GMR AND SOFT MAGNETIC PROPERTIES OF Ni-Mn ALLOYS WITH DISPERSED FERROMAGNETIC NANO PARTICLES

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Abstract. GMR and soft magnetic properties were investigated in nano-scale inhomogeneous \( \text{Ni}_{x}\text{Mn}_{1-x} \) alloys \((x = 0.20 \sim 0.30)\), where ordered single-domain particles are distributed in disordered nonmagnetic or Ni-rich or Mn-rich matrices. The GMR of \( \text{Ni}_{x}\text{Mn} \) alloy depends on the volume fraction of ordered domains \( \varepsilon \). Maximum value of \(-1.8\%\) is obtained at \( \varepsilon \sim 0.2 \). Moreover, the GMR depends remarkably on \( x \): GMR for \( 0.20 \leq x \leq 0.24 \) is small (Type I) and for \( 0.26 \leq x \leq 0.30 \) has a maximum of \(-6\%\) at \( x = 0.30 \) (Type II). Types I and II are caused respectively by ferromagnetic and antiferromagnetic interactions between domains.

1. INTRODUCTION

In the \( \text{Ni}_{x}\text{Mn} \) alloy system, the Cu\textsubscript{3}Au-type ordered phase shown in Fig.1 is formed after suitable heat treatment. The most striking characteristic of this system is as follows: a change in the degree of the long-range order causes a wide variety of the magnetic and transport properties. Many studies of \( \text{Ni}_{x}\text{Mn} \) have been reported so for which concentrate mainly on the completely ordered and disordered states \([1-7]\).

The difference in their texture was observed by Taoka \([8]\) and Marcinkowski and Poliak \([9]\) using transmission electron microscopy. For \( \text{Ni}_{x}\text{Mn} \) alloys annealed in the temperature range of 733-773K, they demonstrated that the ordered ferromagnetic domains are distributed in a disordered nonmagnetic matrix. In previous study \([10, 11]\), we reported that the value of M for \( \text{Ni}_{x}\text{Mn} \) annealed at 693K depends on the atomic short-range order. The alloy reveals a superparamagnetic behavior in a wide temperature range above the Curie point \( T_C \), where the alloy has low degree of order. The magnetic analysis based on a superferromagnetic model \([12,13]\) shows that long-range-ordered magnetic domains with nanometer size are distributed in a disordered nonmagnetic matrix.

Giant magnetoresistance (GMR) was observed in a variety of magnetic granular alloy system such as Co-Cu \([14]\), Co-Ag \([15]\) and Fe-Cr \([16,17]\), where single-domain ferromagnetic particles are embedded in an immiscible medium. The GMR in granular systems is due to the additional scattering by ferromagnetic single domain particles, which are randomly oriented. The spin-dependent scattering decreases when the magnetization of particles in superparamagnetic phase is tilted in the direction of the applied field.

In such an inhomogeneous phase, nano-particles are in contact with each other forming a group, where spontaneous magnetization \( M_s \) of particles has a tendency to be parallel with each other because of exchange interaction. Since each \( M_s \) in a group have magnetization ripple \([18]\), the system is expected to show soft magnetic property \([19]\).
GMR and soft magnetic properties of Ni-Mn alloys with dispersed ferromagnetic nano particles

At first, we report about ferromagnetic particle size, magnetization and GMR for Ni$_3$Mn alloy with various long-range order [20]. Next, GMR and soft magnetic properties of Ni$_{1-x}$Mn$_x$ ($x = 0.20 – 0.30$) alloys which have nano-scale inhomogeneity are investigated [21-23].

2. EXPERIMENTAL PROCEDURE

Ni$_{1-x}$Mn$_x$ ($x = 0.20 – 0.30$) alloys were melted in an rf induction furnace and then cast. These ingots were homogenized by holding in a vacuum for 15 h at 1273K. It was cold-worked into a ribbon (0.5 mm in thickness) and a wire ($\Phi = 0.5$ mm). They were annealed in Ar for various hours at 673–713K to get ordered states. The X-ray diffraction for sheet samples was measured with Cu-$K_\alpha$ radiation. The loop of magnetization $M$ vs. magnetic field $H$ was measured by using a vibrating sample magnetometer. Resistivity measurements were made by the 4-terminal method in an electromagnet with a maximum applied field of 10 kOe at room temperature. The magnetoresistance (MR) ratio is defined by the following equation:

$$\text{MR ratio} = \frac{\Delta \rho}{\rho_0} = \frac{\rho_H - \rho_0}{\rho_0}, \quad (2.1)$$

where $\rho_H$ and $\rho_0$ are the resistivities with and without $H$, respectively.

Permeability of wire specimen for 1~500 kHz high frequency was measured by impedance analyzer. In order to investigate antiferromagnetic interaction between ferromagnetic nano-scale particles in Mn-rich matrices, we studied magnetization and MR in large pulse magnetic field up to 16 T at low temperature 12K.

3. LONG-RANGE ORDER PARAMETER S AND AVERAGE PARTICLE SIZE D

Fig. 2 shows (110) $K_{11}$ peaks with cutting $K_{12}$ obtained for the Ni$_3$Mn alloys, indicating super-lattice formation. A peak at $\theta = 34.2^\circ$ is attributed to an instrumental artifact. The long-range-order parameter $S$ was determined by comparing the integral intensity of the (110) peak to that of the (220) peak.

Average particle size $D$ of samples was determined from the broadening of the X-ray diffraction peak by using the Scherrer’s equation,

$$D = \frac{0.9}{W \cos \theta}, \quad (3.1)$$

where $\lambda$, $W$ and $\theta$ denote the wavelength (0.15405 nm) , FWHM (full width at half maximum intensity) of each (110) peaks and Bragg angle. The values of $S$ and $D$ are given in Table 1. They are 2.8 to 10 nm for $S = 0.26$ to 0.88 states. The $<m>$ in Table 1 is also the average particle size estimated by magnetic analysis [11]. We find that the $D$ value is about 1.5 times larger than the corresponding $<m>$ value.
Thus these values are of the same order in size. The volume fraction $\varepsilon$ of the ordered regions can be evaluated by using the relationship [24] $\varepsilon = S^2 / S_{do}^2$, where $S_{do}$ is the long-range-order parameter in the ordered domains. Assuming $S_{do} = 1$, $\varepsilon$ is 0.017 to 0.78 for $S = 0.13$ to 0.88 states.

Fig. 3 also shows $(110) K_{\alpha}$ peaks obtained for the present Ni$_{1-x}$Mn$_x$($x = 0.20 - 0.30$) alloys annealed for 100 h at 693K. The values of $S$ and $D$ are given in Table 2. The $S$ value increases 0.3 to 0.66 with Mn concentration, $x$ for $0.20 \leq x \leq 0.26$ and reaches to about 0.7 for $0.26 \leq x \leq 0.30$. The $D$ value also increases about 4 to 6.7 nm with $x$. The volume fraction $\varepsilon$ in the ordered regions is about 0.1 to 0.5 for $S = 0.3$ to 0.72 states. They are nearly constant value of 0.5 for Ni$_{1-x}$Mn$_x$ alloys of $0.26 \leq x \leq 0.30$.

4. MAGNETIZATION AND GMR OF Ni$_3$Mn ALLOY

4.1. Magnetization of Ni$_3$Mn alloy

Fig. 4 shows the $M$ vs. temperature $T$ curves of Ni$_3$Mn alloys ordered for 5-1000 h at 673K and 693K [10]. The $S$ values in brackets were determined by X-ray diffraction analysis. It was found that $M$ increases sharply with $S$.

The magnetism of Ni$_3$Mn depends on the number $n$ of the nearest-neighbor Mn atoms around an Mn atom [7, 10, 18], because a ferromagnetic interaction operates for the Ni-Ni and Ni-Mn pairs and an antiferromagnetic one for the Mn-Mn pairs. That is, the average exchange interaction around a Mn atom is considered to be $J_{ex} > 0$ for $n < 3$, $J_{ex} \approx 0$ for $n = 3$ and $J_{ex} < 0$ for $n > 3$. The average number $\langle n \rangle$ of $n$ for a Ni$_3$Mn alloy can be evaluated from $S$ by using Cowley’s equation [10,25]. From Fig.1, $\langle n \rangle$ is evaluated to be 0 and 3, respectively, for the ordered state ($S = 1$) and the disordered state ($S \approx 0$). $\langle n \rangle$ decreases with $S$ and $M$ increases with $S$. It is found that $M$ reaches a maximum of 84 emu/g at $S = 0.88$ ( $\langle n \rangle \approx 0.7$) for Ni$_3$Mn ordered at 693K. The value is 82% of one obtained from $S = 1$ state where the local magnetic moments of $\langle m \rangle_{Ni}$ (~0.31 $\mu_B$) [26] and $\langle m \rangle_{Mn}$ (~ 3.6 $\mu_B$) [26] are parallel to each other.

Table 1. The annealing time (t) at 673K and 693K, the long-range-order parameter ($S$), average cluster size ($D$ and $\langle m \rangle$), the volume fraction of the ordered regions ($\varepsilon = S^2 / S_{do}^2$), ferromagnetic and paramagnetic Curie temperatures $T_F$ (K) and $\theta_p$ (K).

<table>
<thead>
<tr>
<th></th>
<th>673 K</th>
<th>693 K</th>
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<tr>
<td>t (h)</td>
<td>50 70 116 1000</td>
<td>5 25 50 200 1000</td>
</tr>
<tr>
<td>$S$</td>
<td>0.26 0.39 0.52 0.72</td>
<td>0.13 0.29 0.44 0.64 0.88</td>
</tr>
<tr>
<td>$D$ (nm)</td>
<td>2.8 3.3 3.8 5.9</td>
<td>3.2 4.3 6.5 10</td>
</tr>
<tr>
<td>$\langle m \rangle$ (nm)*</td>
<td>1.7 1.8 2.7</td>
<td>1.4 2.1 2.9</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.068 0.15 0.27 0.52</td>
<td>0.017 0.084 0.19 0.41 0.78</td>
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<tr>
<td>$\varepsilon^*$</td>
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<tr>
<td>$T_F$ (K)</td>
<td>273 353 503 657</td>
<td>241 393 581 713 723</td>
</tr>
<tr>
<td>$\theta_p$ (K)</td>
<td>482 594 643</td>
<td>550 650 710</td>
</tr>
</tbody>
</table>

*Ref.[11]
As seen from the $M - T$ curves in Fig.4, the states for $S \geq 0.64$ are found to be ferromagnetic. The Curie temperature $T_C$ for 673K•1000 h, 693K•200 h and 1000 h states are 657, 713 and 723K, respectively. Furthermore, it should be noted that each curve for $S < 0.64$ states has a long tail in the temperature range of $T > T_F$. We have reported that the magnetism in the range of $T_F < T < \theta_P$ for 693K•5, 25 and 50 h states was superparamagnetic, where $\theta_P$ is the paramagnetic Curie temperature. The $T_F$ and $\theta_P$ of the 673K•50, 70 and 116 h states, which are determined by Arrott plot and inverse susceptibility vs. temperature curves, are listed in Table 1. For these states also, the magnetism in the temperature range of $T_F < T < \theta_P$ is superparamagnetic, where magnetization of single domain in disordered nonmagnetic matrix orients randomly.

4.2. GMR of Ni$_3$Mn alloys

Fig. 5 shows the dependence of $\Delta \rho / \rho_0$ // $H$ and $\perp H$ at room temperature on annealing time $t$ at 673 and 693K, where $\Delta \rho / \rho_0$ // $H$ and $\perp H$ are the MR ratios for electric current parallel and perpendicular to the applied field, respectively. Since $\Delta \rho / \rho_0$ // $H$ and $\perp H$ are negative for all states except the 673K•25 h state and nearly equal for the annealing time of $t \leq 100$ h, each $\Delta \rho / \rho_0$ is considered to be caused by the GMR effect. The MR ratio for $t \geq 100$ h consists of GMR and anisotropic magnetoresistance (AMR). AMR is caused by ferromagnetic behavior. As all the particles grow and then make a connecting network to form large ferromagnetic domains where the annealing time is longer, the GMR decreases gradually and reaches zero such as in, for example, $\Delta \rho / \rho_0$ // $H$ of the 693K•1000 h state. The effect of GMR is maximized in the 693K•50 h ($S = 0.44$) and 673K•116 h state ($S = 0.52$) states.

The finding that the decrease in $\Delta \rho / \rho_0$ // $H$ of 673K•1000 h is slight suggests that the average size of each domain in 673K•116 h state ($D = 3.8$ nm) remains nearly constant in the 673K•1000 h state (5.9 nm).

Fig. 6 shows the dependence of the $\Delta \rho / \rho_0$ // $H$ on the volume fraction $\varepsilon$ of the ordered regions for the 673K- and 693K- samples. The two $\Delta \rho / \rho_0$ vs. $\varepsilon$ curves exhibit a similar tendency, that is, $\Delta \rho / \rho_0 \sim 0$ at $\varepsilon \sim 0$, and $\Delta \rho / \rho_0$ increases sharply at $0 < \varepsilon < 0.1$, reaching a maximum of $-1.8\%$ at $\varepsilon \sim 0.27$. Thereafter, it decreases with increasing of $\varepsilon$ and returns to zero at $\varepsilon \sim 0.8$. The tendency resembles the dependence of $\Delta \rho / \rho_0$ on the Fe content $x$ in Cr$_{1-x}$Fe$_x$ granular alloy thin films [16,17]. When these Fe particles of 2.0-3.0 nm in diameter are distributed in Cr matrix at intervals of 5-20 nm, the $\Delta \rho / \rho_0$ has a maximum. The largest effect of spin-dependent scattering in the inhomogeneous phase of Ni$_3$Mn alloy appears under the condition where ordered domains of $\sim 4$ nm are distributed in a disordered nonmagnetic matrix at $0.2 < \varepsilon < 0.3$. At $D > 6.5$ nm, $\varepsilon > 0.4$, as all particles are contiguous with one another form-

<table>
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<th>$x$</th>
<th>$S$</th>
<th>$D$ (nm)</th>
<th>$\varepsilon$</th>
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<td>~0.3</td>
<td>~4</td>
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<td>0.66</td>
<td>4.3</td>
<td>0.44</td>
</tr>
<tr>
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<td>0.70</td>
<td>5.1</td>
<td>0.49</td>
</tr>
<tr>
<td>0.28</td>
<td>0.66</td>
<td>6.5</td>
<td>0.44</td>
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<tr>
<td>0.29</td>
<td>0.72</td>
<td>6.1</td>
<td>0.52</td>
</tr>
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</table>

Fig. 4. Magnetization vs. temperature curves of Ni$_3$Mn alloys ordered for $5 - 1000$ h at 673K and 693K. $S$ indicated in brackets is the long-range order parameter.

**Table 2.** The long-range-order parameter ($S$), average particle size ($D$) and the volume fraction of the ordered regions ($\varepsilon = S^2/S_{do}$) for Ni$_{1-x}$Mnx alloys ($x = 0.20 - 0.30$).
ing large ferromagnetic clusters, GMR decreases and disappears in homogeneous ferromagnetic alloys.

4.3. DEPENDENCE OF GMR ON THE MAGNETIC FIELD

If the GMR in granular systems is proportional to the average \( \langle \cos \theta_{ij} \rangle \), where \( \theta_{ij} \) is the relative angle between the magnetization of two ferromagnetic particles \( M_i \) and \( M_j \), the MR ratio can be described as [15]

\[
\frac{\Delta \rho}{\rho_0} \propto 1 - \langle \cos \theta_{ij} \rangle = 1 - \langle \cos \theta_i \rangle^2 = 1 - \left( \frac{M}{M_s} \right)^2,
\]

(4.1)

where \( \theta_i \) denotes the angle between \( M_i \) and \( H \), and \( M \) and \( M_s \) the global and saturation magnetization.

Provided that the GMR in Fig. 5 is caused by spin-dependent scattering on ordered single domains precipitated in a disordered matrix, the dependence of MR ratio on \( H \) must satisfy equation (4.1).

Fig. 7 shows the dependence of the MR ratio on \( H \) for (a) 693K•5h and (b) 673K•50h states which have superparamagnetic phase at room temperature. The resistivity decreases with the applied field. For comparison, Fig. 7 also shows the theoretical \( 1-(MM_s)^2 \) vs. \( H \) curves at room temperature, where \( M_s \) is obtained by extrapolating the \( M-H \) curve to the value of \( H = 10 \) kOe. The theoretical curves fit well to the experimental curves, \( \Delta \rho/\rho_0 \) vs. \( H \), for both states in Fig. 7.

From the results described above, the GMR in the inhomogeneous phase of a Ni₄Mn alloy is considered to be due to spin-dependent scattering by ferromagnetic particles, and is therefore of the granular type.
5. MAGNETIZATION AND GMR OF Ni$_{1-x}$Mn$_x$ ($x=0.20-0.30$) ALLOYS

5.1. GMR of Ni$_{1-x}$Mn$_x$ ($x=0.20-0.30$) alloys

From Table 2, we find that the ferromagnetic ordered particles of the size $D$ of 4~6.7 nm distribute in a disordered matrix for the present Ni$_{1-x}$Mn$_x$ ($x=0.20$--0.30) alloys. Fig. 8 shows the dependence of $\Delta \rho / \rho_0$ // $H$ and $\perp H$ for all samples at room temperature on Mn concentration. Since $\Delta \rho / \rho_0$ // $H$ and $\perp H$ are negative and nearly equal to each other for Ni$_{1-x}$Mn$_x$ ($x \geq 0.25$) alloys, each $\Delta \rho / \rho_0$ is caused by the GMR effect. The MR ratio for $x<0.25$ alloys consists of GMR and anisotropic behavior (AMR) which arises from ferromagnetic phase (Type I). Moreover, the GMR for $x>0.25$ alloys increases steeply with annealing time $t$ of 50 h < $t$ < 100 h and reaches maximum (~3.6 %) for the Ni$_{0.73}$Mn$_{0.27}$ alloy of 693K•100 h state (Type II). While, one for $x<0.25$ alloys decreases slightly with $t$.

In Mn concentration of 0.30 $\geq x \geq 0.26$, every alloy is occupied with ferromagnetic particles of about 6 nm at the rate of 50%. Nevertheless, the observed GMR varies from ~0.5% to ~3.5%. In order to clear this situation, we investigate an interaction between ferromagnetic particles.

5.2. Magnetization of Ni$_{1-x}$Mn$_x$ ($x=0.20-0.30$) alloys

Fig. 9 shows the magnetization $M$ vs. temperature $T$ curves of Ni$_{0.80}$Mn$_{0.20}$, Ni$_{0.73}$Mn$_{0.27}$, and Ni$_{0.70}$Mn$_{0.30}$ alloys of 693K•100h. In Fig.9, it is seen that magnetic feature in inhomogeneous phase of the three alloys are quite different. First, saturation magnetization, $M_s$ at 77K decreases from 59 to 14 emu g$^{-1}$ for $x=0.20$ to 0.30 with Mn concentration. Secondly, $M$ vs. $T$ curve in Figs. 9b and 9c has a cusp in temperature range of 600K $< T < 750$K which grows with $x$, but in Fig.9a has not.

Fig. 10 shows the inverse susceptibility (1/\chi) vs. temperature curves for Ni$_{0.80}$Mn$_{0.20}$, Ni$_{0.73}$Mn$_{0.27}$, and...
Fig. 9. Magnetization vs. temperature curves of (a) Ni$_{0.80}$Mn$_{0.20}$, (b) Ni$_{0.73}$Mn$_{0.27}$ and (c) Ni$_{0.70}$Mn$_{0.30}$ alloys annealed for 100 h at 693K.

Fig. 10. The inverse susceptibility ($1/\chi$) vs. temperature curves for Ni$_{0.80}$Mn$_{0.20}$, Ni$_{0.73}$Mn$_{0.27}$ and Ni$_{0.70}$Mn$_{0.30}$ alloys at applied field of 500 Oe.

Ni$_{0.70}$Mn$_{0.30}$ alloys at applied field of 500 Oe. The curves of Ni$_{0.70}$Mn$_{0.30}$ and Ni$_{0.70}$Mn$_{0.30}$ alloys have a minimum at 673K and 743K, respectively, that is Neel point $T_N$, where antiferromagnetic interaction between ordered domains disappears. While, there is no minimum in $1/\chi - T$ curve of Ni$_{0.80}$Mn$_{0.20}$. The paramagnetic Curie point $\theta_p$ of each alloys determined by $1/\chi - T$ curves is shown by an arrow in Fig. 10.

The values of $M_s$, $T_N$, $\theta_p$ and Curie point $T_C$ determined by Arrott plot of the present alloys are shown in Fig. 11. From the results of magnetic analysis, the Ni$_{0.80}$Mn$_{0.20}$ alloy in which $T_N$ is nearly equal to $\theta_p$ is found to be a typical ferromagnetic substance. There is a superparamagnetic phase between $T_F$ and $\theta_p$ for the Ni-Mn alloys of $0.26 > x > 0.23$. The Ni-Mn alloys of $x \geq 0.26$ have $T_N$ in high temperature range of $743K > T > 643K$, which increases with Mn concentration and is near or equal to $\theta_p$.

5.3. Interaction between ordered domains

We think that interaction between ordered domains is caused through disordered matrix. The magnetism of Ni$_x$Mn depends on the number of the nearest-neighbor Mn atoms around a Mn atom [7], because a ferromagnetic interaction operates for the Ni-Ni and Ni-Mn pairs and an anti-ferromagnetic one for Mn-Mn pairs. In section 4.2, we report that the inhomogeneous Ni$_{0.75}$Mn$_{0.25}$ alloy annealed at 693K consists of nano-scale ordered domains distributed in disordered nonmagnetic matrix (the average exchange coupling around a Mn atom, $J_{ex} \sim 0$), where
GMR in granular ferromagnetic systems arises. The present alloys with Mn concentration of $x<0.25$ or $x>0.25$ have Ni-rich ($J_{ex}>0$) or Mn rich ($J_{ex}<0$) matrices, respectively, after super-lattice Ni$_3$Mn particles are precipitated and formed in the alloys. Consequently, the ferromagnetic interaction between particles in Type I of GMR increases with decreasing $x$ and makes AMR arise in MR ratio. The anti-ferromagnetic interaction between particles in Type II of GMR increases and makes $M_S$ decrease with increasing $x$. Therefore, a maximum of GMR in Fig. 8 arises at Ni$_{0.73}$Mn$_{0.27}$ composition in which opposite directed domains is reversed by applied field of 10 KOe as anti-ferromagnetic interaction is weak. While, the rapidly decrease of GMR for Mn concentration of $x>0.27$ is caused by insufficiency of applied field to reverse opposite directed domains.

From the results of magnetic analysis, Types I and II of GMR, respectively, are caused by ferromagnetic and antiferromagnetic interactions between ordered domains distributed in Ni-rich ($J_{ex}>0$) and Mn-rich ($J_{ex}<0$) matrices.

5.4. Magnetization and GMR of Ni$_{0.70}$Mn$_{0.30}$ alloy in magnetic field up to 16 T

Next, we investigate GMR of Ni-Mn alloys with $x>0.25$ under high magnetic field at low temperature. Ni-Mn alloys with $x>0.25$ at 693K•100 h state consists of ferromagnetic nano-particles( about 6 nm, $\varepsilon \sim 0.50$) dispersed in Mn-rich matrix. Since the interaction between single domains is mediated by disordered matrix, that is antiferromagnetic. Especially, antiferromagnetic interaction between nano particles for Ni$_{0.70}$Mn$_{0.30}$ alloy is stronger than other’s one as shown in Fig.11.

Figs. 12a and 12b are dependency of magnetization and GMR for Ni$_{0.70}$Mn$_{0.30}$ on $H$ which is pulse magnetic field up to 16 T at low temperature12K. Magnetization in Fig.12a increases rapidly with $H<6T$, slowly at $H>6T$, and then reaches to 73 emug$^{-1}$ at 13 T. The value is about 71% of that all magnetic moments of Ni and Mn atoms are parallel to applied magnetic field direction. Moreover, magnetic processes up to 2 T and down to zero are reversible.
On the other hand, the processes up to 13 T and down to zero are irreversible.

Resistance in Fig. 12b dose not change within \( H < 1 \) T, and decreases rapidly with increasing of \( H \). Especially, it decreases in steps as the field increases 4 T to 12 T. It is considered that the phenomenon is due to spin-flopping of single domains with various antiferromagnetic interactions. On the other hand, as the field decreases, spins rotate continuously. Consequently, GMR curve against \( H \) also has hysteresis loop.

### 6. SOFT MAGNETIC PROPERTY DUE TO FERROMAGNETIC NANOCRYSTAL

#### 6.1. Coercive force of Ni\textsubscript{3}Mn alloy

Table 1 indicates that the ferromagnetic ordered particles of the size \( D \) of 2.8~10nm distribute in a disordered nonmagnetic matrix (\( J_{ex} \sim 0 \)) in the present Ni\textsubscript{3}Mn alloys.

In nano-scale inhomogeneous magnetic alloy, exchange and magnetic dipole interactions between particles overcome magnetocrystalline anisotropy of particles, making \( M_s \) of particle parallel to each others in one group, because the effective anisotropy constant \( K_{eff} \) is described by \( K_{eff} \sim K/N \), where \( N \) is the number of particles included in one group. The coercive force \( H_c \) in nanocrystalline material can be described as [18]

\[
H_c = \text{const} \ K_{eff} \left( \frac{D}{W} \right)^{\frac{3}{2}} \frac{M_s L}{W^2},
\]

where \( W \) and \( L \) denote a domain wall thickness and a characteristic length of exchange interaction. Assuming that \( W, L \) and \( M_s \) in Eq. (6.1) are constant, \( H_c \) is proportional to \( K_{eff} \) and \( (D/W)^{\frac{3}{2}} \). Consequently, we expect soft magnetic properties in nano-scale inhomogeneous Ni\textsubscript{3}Mn alloys.

Fig. 13 shows the \( M \) vs. \( H \) loops for (a) 693K\textcdot2h and (b) 693K\textcdot1000 h states obtained by applied \( H_{max} = 500 \) Oe. The scale of \( M \) axis in (b) is 50 times of one in (a). Coercive force \( H_c \) in (a) is slightly wide, 5.5 Oe, while one in (b) becomes narrower to be 3 Oe.

The relations of \( H_c \) to annealing time \( t \) at 673 and 693K are shown in Fig. 14. It is seen that \( H_c \) for Ni\textsubscript{3}Mn annealed at 693K shows an increase with \( t \) for 0 < \( t \) < 2h, a maximum, 5.5 Oe at 2h, a rapid decrease for 2h < \( t \) < 5h, a minimum, 1.7 Oe at 25h and finally a slight increase up to 3 Oe at \( t = 1000h \), where ferromagnetic particles of about 10 nm are in contact with each other. The overall \( t \)-dependence behavior of \( H_c \) for alloys annealed at 673K is rather similar, aside from the factor of two larger maximum of \( H_c \). 10.7 Oe at \( t = 25h \), for 673K – annealed alloy compared to the that for 693K – annealed alloy. The dotted line in Fig.14 displays \( H_c \) estimated from magnetoelastic energy \( \lambda_s \sigma \) for 693K annealed alloy. Here, \( \lambda_s \) and \( \sigma \) are saturation magnetostriiction and internal stress caused by magnetostriction \( \lambda \). These \( H_c \) values are 0 ~ 2 Oe.
and can be compared with the $H_c$ at $5 < t < 25$ h for 693K-annealed alloy (solid line). From these results, the peaking of $H_c$ (maximum 5.5 Oe) at 2h for 693K-annealed alloy is considered to be caused by two contributions: one is $H_c$ due to magnetostriction (~2 Oe) and the other is $H_c$ due to internal strain of nearly completely disordered state (~3.5 Oe).

The dependence of $H_c$ and saturation magnetic flux density $B_s$ on $\varepsilon$ are shown in Fig. 15, where $B_s$ is the one measured at $H_{\text{max}}$ = 500 Oe in Fig. 13. As seen in Fig.15, $H_c$ rapidly increases and decreases for $\varepsilon < 0.1$, increases gradually for $0.2 < \varepsilon < 0.8$, and comes to 3 Oe. The $B_s$ increases as the ordered region grows and reaches to 0.92 T for $\varepsilon = 0.78$.

However, the $\varepsilon$ value estimated by $S$ is uncertain in the small $S$ range, where x-ray diffraction (110) peaks are very weak to determine $S$ correctly as shown in Fig. 2. The $\varepsilon$ value of ordered region obtained by the magnetic analysis [11] is about 0.10, 0.16 and 0.32 for 693K-5h, 693K-25h and 693K-50h states, respectively.

These results indicate that the decrease of $H_c$ for $8 \leq \varepsilon \leq 16$ is due to the decrease of $K_{\text{eff}}$ where magnetic particles come in contact with each other to form groups. Moreover, it is considered that the increase of $H_c$ for $\varepsilon > 16$% is due to the growth of $D$ which changes 3.2 nm to 10 nm as shown in Table 1. The alloy for $\varepsilon = 0.8$ still maintains soft magnetic properties where $B_s = 0.92$ T and $H_c = 3$ Oe.

6.2. Soft magnetic property of Ni$_{1-x}$Mn ($x = 0.20-0.25$) alloys in high frequency range

Nano-scale inhomogeneous Ni$_x$Mn alloy has soft magnetic properties where the particles couple to each other ferromagnetically [21]. That is, the saturation magnetic flux density increases but the coercive force decreases with the ferromagnetic particle size.

Fig. 16 shows the dependency of $H_c$ ($H_{\text{ext}}$=500 Oe) and $M_c$ ($H_{\text{ext}}$=5 kOe) of wire-samples annealed for 100 h at 693K and 713K on Mn concentration. Both values depend on $x$ remarkably. The value of $H_c$ is small and equal to about 2.5 Oe for wire of $0.20 \leq x \leq 0.24$, but it increases with $x > 0.25$. It is considered that the wire of $0.24 \leq x \leq 0.26$ annealed for 100 h at 693K consists of nano particle being almost ordered state of $S=1$, because their $B_s$ equal to 1 T.

From the results, soft magnetic property due to the nanocrystalline morphology in high frequency range is expected to occur in wire of $x < 0.26$.

Fig. 17 shows 1~500 kHz high frequency permeability of $x = 0.20, 0.21, 0.24, 0.25$ wires annealed for 100 h at 693K. The permeability for $f = 1$~20 kHz is high, 200~600, but decreases slowly for $f > 20$ kHz, because of loss due to eddy currents. To overcome these limitations, it should be necessary to prepare and study fiber or foil samples.
7. CONCLUSIONS

The long-range-order parameter $S$, the magnetization and GMR were investigated for inhomogeneous Ni$_{1-x}$Mn$_x$ $(x = 0.20\sim0.30)$ alloys in which nano-scale ordered magnetic particles are distributed in a disordered nonmagnetic or Ni-rich or Mn-rich matrices. The main conclusions are as follows:

1. Ni$_3$Mn alloy with various $S$:
   The average size of ferromagnetic particle increases with the long-range-order parameter $S$, i.e., 1.4 nm to 10 nm with $S = 0.13$ to 0.88. GMR depends on the volume fraction of ordered domains $\varepsilon$: GMR of $-1.8\%$ is obtained at $\varepsilon \sim 0.27$ and zero at $\varepsilon \sim 0.8$. The saturation magnetic flux density increases with $\varepsilon$ and reaches to 0.92 T where Ni$_3$Mn alloy maintains soft magnetic properties due to the nanocrystalline structure.

2. Ni$_{1-x}$Mn$_x$ $(x = 0.20\sim0.30)$ alloys annealed for 100 h at 693K:
   The values of $S$, average particle size and the volume fraction in the ordered regions are $0.3\sim0.7$, $4\sim6$ nm and $0.1\sim0.5$, respectively, and increase with Mn concentration. The GMR depends remarkably on Mn concentration, $x$: the GMR increases from $-0.5\%$ to $-1.2\%$ for $x = 0.20$ to 0.24 alloys (Type I), while, for alloys of...
0.26 ≤ x ≤ 0.30, one has maximum of –6% at x = 0.30 at 16 T (Type II). From the results of magnetic analysis, Types I and II of GMR, respectively, are caused by ferromagnetic and antiferromagnetic interactions between ordered domains distributed in Ni-rich (J<sub>e</sub> < 0) and Mn-rich (J<sub>e</sub> > 0) matrices. On the other hand, Ni<sub>x</sub>Mn<sub>1-x</sub> alloys of x ≤ 0.24 exhibit soft magnetic property with permeability of 400–600 for 1–500 kHz high frequency.

REFERENCES