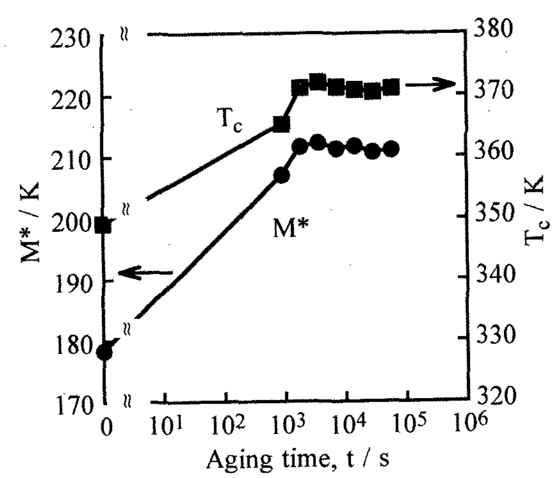

Fig. 1. Changes in M* and T_c by aging at 673 K in Ni - 23.0 Mn - 25.6 Ga.

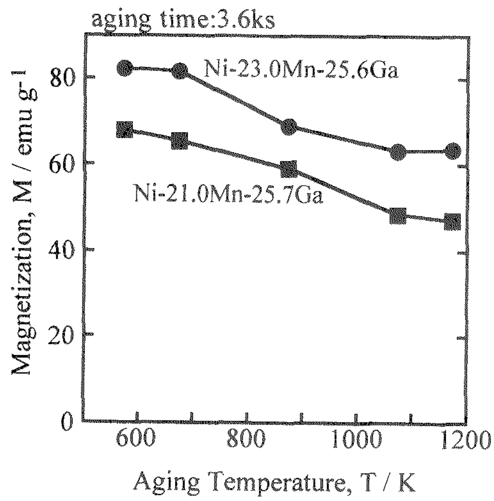

Fig. 2 Effect of aging temperature on M* and T_c in Ni - 23.0 Mn - 25.6 Ga.

3. RESULTS

Martensitic transformation temperature, M*, and paramagnetic/ferromagnetic transition temperature (the Curie temperature), T_c, are plotted as a function of aging time at 673 K for the Ni - 23.0 at% Mn - 25.6 at% Ga alloy in Fig. 1. M* increased and saturated at around 213 K by aging of 1 hour. T_c also increased and saturated at 372 K after 1 hour of aging. M*

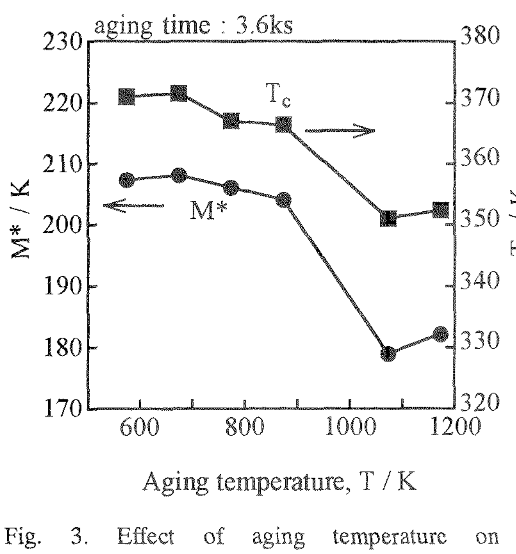

Fig. 3. Effect of aging temperature on magnetization in Ni - 23.0 Mn - 25.6 Ga and Ni - 21.0 Mn - 25.7 Ga.

and T_c showed similar time dependence but M* exhibited a larger increase of 30 K on aging than T_c (an increase of 20 K).

In Fig. 2, M* and T_c after 1 hour of aging are plotted as a function of aging temperature. Both M* and T_c change markedly in the temperature range between 873 K and 1073 K; below 873 K and above 1073 K, no significant dependence can be found.

Saturation magnetization measured at room temperature also depends on aging temperature as shown in Fig. 3. The values of magnetization in aged samples at 573 K were about 30 % higher than in the as-quenched samples.

TEM observations of the as-quenched and aged samples revealed no apparent microstructural change. Selected area diffraction (SAD) patterns along the [011] -zone axis of the parent phase are shown in Fig. 4. Figure 4 (a) is the SAD for an as-quenched sample of Ni - 23.0 Mn - 25.6 Ga. The {200} and {111} spots are B2 and $L2_1$ superlattice reflections, respectively. It was

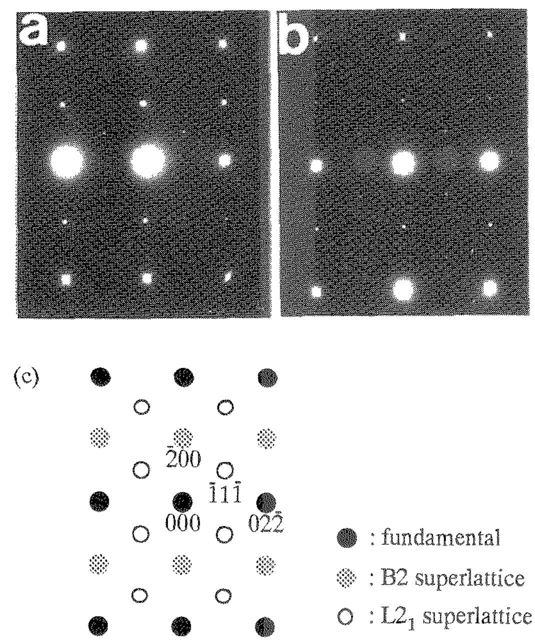

Fig. 4. Selected area electron diffraction patterns obtained for (a) an as-quenched sample, (b) a sample aged at 673 K for 1 hour of Ni - 23.0 Mn - 25.6 Ga alloy, and (c) a key diagram.

confirmed by in situ cooling observation that this alloy transforms to martensite with monoclinic structure. The appearance of the {111} spot indicates that the alloy orders to $L2_1$ Heusler structure on quenching from homogenization temperature, although the degree of order is not high, since intensity of the $L2_1$ spots is much lower than the B2 spots. By aging for 1 hour at 673 K, intensity of the (111) spot increased and became comparable with those of the B2 spots as shown in Fig. 4 (b). This qualitatively indicates that the degree of $L2_1$ order increased to some extent by the aging.

4. DISCUSSION

Since the observed changes in both M* and T_c exhibit quite similar dependence on aging time and temperature, it is likely that they have a common origin. Since martensitic transformation does not involve long range diffusion of constituent atoms, a martensite phase inherits ordered atomic arrangements from its high temperature parent phase on transformation. It was shown for several shape memory alloys that relative stability of martensite phase with respect to its parent phase is extremely sensitive to a ordered structure [2, 3]. T_c is also a function of a degree of order in LRO alloys [6].

Recently, temperature dependence of a long range order (LRO) parameter in Ni-Mn-Ga alloy has been studied by Overholser et al. by high temperature neutron diffraction [7]. It was found that the alloy orders directly to the B2 structure on solidification at 1382 K and then to the $L2_1$ structure at 1071 K in a stoichiometric Ni_2MnGa. The present TEM results indicated that the $B2/L2_1$ transition cannot be suppressed by quenching. This is in contrast to the case of Ni - Mn - Al alloys, in which the $B2/L2_1$ ordering temperature is low and thus the reaction is sluggish. The B2 phase can be retained on quenching [8].

The degree of order changes most significantly within the temperature range of about 100 K below the $B2/L2_1$ ordering temperature; below this temperature range the degree of order is almost constant[7]. The aging temperature dependence shown in Fig. 2 reflects this tendency; both M* and T_c are almost constant for the aging temperatures below 873 K. The TEM results also revealed that the $L2_1$ spots intensity increases by aging at 673 K, indicating that the quenched-in order is not the highest degree and can be increased by a heat treatment below the $B2/L2_1$ ordering temperature. Therefore it is most likely that the observed changes in M* and T_c by aging is caused by an increase in the degree of $L2_1$ order.

The changes in the magnetization can be also explained by the change in the $L2_1$ order. Neutron diffraction study by Webster et al. [9] has shown that most of the magnetic moment in Ni_2MnGa resides on Mn-sites in the Heusler sublattice. Electronic structure calculations by Fujii et al. [10] also support the results. The Mn-sites form fcc sublattices in the Heusler structure with the nearest neighbor distance of 4.2 Å; ferromagnetic coupling of the neighboring Mn atoms is due not to a direct interaction but sought to be via the conduction electrons (the RKKY interaction). If the $L2_1$ ordering is incomplete, some Mn atoms present on the nearest neighbor (nn) Ni-sites or the next nearest neighbor (nnn) Ga-sites. The distance between such Mn atoms is about 2.06 Å for nn 2.9 Å for nnn, which results in a direct antiferromagnetic interaction between the Mn atoms[11]. Thus the incomplete $L2_1$ order leads to an overall decrease in magnetization in Ni - Mn - Ga alloy.

5. CONCLUSION

The aging at the temperature below $B2/L2_1$ ordering temperature caused an increase in both M* and T_c. The maximum increase observed was about 30 K for M* and 20 K for T_c. Magnetization also increased by aging. These changes are most likely caused by an increase in the degree of $L2_1$ long range order.

References

1) K. Ullakko, J. K. Huang, V. V. Kokorin and R. C. O'Handley, Scrip. Metall., **36** (1997) 1133.
2) K. Tsuchiya, D. Miyoshi, K. Tateyama, K. Takezawa and K. Marukawa, Scrip. Metall. Mater., **31** (1994) 455.
3) K. Tsuchiya, K. Takahashi and K. Marukawa, Mater. Trans. JIM, **37** (1996) 304.
4) M. Ahlers, ICOMAT-'86, ed. by , Japan Institute of Metals (1986) 786.
5) Y. Sutou, I. Ohnuma, R. Kainuma and K. Ishida, Metall. Mater. Trans, **29A** (1998) 2225.
6) G. Inden and W. Pitsch, Z. Metallkde., **62** (1971) 627.
7) R. W. Overholser, M. Wuttig and D. A. Neumann, Scripta Mater., **40** (1999) 1095.
8) R. Kainuma, H. Nakano and K. Ishida, Metall. Mater. Trans, **27** (1996) 4153.
9) P. J. Webster, K. R. A. Ziebeck, S. L. Town and M. S. Peak, Philos. Mag., **49B** (1984) 295.
10) S. Fujii, S. Ishida and S. Asano, J. Phys. Soc. Japan, **58** (1989) 3657.
11) Y. Endo and Y. Ishikawa, Solid State Physics, **5** (1970) 245.

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