Magnetism and Nano-cluster in Inhomogeneous Phase of Ni-Mn Alloy

T. Okazaki, T. Miyanaga, Y. Kondo, Y. Aono and M. Homma
Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan.
Faculty of Engineering, Tohoku University, Sendai 980-77, Japan.

(Received: April 30, 1998) [Accepted: August 26, 1998]

Ni$_{15}$Mn and Ni$_{0.77}$Mn$_{0.23}$ alloys which are ordered at 420°C have inhomogeneous phase, where long-range ordered magnetic domains distribute in a disordered non-magnetic matrix. Magnetism of these alloys with long-range ordered parameter S from 0.13 to 0.44 shows a ferromagnetic and a glass-like phases below and above the Curie temperature, respectively. The ferromagnetic cluster size obtained by magnetic analysis of the glass-like phase for those alloys is $1^3 \times 3^1$ nm$^3$ and increases with $S$. Minimum cluster size which forms a single domain is about $1^3$ nm$^3$. Magnetism of alloy in which the volume fraction of ordered region is greater than 0.32 (cluster size $> 3^1$ nm$^3$), is wholly ferromagnetic.

key words: super lattice Ni$_{15}$Mn, inhomogeneous phase, glass-like phase, super paramagnetic model, nano-cluster.

1. Introduction

Magnetic and electronic properties of Ni$_{15}$Mn which forms the Cu$_3$Au type superlattice depend$^{(1)(2)}$ on atomic short range order, that is, the probability of finding Mn atom at neighboring site of one particular Mn atom. Magnetization $M$, vs. temperature, $T$ curve of Ni$_{15}$Mn with the long-range parameter, $S$=0.13 - 0.44 which is ordered at 693K shows double-stage behavior. That is, a ferromagnetic and a glass-like phases which was predicated theoretically in Ni-Mn alloy by Kakehashi$^{(9)}$ exist in temperature range below and above the Curie temperature, $T_C$, respectively. We analyzed$^{(9)}$ the magnetization in the glass-like phase by a superferromagnetic model$^{(9)}$ involving inter-and intra-cluster ferromagnetic coupling. It is seen that these Ni$_{15}$Mn have an inhomogeneous phase, where long-range ordered magnetic domains (cluster size, $2 \times 10^2 - 2 \times 10^3 \mu_0$) distribute in a disordered non-magnetic matrix. But, the mechanism of magnetization in the inhomogeneous phase, especially the relationship between the magnetism and cluster size is not clear yet.

In the present paper, we investigate the magnetism of the glass-like phase which exists in Ni$_{0.77}$Mn$_{0.23}$ ordered at 693K. The magnetic analysis of the phase is done by using a modified superparamagnetic model involving inter-cluster ferromagnetic coupling. Moreover, we report that the magnetism of Ni$_{15}$Mn and Ni$_{0.77}$Mn$_{0.23}$ alloys with 0.13 $< S < 0.44$ states is dependence on the cluster size and the volume fraction of ordered region in inhomogeneous phase.

2. Experimental Procedure

The sample preparations were done by the same methods as before$^{(9)}$. Ni$_{0.77}$Mn$_{0.23}$ melted with rf induction furnace was ordered in Ar by annealing for 10, 50 and 1000h at 693K. The $S$ was determined by the X-ray diffraction analysis. The magnetization was measured using a magnetic balance (300 – 800K, $H=2.0$, 3.3, 4.7, 6.7 KOe). Hereafter, the specimens annealed for 10, 50 and 1000h are denoted by the states of $A_{10h}$, $A_{50h}$ and $A_{1000h}$, respectively.

3. Results and Discussion

3.1 Magnetization

Figure 1 shows the $M$ – $T$ curves obtained for $A_{10h}$, $A_{50h}$, $A_{1000h}$ states of Ni$_{0.77}$Mn$_{0.23}$ and for $A_{25h}$, $A_{50h}$, $A_{1000h}$ states of Ni$_{15}$Mn$^{(9)}$. The $M$ increases with annealing time. That is due to the increase of the number of ferromagnetic Ni – Mn pairs accompanied with the decrease of antiferromagnetic Mn – Mn ones (atomic short-range order). In completely ordered state ($S$=1), there is no Mn – Mn pair because each Mn atoms are surrounded with 12 Ni one. The magnetism of $A_{1000h}$ states of Ni$_{0.77}$Mn$_{0.23}$ ($S$=0.77) and Ni$_{15}$Mn ($S$=0.88) which are controlled by the magnetic coupling of the exchange interaction, $J_{ex}^{Ni\rightarrow Mn}$ > 0 and $J_{ex\rightarrow Ni\rightarrow Ni}$ > 0 are ferromagnetic and show the high $T_C$.

![Fig.1 Magnetization vs. temperature curves for Ni$_{0.77}$Mn$_{0.23}$ and Ni$_{15}$Mn$^{(9)}$. Arrows indicate the inflection points of the M – T curves applied $H=2.0$ kOe.](image-url)
683 and 723K, respectively. While, the $M - T$ curves at low ordered states, $\Lambda_{10h}$ ($S=0.21$), $\Lambda_{10w}$ ($S=0.24$) of Ni$_{87}$Mn$_{13}$ in Fig.1 also have inflection point (denoted by arrows) near $T_p$ which is similar to $\Lambda_{1w}$ ($S=0.13$) and $\Lambda_{2sh}$ ($S=0.29$) states for Ni$_7$Mn. These curves show the ferromagnetic phase profile and a long tail as a glass-like phase below and above $T_p$, respectively, because a latter is controlled by three magnetic couplings of $J_{ex}$ $\ln{\text{Ni-Mn}} < 0$, $J_{ex}$ $\ln{\text{Mn-Ni}} > 0$ and $J_{ex}$ $\ln{\text{Mn-Mn}} > 0$.

Figure 2 shows the spontaneous magnetization $M_s$ obtained by Arrott plot and the inverse susceptibility vs. temperature, $1/\chi - T$ curve for $\Lambda_{10h}$ of Ni$_{87}$Mn$_{13}$. The $T_p$ where the $M_s$ becomes to zero is 445K. The paramagnetic Curie temperature from the glass-like phase to the paramagnetic one $\theta_p$, 571K is obtained by extrapolating the linear $1/\chi - T$ curve in the range of $T > 620K$ to $1/\chi = 0$. The values of $T_p$ and $\theta_p$ for $\Lambda_{10w}$ obtained by same method as $\Lambda_{10h}$ are 334 and 448K, respectively. The curve deviates from the Curie-Weiss law in intermediate temperature range corresponding to the glass-like phase ($T_p < T < \theta_p$).

### 3.2 Superparamagnetic analysis.

The glass-like phase for $\Lambda_{10h}$ and $\Lambda_{10w}$ of Ni$_{87}$Mn$_{13}$ is considered that a set of ferromagnetic clusters with a high $T_p$ is randomly distributed in a matrix of nonmagnetic almost disordered one with a lower $T_p$ as that of Ni$_7$Mn.

At first, we analyze the magnetization in the glass-like region by a noninteracting superparamagnetic mode. The magnetization of a specimen is expressed as

$$ M = N\mu L(\alpha) $$

$$ \alpha = mH / (kT) $$

where $L(\alpha)$ is the Langevin function, $N$ the number of clusters per unit volume, $m$ the magnetic moment per cluster, $H$ the applied field and $k$ the Boltzmann constant. Figure 3(a) shows the plot of $M$ against $H / T$ for $\Lambda_{10h}$ state. However, $M$ is not uniquely determined by a universal function of $H / T$ expected from Eqs. (1) and (2).

Next, we introduce the inter-cluster coupling. By taking into account the inter-cluster coupling as a molecular-field, the effective magnetic field $H_{eff}$ is expressed as $H_{eff} = H + WM$, where $W$ is the molecular-field constant. The $W$ can be estimated from Fig.2 as follows. The superparamagnetic Curie temperature, $\theta_C$ of 417K taken from linear part of 440-540K in Fig.2 yields the $W$ of 6.04 $\times 10^3$ Oe $\cdot$ emu$^{-1} \cdot$ g for $\Lambda_{10h}$ by the ratio $\theta_C / [x (T)(T - \theta_C)] = W$. The value for $\Lambda_{10w}$ is 12.5 $\times 10^3$ Oe $\cdot$ emu$^{-1} \cdot$ g. Figure 3(b) shows the plots of $M$ against $H_{eff} / T$ for $\Lambda_{10w}$ (445K $< T < 563K$), in which these plots are nearly universal relation. While, a universal relation of the $M - H_{eff} / T$ plots for $\Lambda_{2sh}$ states$^{(6)}$ of Ni$_7$Mn in Fig.1 was limited in a narrow temperature range of 500K $< T < 550K$. Taking into account both intra- and inter cluster coupling$^{(6)}$, the plot of $M / b(T)$ against $b(T)H_{eff} / T$ could fit to universal relation in much wider temperature range.

where we assume a Brillouin function, $b(T)$ with $x = 1/2$ spins$^{(6)}$, as intra-cluster coupling. It is caused by that the magnetization of each cluster, $m$ depends on temperature in higher temperature range than 360K.

$$ m = 3kT \mu / [M_C(T = 0)] $$

$$ (3) $$

Fig.3 Magnetization against $H / T$, (a) and $(H + WM) / T$, (b) for $\Lambda_{10h}$ state.
where $K_m$ and $M_e(T=0)$ denote the slope at the origin in $M - H_m / T$ curve and magnetization arisen from ferromagnetic clusters at 0K. We substitute the $M_e(T=T_R)$, 8.3 emu $\cdot$ g$^{-1}$ for $M_e(T=0)$, because it is difficult to separate the $M_e(T=0)$ from the magnetization caused by atomic short-range order with a lower $T_R$. The values of $<m^2>$ were determined to be $4.2 \times 10^5 \mu_B$ for $A_{108}$ and $2.7 \times 10^7 \mu_B$ for $A_{108}$ of $Ni_{17}Mn_{83}$ from Eq.(3). Since average atomic moment of $Ni_{17}Mn$ ordered at 693K is 0.87 $\mu_B$ in the equilibrium state ($A_{1000}$ state of $Ni_{17}Mn$ in Fig.1), these clusters are considered to be consisted of few $10^8$ atoms of nearly ordered $Ni_{17}Mn$ ($S=0.88$).

3.3 Cluster Size and Magnetism

We assume that these clusters are cubic of $L^3$. The average size of $L$ increases from 1 to 2 nm with $S$ increases from 0.21 ($A_{108}$) to 0.24 ($A_{108}$), while the number of cluster $N$ decreases from $3 \times 10^{18}$ to $2 \times 10^{18}$ cm$^{-3}$. Many nuclei created in $A_{108}$ state are contiguous with one another as the annealing time increases. These values are comparable to one obtained by use of superferromagnetic model for 0.13 ($A_{108}$) $\leq S \leq$ 0.44 ($A_{108}$) states of $Ni_{17}Mn$ ($\theta$), 1 nm $\leq L \leq$ 3 nm, $4 \times 10^{18} \leq N \leq 1 \times 10^{19}$ cm$^{-3}$. The volume fraction of the ordered regions, $L^3/N$ is about 0.1 for two states of $Ni_{17}Mn_{83}$ which is smaller than one for three states of $Ni_{17}Mn_{83}$ as shown in Fig.4.

Moreover, the magnetization of ordered domain, $M_{so}$ which can be evaluated from the relationship, $M_{so} = M_e(T=0) / (L^3/N)$, is 84~89 emu $\cdot$ g$^{-1}$. These values are nearly equal to the magnetization at 0K for $Ni_{17}Mn$ with $S \approx 0.88$, 84.1 emu $\cdot$ g$^{-1}$ in Fig.1.

From the results obtained by magnetic analysis for five states of $Ni_{17}Mn$ and $Ni_{17}Mn_{83}$, it is seen that a minimum cluster size forming a single domain is about 1$^3$ nm$^3$, where the $M - T$ curve shows a ferromagnetic and a glass-like phases. Whereas, magnetism of $Ni_{17}Mn$ alloy in which the volume fraction of ordered region is greater than 0.3 ($\sim 3^3$ nm$^3$) is wholly ferromagnetic. Since the values of $L$ and $NL^3$ are dependence on long-range order parameter, the outline of magnetic phase is shown in Fig.4.

4. Conclusion

$Ni_{17}Mn_{83}$ and $Ni_{17}Mn$ alloys which are ordered at 693K have inhomogeneous phase. The magnetization vs. temperature curves of partially ordered alloys profile ferromagnetic and glass-like phases. The main conclusions obtained by magnetic analysis are as follows.

(1) The inhomogeneous phase with 0.13 $S < 0.44$ is consisted of that ferromagnetic domains of long-range ordered $Ni_{17}Mn (S \sim 0.88)$ are distributed in the atomic short-range ordered non-magnetic matrix with a lower $T_R$.

(2) Minimum ferromagnetic cluster size forming a single domain is about 1$^3$ nm$^3$.

(3) The $M - T$ curves of alloys in which cluster size is $1^3$ $- 3^3$ nm$^3$ show a ferromagnetic and a glass-like phases.

(4) Magnetism of alloys in which the volume fraction of ordered region is greater than 0.3 is wholly ferromagnetic.

Reference