Magnetic Properties and Phase Change of $\text{Ni}_{3-y}\text{Mn}_y\text{Sn}$ Alloy

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The correlation between the phase change and the appearance of ferromagnetism in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy was studied. There appeared three kinds of phases with the DO_{19} -type hexagonal, the DO_3 - and the Heusler (L2_1)-type cubic structures in this alloy. In each phase, the ferromagnetic Curie temperature, T_c , had a tendency to increase with increase in Mn content, x . The T_c vs x curve showed a discontinuous drop by the phase change from DO_{19} to DO_3 , and had a bend at $x=25$ and a small minimum at $x=32$ in the cubic phase. The composition dependence of T_c in the DO_3 and L2_1 phases was analyzed by the molecular field approximation taking into account the magnetic interaction energies of Mn-Mn pairs between the 1st, 2nd and 3rd near neighbors.

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I. Introduction

The Heusler alloys such as Cu_2MnAl and Ni_2MnSn have extensively been studied to investigate the origin of ferromagnetism in such nonferrous alloys. For example, the ferromagnetism of Ni_2MnSn alloy has been studied by means of magnetic measurements⁽¹⁾, the Mössbauer effect⁽²⁾⁽³⁾, nuclear magnetic resonance⁽⁴⁾, neutron diffraction⁽⁵⁾⁽⁶⁾ and theoretical analyses^{(7)~(9)}. As a result, it has been reported that the ferromagnetic Curie temperature, T_c , of Ni_2MnSn alloy is 345 K and that the magnetic moment in Ni_2MnSn alloy is $4.04 \mu_B/\text{mol}$ and localized on the Mn site. Campbell *et al.*⁽¹⁾ have studied the effect of the third alloying elements ($M=\text{Ti}, \text{V}, \text{Cr}$) on T_c of Ni_2MnSn alloy and shown that T_c of $\text{Ni}_{50}\text{Mn}_{25-p}\text{M}_p\text{Sn}_{25}$ alloys decreases with increase in p . These alloys are always of the Heusler(L2_1)-type cubic structure. However, any magnetic ordering has not been observed in Ni_3Sn alloy with the DO_{19} -type hexagonal structure⁽¹⁰⁾.

In the preceding paper⁽¹¹⁾, the present authors have reported the phase diagram of $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy and shown that there

appeared 3 kinds of phases with the DO_{19} -type hexagonal, the DO_3 - and the L2_1 -type cubic structures. The martensitic transformation has also been observed in this alloy. On the other hand, the effect of the B2- or DO_3 -type ordering on the composition dependence of T_c in alloys such as Fe-Co, Fe-Al and Fe-Si has been studied by several investigators^{(12)~(17)}. Then, in this work, the magnetic properties in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy was studied in various ranges of Mn content, and the composition dependence of T_c in the cubic (DO_3 or L2_1) phases were analyzed theoretically by the molecular field approximation.

II. Experimentals

Alloy specimens were prepared by powder metallurgy techniques using powders of the constituent metals with high purity (99.99% Ni, 99.99% Sn and 99.9% Mn). Powders were formed into compacts by a pressure of 5 MPa and sintered at 1200 K for 580 ks in an evacuated quartz tube, and finally, quenched into water. This specimen was filed into fine powders and quenched from 873 to 273 K. Using this powdered specimen, the structure of alloy was studied by means of X-ray analysis with the Debye-Scherrer method. The temperature dependence of the magnetic susceptibility, χ , of the alloy specimen was measured by a magnetic torsion balance in the magnetic field of 560 kA/m. The temperature

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dependence of the molar permeability was measured by a magnetic torsion balance and by a vibrating specimen magnetometer in a weak magnetic field of 56 kA/m in order to determine T_c . These measurements were carried out in the temperature range from 80 to 600 K.

III. Results

1. Phase change in Ni-Mn-Sn alloy

The structure of $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K is of the DO_{19} -type hexagonal in the range of Mn content (x) with 0~6.5 at %, the DO_3 -type cubic in the ranges of $x=9\sim15$ and $32\sim47$, and the L_{21} -type cubic in the range of $x=15\sim32$ at room temperature⁽¹¹⁾. In the range of x below about 9, the high temperature DO_3 -type cubic structure has been shown to undergo a martensitic transformation to the β - $\text{Cu}_3\text{Ti}(2\text{H})$ -type orthorhombic structure during quenching⁽¹¹⁾. In the range of x above 47, the precipitation of unknown phase was observed. The unit cells of the DO_{19} , 2H, DO_3 and L_{21} -type structures are shown in Figs. 1 and 2.

The composition dependence of the lattice parameters, a , in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K is shown in Fig. 3. The a vs x curve in the cubic phase has a maximum at the composition $x=25$ and two bends at $x=15$ and

Fig. 1 The configuration of atoms in the DO_{19} and 2H structures. The closed circles and triangles represent atoms in this plane, and the open ones those above this plane.

Fig. 2 Unit cell of the DO_3 - and the Heusler (L_{21})-type cubic structures. In the DO_3 structure of Ni_2MnSn alloy, α and β sites are occupied by Ni and Mn atoms with equal probabilities and γ site by Sn atoms. In the L_{21} structure, α , β and γ sites are occupied by Ni, Mn and Sn atoms, respectively.

Fig. 3 Composition dependence of the lattice parameters in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K, measured at room temperature.

$x=32$, i.e. at the phase boundaries between DO_3 and L_{21} phases. As seen in Fig. 3, the lattice parameter in the cubic phase is considered to increase by the phase change from DO_3 to L_{21} .

In order to clarify the effect of the chemical long range order on the composition dependence of T_c in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy, the probabilities of finding Mn atoms on the three sublattice sites were analyzed by X-ray analysis. The structure factor of the X-ray diffraction

lines such as 111, 200 and 220 can be given by the following equation†:

$$\begin{aligned} F_{111} &= f_{\text{Sn}} - f_{\text{Ni}} + B_{\beta}(f_{\text{Ni}} - f_{\text{Mn}}), \\ F_{200} &= f_{\text{Sn}} - f_{\text{Ni}} + (4x_{\text{B}} - 2B_{\beta})(f_{\text{Ni}} - f_{\text{Mn}}), \\ F_{220} &= 4x_{\text{A}}f_{\text{Ni}} + 4x_{\text{B}}f_{\text{Mn}} + 4x_{\text{C}}f_{\text{Sn}}, \end{aligned} \quad (1)$$

where f_{Ni} , f_{Mn} and f_{Sn} represent the atomic scattering factor of Ni, Mn and Sn atoms, respectively. The probabilities of finding Ni and Mn atoms on the α and β sites were obtained by analyzing the intensities of the X-ray diffraction lines, obeying the method shown by Matsuda *et al.*⁽¹⁹⁾, using the structure factors shown in eq. (1). The obtained probabilities of finding Mn atoms on the α and β sites, B_{α} and B_{β} respectively, in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy are shown in Fig. 4 as a function of composition. The error of the measurement of probabilities was estimated to be ± 0.07 . In the DO_3 phase, B_{α} and B_{β} are given by $B_{\alpha} = B_{\beta} = 4x_{\text{B}}/3$ from eq. (1') and accordingly, they increase with increase in Mn content. In the range of Mn content from 18 to 28 at%, the obtained values of B_{α} and B_{β} are close to the expected values, i.e. $B_{\beta} = 4x_{\text{B}}$ and $B_{\alpha} = 0$ when $x_{\text{B}} < 0.25$, and $B_{\beta} = 1$ and $B_{\alpha} = 2(x_{\text{B}} - 0.25)$ when $x_{\text{B}} > 0.25$: this means that the alloy has the completely ordered L2_1 -type structure in this range of composition. This result gives an important information to analyze the composition dependence of T_{c} described later.

2. Magnetic properties of Ni-Mn-Sn alloy

The temperature dependence of the molar paramagnetic susceptibility††, χ , in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K

Fig. 4 Probabilities of Mn atoms located on α and β sites, B_{α} and B_{β} respectively, as a function of Mn content in the cubic phase of $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K.

Fig. 5 Inverse of the molar magnetic susceptibility, χ^{-1} , as a function of temperature in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K, measured in the magnetic field of 560 kA/m. Numbers in the figure represent the Mn content (x).

† Ordering of atoms in the ternary *bcc* alloy can be described by nine probabilities of finding the specified atoms on the three sublattice sites⁽¹⁸⁾. The probabilities of finding Ni, Mn and Sn atoms on i site are shown by A_i , B_i and C_i ($i = \alpha, \beta, \gamma$), respectively, and the mole fraction of Ni, Mn and Sn atoms by x_{A} , x_{B} and x_{C} . The following relations between probabilities are given from the equations shown in a previous paper⁽¹⁸⁾, assuming $A_{\gamma} = B_{\gamma} = C_{\gamma} = 0$ in this alloy system, i.e. the γ site is always occupied by Sn atoms:

$$\begin{aligned} 2A_{\alpha} + A_{\beta} &= 4x_{\text{A}}, \quad 2B_{\alpha} + B_{\beta} = 4x_{\text{B}}, \quad C_{\gamma} = 4x_{\text{C}} = 1, \\ A_{\alpha} + B_{\alpha} &= 1, \quad A_{\beta} + B_{\beta} = 1 \quad \text{and} \quad x_{\text{A}} + x_{\text{B}} = 0.75. \end{aligned} \quad (1')$$

†† One mole represents $\text{Ni}_{0.75-x}\text{Mn}_{x\text{B}}\text{Sn}_{0.25}$ ($x_{\text{B}} = x/100$).

was measured in an external magnetic field of 560 kA/m. The χ^{-1} vs T plot shown in Fig. 5 indicates that the susceptibility obeys the Curie-Weiss law:

$$\chi^{-1} = (T - \theta_p)/C \quad \text{and} \quad C = (m\mu_{\text{B}})^2 N/3k, \quad (2)$$

where T is the temperature, θ_p the paramagnetic

Curie temperature, C the Curie constant, μ_B the Bohr magneton, N the Avogadro number, k the Boltzman constant, $m\mu_B$ the effective paramagnetic moment per molecule. The paramagnetic moment per Mn atom, μ_{eff} , is obtained by dividing $m\mu_B$ by the mole fraction of Mn atom, x_B . By analyzing the χ^{-1} vs T curves shown in Fig. 5 using eq. (2), θ_p and μ_{eff} in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy are obtained as a function of Mn content, as shown in Fig. 6. In the range of small Mn content, μ_{eff} is near 6 and decreases with increase in Mn content. θ_p has a tendency to increase with increase in Mn content in each phase. When the alloy phase changes from DO_{19} to DO_3 at the composition near $x=7\sim 10$, θ_p drops discontinuously.

The temperature dependence of the molar permeability, μ_{56k} ,^{†††} in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K was measured during heating. The example of μ_{56k} vs T curves is shown in Fig. 7. The ferromagnetic Curie temperature, T_c , was given by the temperature where the tangent of a μ_{56k} vs T curve with the largest slope intersected the horizontal axis. The composition dependence of T_c in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy is shown in Fig. 8. T_c was also recognized by the differential thermal

Fig. 6 The paramagnetic moment per Mn atom, μ_{eff} , and the paramagnetic Curie temperature, θ_p , as a function of composition in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy.

††† μ_{56k} represents the molar permeability measured in the weak magnetic field of 56 kA/m.

Fig. 7 The molar permeability, μ_{56k} , measured in the magnetic field of 56 kA/m as a function of temperature in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K. Numbers in the figure represent the Mn content (x).

Fig. 8 Composition dependence of the ferromagnetic Curie temperature, T_c , in the hexagonal (DO_{19}) and the cubic (DO_3 and L_{21}) phases of $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy quenched from 873 K. T_c of the martensite (2H) phase is also shown in this figure.

analysis above room temperature, which was consistent with that obtained by the magnetic measurement. T_c has a tendency to increase with increase in Mn content in each phase. In the cubic phase, the T_c vs x curve has a bend at the composition $x=25$ and a small minimum at $x=32$. When the phase changes from DO_{19} to DO_3 , T_c drops discontinuously. T_c of the martensite phase with the 2H-type orthorhombic structure in alloys with com-

positions $x=5$ and 6, which was obtained by quenching from 1170 to 273 K, is also measured and found to be lower than that of the DO_{19} phase. Details of the magnetic properties in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy with x below 5 is not clear at present, which should be studied in a temperature range below 77 K. The composition dependence of T_c in the cubic phase will be discussed in the next section.

IV. Thermodynamical Consideration

The magnetic moment in Ni_2MnSn alloy has been reported to be localized on Mn site^{(1)~(9)}. The temperature dependence of the chemical long range order in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy is considered to be negligible at a temperature range below 450 K⁽¹¹⁾. Thereby, the magnetic ordering in this alloy system is reasonably described by considering only the magnetic contribution to the free energy on the basis of the molecular field approximation^{(14)~(17)}. If the numbers of Mn atoms on the α and β sites are given by N_α and N_β , respectively, the following relations are obtained:

$$N_\alpha + N_\beta = x_B N, \quad N_\alpha = NB_\alpha/2 \text{ and } N_\beta = NB_\beta/4, \quad (3)$$

where N is the number of lattice points. The parameter of magnetic order, S , is given by the following equation:

$$S = (N_\alpha^+ - N_\alpha^-)/N_\alpha = (N_\beta^+ - N_\beta^-)/N_\beta,$$

and

$$N_\alpha^+ + N_\alpha^- = N_\alpha, \quad N_\beta^+ + N_\beta^- = N_\beta, \quad (4)$$

where N_α^+ and N_α^- represent the number of up and down spins on Mn atoms in the α site, and N_β^+ and N_β^- those in the β site, respectively. It is assumed in eq. (4) that the parameter of magnetic order in the α site is identical with that in the β site. From eq. (4), the numbers of up and down spins on the α and β sites are given as follows:

$$\begin{aligned} N_\alpha^+ &= N_\alpha(1+S)/2, \quad N_\alpha^- = N_\alpha(1-S)/2, \\ N_\beta^+ &= N_\beta(1+S)/2 \text{ and } N_\beta^- = N_\beta(1-S)/2. \end{aligned} \quad (5)$$

The magnetic free energy of the system is given by the molecular field approximation taking into account the magnetic interaction energies

of Mn-Mn pairs with the 1st, 2nd and 3rd nearest neighbors, which are written by J_1 , J_2 and J_3 , respectively:

$$F = E - kT \ln Z, \quad (6)$$

$$\begin{aligned} E = & -16J_1 N_\alpha N_\beta S^2/N - 6J_2 N_\alpha^2 S^2/N \\ & - 12J_3 (N_\alpha^2 + 2N_\beta^2) S^2/N, \end{aligned} \quad (7)$$

$$Z = N_\alpha! N_\beta! / (N_\alpha^+! N_\alpha^-! N_\beta^+! N_\beta^-!). \quad (8)$$

T_c is given by the condition, $\partial^2 F / \partial S^2 = 0$ and $S=0$ at $T=T_c$, as follows:

$$kT_c = \{4J_1 B_\alpha B_\beta + 3J_2 B_\alpha^2 + 3J_3 (2B_\alpha^2 + B_\beta^2)\} / x_B. \quad (9)$$

The composition dependence of T_c can be analyzed by eq. (9), which will be described in the next section.

V. Discussion

The composition dependence of the Curie temperature, T_c , in the cubic phase of $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy was calculated by eq. (9), using the obtained values of B_α and B_β in Fig. 4 and assuming following parameters:

$$J_1 = 62.6 \text{ k}, \quad J_2 = 23.6 \text{ k} \text{ and } J_3 = 28.7 \text{ k}.$$

The calculated result is shown in Fig. 9, compared with the experimental result of T_c shown in Fig. 8. In the DO_3 phase, T_c is

Fig. 9 Composition dependence of the ferromagnetic Curie temperature, T_c , calculated by eq. (9) in the cubic phase of $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy. The experimental result of T_c is also shown for comparison.

expected to be proportional to Mn content, $x(=100x_B)$. And in the $L2_1$ phase, T_c vs x curve is expected to have a bend at the stoichiometric Ni_2MnSn composition (i.e. at $x=25$). And moreover, T_c is expected to increase by the phase change from DO_3 to $L2_1$. The calculated result of T_c vs x curve can well explain the experimental one especially in the range of x above 18, as shown in Fig. 9. In the range of x below 18, the experimental value of T_c is higher than the calculated one. As shown in Fig. 7, the slope of a μ_{56k} vs T curve near T_c was found to be mild in the range of x below 18. This result suggests that the local fluctuation of concentration of Mn atoms may exist even in the well-annealed specimen, which results in a raise of T_c . This may be one of the reason of the discrepancy between the calculated and the experimental values of T_c in the range of x below 18. The other may come from the variation of the magnetic interaction energies dependent on composition. When the phase changes from DO_{19} to DO_3 , T_c decreases discontinuously as shown in Fig. 8. This is attributable mainly to the fact that the coordination number (z) of the DO_{19} -type hexagonal ($z=12$) is larger than that of the DO_3 -type cubic ($z=8$).

As shown in Fig. 6, μ_{eff} in $Ni_{75-x}Mn_xSn_{25}$ alloy is about $6.0 \mu_B$ in a range of small Mn content and decreases with increase in x . This phenomenon is similar to that reported in the dilute solid solution such as Ag-Mn and Ag-Sn-Mn⁽²⁰⁾. In the stoichiometric Ni_2MnSn composition, μ_{eff} is $5.10 \mu_B$, which is in good agreement with the result of Campbell *et al.*⁽¹⁾ For the electronic configuration of Mn atom with $3d^5 4s^2$, μ_{eff} is $5.91 \mu_B$ and for that with $3d^6 4s^1$, μ_{eff} is $4.90 \mu_B$ ⁽²⁰⁾. Therefore, in a range of small Mn content, Mn atoms are considered to have 5 unpaired electrons. According to the calculated result of the band structure of Ni_2MnSn alloy⁽⁹⁾, the majority spin band of Mn atoms overlaps partially the minority spin band and the Fermi level lies below the top of the majority spin band. Both spin bands have electron holes. Then, the localized magnetic moment of Mn atoms in Ni_2MnSn alloy is reduced to $4.01 \mu_B$ ⁽⁹⁾. In the present study, the measurement of the saturated

magnetization at a temperature near 4 K was not carried out, and the magnetic moment of Mn atom in the ferromagnetic state is not clear. This investigation should also be performed in the future in order to clarify the details of the magnetic properties in this alloy.

The Curie temperature, T_c , of $Ni_{75-x}Mn_xSn_{25}$ alloy is represented as a function of the electron concentration, e/a^* , in Fig. 10, together with the starting temperature of the martensitic transformation, M_s , of $Ni_{75-x}Mn_xSn_{25}$ and $Ni_{75-x}Cu_xSn_{25}$ alloys reported in the preceding paper⁽¹¹⁾. Hereby, e/a^* represents an averaged number of d+s+p electrons in the outer shell of the constituent atoms. In Fig. 10, e/a^* of Ni_3Sn is 11.0 and e/a^* of $Ni_{75-x}M_xSn_{25}$ ($M = Cu$ or Mn) increases (or decreases) with increase in Cu (or Mn) content. It has been already shown that the DO_3 phase of these alloys becomes unstable in the range of e/a^* from 10.7 to 11.2 and undergoes a martensitic transformation from the DO_3 -type cubic to the 2H-type orthorhombic structure⁽¹¹⁾. In the range of e/a^* above 11.0, the alloy has no magnetic moment and the constituent atoms are considered to have the closed shell of d electrons. When e/a^* increases up to 11.5, the concentration of free electrons increases, and as a result, the cubic phase becomes stable as

Fig. 10 The ferromagnetic Curie temperature, T_c , in the cubic (DO_3 and $L2_1$) and the martensite (2H) phases in $Ni_{75-x}Mn_xSn_{25}$ alloy as a function of the electron concentration e/a^* . The starting temperature of the martensitic transformation, M_s , in $Ni_{75-x}Mn_xSn_{25}$ and $Ni_{75-x}Cu_xSn_{25}$ alloys⁽¹¹⁾ is also shown in this figure.

shown already in $\text{Ni-Cu-Zn}^{(21)}$, $\text{Cu-Zn}^{(22)}$ and Au-Cd alloys⁽²³⁾. When e/a^* decreases below 11.0, the alloy shows ferromagnetism and the cubic phase becomes stable again in the range of e/a^* below 10.7. As shown in Fig. 10, T_c of the martensite (2H) phase is slightly higher than that of the cubic phase extrapolated to the range of e/a^* above 10.7. Then, the influence of the ferromagnetism on the martensitic transformation is expected also in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy. The relation between these phenomena has also been discussed in Fe-Ni alloy⁽²⁴⁾⁽²⁵⁾. Detailed study of the electronic structure and the magnetic property is hoped to clarify the origin of the ferromagnetism and the martensitic transformation in this alloy.

In summary, the phase change and the ferromagnetism in $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloy was studied. There appeared three phases with the DO_{19} -type hexagonal, the DO_3 -type and the L2_1 -type cubic structures. The composition dependence of the ferromagnetic Curie temperature, T_c , was investigated as a function of Mn content in each phase. The composition dependence of T_c in the cubic phase was analyzed by the molecular field approximation taking into account the magnetic interaction between Mn-Mn pairs of the 1st, 2nd and 3rd near neighbors. The starting temperature of the martensitic transformation, M_s , and T_c were discussed as a function of electron concentration.

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