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EFFECT OF RARE EARTH ELEMENTS ADDITION ON PROPERTIES OF Ni-Mn-Ga FERROMAGNETIC SHAPE MEMORY ALLOYS.

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Effect of addition of rare earth elements, such as, Nd, Sm and Tb, was investigated on the phase transformation and magnetic property of Ni-Mn-Ga ferromagnetic shape memory alloy. The prepared alloys were found to be in almost single phase of $L2_1$ structure; but, precipitates containing the rare earth element were occasionally found along the subgrain boundaries. Solubility limit of the Nd, Sm and Tb into the $L2_1$ matrix seems to be very low, possibly less than 0.1 mol%. Nevertheless they noticeably affected the transformation temperatures and magnetic properties of the alloys.

Key words: martensitic transformation, magnetostriction, Heusler compounds.

1. INTRODUCTION

Ni_2MnGa is one of the Heusler compounds and undergoes thermoelastic martensitic transformation in a ferromagnetic state[1]. Large magnetostriction in the martensite phase of Ni-Mn-Ga alloy was found by Ullakko; the strain was attributed to the field induced twinning/detwinning (twinning magnetostriction)[2]. Since then ferromagnetic shape memory alloys have attracted much interest as potential materials for magnetic actuators. Ferromagnetic shape memory alloys can produce a large strain of several percent , which is much larger than that of giant magnetostrictive Terfenol-D[3]. One disadvantage of this material is its low output energy density. In order to improve the output power, one has to increase the magnetocrystalline anisotropy energy. One of the possibilities to increase the anisotropy energy is to introduce 4f rare earth elements. The 4f electrons locate relatively far inside the atoms and they are shielded from the effect of surrounding atoms. Thus the orbital angular momentum makes large contribution to the total angular momentum [4].

In the present study, effect of addition of rare earth elements, such as, Nd, Sm and Tb, on various properties of Ni-Mn-Ga ferromagnetic shape memory alloy was investigated.

2. EXPERIMENTAL

Alloy ingots were prepared by an argon arc melting furnace. They were homogenized at 1073 K for 72 hours in an Ar atmosphere, and then quenched into water at room temperature. 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. Sample composition was analyzed by ICP method. DSC measurements were conducted on RIGAKU-8230L 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 on Hitachi H-800 and JEOL JEM-2010 both operated at 200 kV.

3. RESULTS

Fig. 1 is the X-ray diffraction patterns for Ni-22.4 mol%Mn-25.1 mol%Ga-0.2 mol%Sm alloy. The most of the observed peaks can be indexed as those from $L2_1$ phase. The $L2_1$ superlattice reflections (*e.g.*, 111) and B2 (*e. g.*, 200) reflections are clearly seen. It was also revealed by TEM selected area diffraction that the alloys possess a high degree of $L2_1$ order. Minor peaks

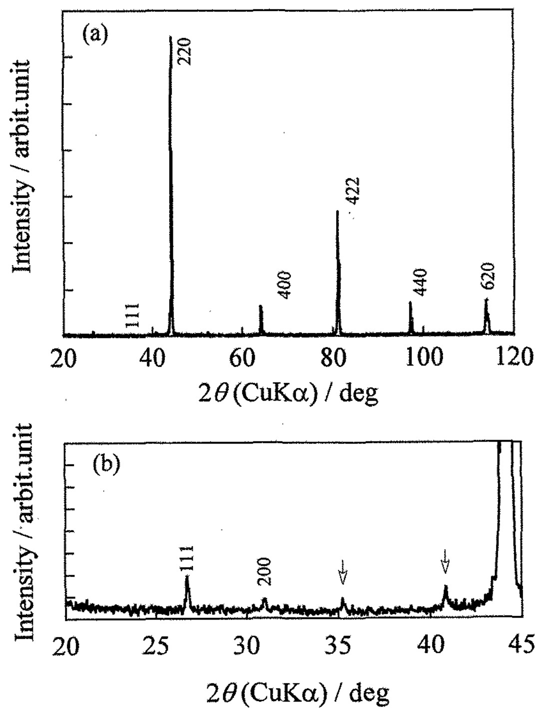

Fig. 1 (a) X-ray powder diffraction pattern of Ni- 22.4 mol%Mn-25.1 mol%Ga-0.2 mol%Sm alloy. (b) an enlarged view of lower angle part. Peaks not correspond to those from the $L2_1$ structure are denoted by the arrows.

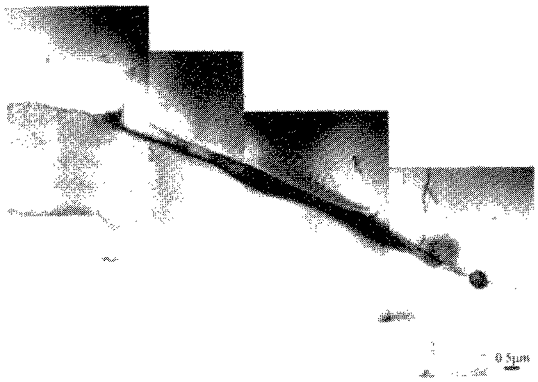

Fig. 2 TEM micrograph of Ni- 22.4 mol%Mn-25.1 mol%Ga-0.2 mol%Sm alloy.

(indicated by the arrows in Fig. 2(b)), which do not correspond to those from the $L2_1$ phase, can be also seen.

Fig. 2 is a TEM micrograph obtained for the same alloy. Precipitates with an elongated shape along the subgrain boundary can be seen. An EDX analysis in analytical TEM revealed that the precipitates contain about 16 mol% of Sm. The Sm content in the matrix $L2_1$ phase was under the detection limit of the EDX. The identification of the precipitates is underway.

In Fig. 3 martensitic transformation temperature (M^*) and the Curie temperature (T_C) was plotted as a function of valence electron concentration(e/a) of the matrix. The data for ternary alloys obtained by the present authors are also indicated for comparison[5, 6]. The contribution of rare earth to the matrix concentration was neglected. The rare earth containing alloys exhibit higher martensitic transformation temperatures compared to ternary alloys, while the T_Cs are similar to those in ternary alloys. This indicates that, although the amount of rare earth content is very low, it significantly affects the martensitic transformation temperature.

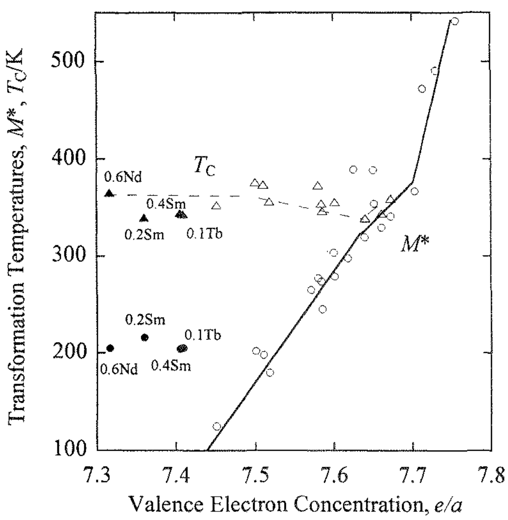

Fig.3 Transformation temperatures as a function of valence electron concentration. M^*: martensitic transformation temperature. T_C: Curie temperature. Open and solid symbols indicate the data for ternary alloys and rare earth containing alloys, respectively.

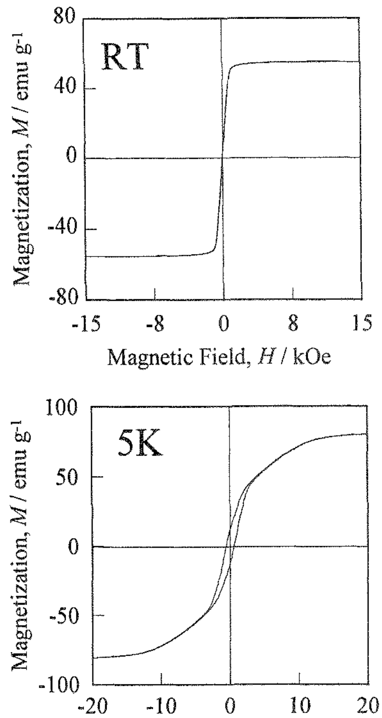

Fig. 4 Magnetization curves of Ni - 22.4 mol%Mn - 25.1 mol%Ga - 0.2 mol%Sm alloy obtained at room temperature (parent phase) and at 5 K (martensite phase).

Fig. 4 is the magnetization curves obtained in the parent phase at 220 K and in the martensite phase at 5 K. It should be noted that the deflection points exist in the curve obtained for martensite phase. The similar tendency was also observed for Nd and Tb containing alloys. The reason for the observed deflection in the magnetization curves of martensite in rare earth containing alloys is not clear at this point. But it seems that the rare earth elements has noticeable effect on the magnetization process of martensite phase.

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