Effects of Composition and Structure on Mechanical Properties of Polycrystalline Ni₂MnGa Alloy

Hiroyuki Ogasawara^{*,+}, Makoto Ohtsuka^{**,++}, Minoru Matsumoto^{**}and Kimio Itagaki^{**}

Graduate Student, Tohoku University, Sendai 980-8577, JAPAN Fax: 81-22-217-5211, ⁺e-mail: ogaline@mail.tagen.tohoku.ac.jp **IMRAM, Tohoku University, Sendai 980-8577, JAPAN Fax: 81-22-217-5211, ⁺⁺e-mail: ohtsuka@tagen.tohoku.ac.jp

The ternary intermetallic compound Ni₂MnGa is a very attractive material because it has both shape memory effect (SME) and ferromagnetic property. However, polycrystalline Ni₂MnGa alloy is too brittle to be formed in a required shape. In the present study, the composition and structure of non-stoichiometic Ni₂MnGa alloy, whose matrix is martensitic phase (β) at room temperature, were controlled in order to improve the mechanical properties. The ingots of several samples having different compositions were prepared by arc-melting and heat-treated at 1073 K for 360 ks. The sample alloys have three different phase conditions: single phase of β , multi phase of $\beta + \alpha'(Ni_3Ga)$ and multi phase of $\beta + \gamma(Mn,Ni)$. Vickers hardness (HV) of the multi phase range alloys is superior to that of the single phase range alloys. The strength of the multi phase range alloys is also superior. It is clarified that the precipitation of additional α' or γ phase in the parent β phase is effective to improve hardness and strength of polycrystalline Ni₂MnGa alloys.

Key words: nickel-manganese-gallium, ferromagnetic shape memory alloy, polycrystal, mechanical property, martensitic transformation

1. INTRODUCTION

The ternary intermetallic compound Ni_2MnGa is a very attractive material because it has both shape memory effect (SME) and ferromagnetic property. It has the Heusler type crystal structure at high temperature and some martensitic crystal structures at low temperature [1-3]. The martensitic transformation of stoichiomeiric composition Ni_2MnGa occurs in the ferromagnetic region below Curie temperature and can be controlled not only by temperature and stress but also by magnetic field [4]. However, polycrystalline Ni_2MnGa alloy is too brittle to be formed in a required shape.

In recent research to improve the mechanical properties of Ni-Mn-Ga shape memory alloy, thin film [5-7], melt spun ribbon [8] and pulse discharged sintered (PDS) [9] processes are mainly discussed. For the bulk alloy, single crystal and single phase Ni-Mn-Ga alloys are mainly discussed, however, there are few reports about polycrystalline and multi phase Ni-Mn-Ga alloys.

Fig. 1 shows the phase diagram of Ni-Mn-Ga system at 1073 K reported by Wedel [10]. According to the phase diagram, stoichiometric Ni₂MnGa represents a single phase of β . It was also reported that the maximum tensile stress and strain of Ni₅₄Mn₄₀Ga₆ in a range of multi-phase of $\beta + \gamma$ and Ni₆₃Mn₁₀Ga₂₇ in a range of multi-phase of $\beta + \alpha'$ were superior to those of the stoichiometric Ni₂MnGa [11].

In the present study, by controlling the chemical composition and by heat treatment, the effects of composition, structure and additional phase on the mechanical properties of polycrystalline Ni-Mn-Ga alloy were investigated.

2. EXPERIMENTAL PROCEDURE

All samples were arranged by two parameters: valence electron concentration (e/a) and Mn content. E7.7-series were arranged by controlling Mn content in a range from 10.0 to 25.0 mol%Mn, keeping e/a at 7.7. While, Mn17.5-series were arranged by controlling e/a in a range from 7.7 to 8.1, keeping the Mn content at 17.5 mol%.



Fig. 1 Phase diagram of ternary Ni-Mn-Ga alloy at 1073K [10].

Small ingots of each sample were prepared by arc-melting of high-purity initial elements: Ni (99.9 %), Mn (99.9+%) and Ga (99.9999 %).

They were encapsulated into a quartz tube under vacuum and homogenized at 1273 K for 86.4 ks followed by quenching into ice water. Then, the homogenized ingots were heat-treated in the evacuated tube at 1073 K for 360 ks followed by quenching into ice water. A part of alloys was spark-cut into rectangular specimens with dimension of 3 mm \times 3 mm \times 6 mm.

The chemical compositions of alloys were determined by the inductively coupled plasma (ICP) spectrometry (Seiko SPS-1200A) and electron prove micro analyser (EPMA, JEOL JXA-8100). In order to identify apparent phases, the conventional $\theta - 2\theta$ XRD analysis using Rigaku Rint 2200 was carried out at room temperature (RT) using Cu-K α radiation of 20 mA and 36 kV. The micostructures of alloys were observed by an optical microscope (OM). By using Akashi MVK-H0 Vickers Hardness Tester, micro Vickers hardness (HV) was measured at more than 9 points on a surface of the alloy sample where applied load and time were 500 g and 15 s, respectively. Compression tests were performed at room temperature with the same speed (5×10^4 mm/s) by advanced materials testing system (Instron 5582).

3. RESULTS AND DISCUSSION

3.1 Constitution of Phase

Fig. 2 shows the XRD diffraction pattern of the E7.7 and Mn17.5-series. In E7.7-series, only the peaks corresponding to β -phase appear in a range of 15.0-25.0 mol%Mn, while, under 12.5 mol%Mn, the peaks corresponding to $\alpha'(Ni_3Ga)$ -phase and $\gamma'(Ni_3Ga_2)$ -phase appear in addition to the β -phase. In Mn17.5-series, in a range of e/a over 7.9, the peaks of $\gamma(Mn,Ni)$ -phase appear in addition to β -phase. These results correspond very well with the phase diagram shown in Fig. 1.

3.2 Microstructure

Fig. 3 shows the micrographs of the samples of single and multi phase alloys, respectively. Several crystal



Fig. 2 X-ray diffraction patterns of the alloys of (a) E7.7-series and (b) Mn17.5-series



Fig. 3 Microstructure of alloys with the composition in a range of (a) single phase (Ni_{52.9}Mn_{25.0}Ga_{22.1}, β), (b) multi phase (Ni_{61.4}Mn_{10.0}Ga_{28.6}, $\beta + \alpha'$) and (c) multi phase (Ni_{62.9}Mn_{17.5}Ga_{19.6}, $\beta + \gamma$).



Fig. 4 Vickers hardness of alloys as a function of (a) Mn content (E7.7-series) and (b) e/a (Mn17.5-series).



Fig. 5 Proof stress ($\sigma_{0,2}$) as a function of Vickers hardness for both series.

grains with martensitic twins are observed in the alloys with the composition in a range of single phase (β), as shown in Fig 3(a). In addition, the crystal grains grow along the cooling direction after arc-melting. While, in the alloys with the composition in a range of multi phase, a quite different microstructure is observed. In E7.7-series, the precipitation of additional phase is observed in the enormously coarse grain, as shown in Fig. 3(b). In Mn17.5-series, the dendritic precipitation of additional phase is observed in the coarse grain, as shown in Fig. 3(c). It was identified by EPMA analysis that the compositions of these precipitations observed in E7.7-series and Mn17.5-series are in a range of α '-phase and γ -phase, respectively.

3.3 Vickers Hardness Test

Fig. 4 shows Vickers hardness as a function of Mn-content in E7.7-series and e/a in Mn17.5-series. In E7.7-series, hardness increases with decreasing Mn content, as shown in Fig. 4(a). In addition, the increase in hardness of the alloys with the composition under 15.0 mol%Mn (multi phase range alloys) is remarkable in comparison with the alloys with the composition over 15.0 mol%Mn (single phase range alloys). The

gradient of hardness-Mn content plots for the single and multi phase range alloys are 2.94 and 13.8, respectively. So, it is clear that precipitation of the additional phase is very effective on the improvement of hardness of the alloys in E7.7-series.

In Mn17.5-series, the hardness values of the alloys with e/a over 7.9 (multi phase range alloys) are larger than that of the alloys with e/a of 7.7 (single phase range alloys), as shown in Fig. 4(b). However, the hardness of the alloy with e/a of 8.1 is decreased in spite of the multi phase range alloys. This decrease is considered to be ascribed to caused the precipitation of coarse particle of additional phase.

3.4 Compression Test

In both series, stress-strain curve is improved for the multi phase range alloys in comparison with the single phase range alloys. Fig. 5 shows proof stress ($\sigma_{0.2}$) as a function of the Vickers hardness for both series. Strength of the multi phase range alloys having the improved hardness is also improved in comparison with the single phase alloys. So, it is clear that the precipitation of the additional phase is very effective on the improvement of not only hardness but also stress-strain curve and strength of the alloys.

4. SUMMARY

- (1) In E7.7-series, in addition to β phase, α' and γ' phases appear in the alloys with the composition under 12.5 mol%Mn, and in Mn17.5-series, an additional phase (γ) appears in the alloys with *e/a* over 7.9. These results correspond very well with the reported phase diagram at 1073K.
- (2) The grain size becomes coarse with decreasing Mn content or increasing e/a.
- (3) Vickers hardness (HV) of alloys increases in a range of multi phase, while, in Mn17.5-series, HV decreases at e/a of 8.1. This decrease is caused by the precipitation of coarse particle.

- (4) Stress-strain curve and strength are also improved in a range of multi phase.
- (5) In both series, additional phases are effective on the improvement of mechanical properties (hardness, strength) of Ni₂MnGa alloys.

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