Pressure-induced new spin-states in Ni-25at%Mn mechanical alloy under high pressure

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Abstract. AC-susceptibility measurements in mechanically alloyed Ni-25at%Mn were made under high hydrostatic pressures up to 7.5 GPa by using a cubic anvil press in the low-temperature range from 4.2 K to 300 K. At ambient pressure a reentrant spin glass (RSG) state was observed below 58 K, followed by a ferromagnetic (FM) state with the Curie temperature (T_C) at 120 K. T_C decreased with increasing pressure up to 4.3 GPa, while the transition temperature from RSG to FM increased to merge with T_C at 70 K, and then, with further increasing pressure the FM state disappeared, and a spin glass (SG) state appeared. The local moments of this high-pressure SG phase decreased with pressure. The results were compared with a bulk alloy made by the conventional method of melting. In the bulk alloy, a new high-pressure magnetic phase appeared having almost pressure-independent local magnetic moments.

1. Introduction
Ni-rich Ni-Mn alloys crystallize into a face-centered cubic structure. They have an ordered state of Cu₃Au-type structure around Ni₃Mn composition. It is well known that the magnetic structure of these alloys is sensitive to the short-range structure of atomic ordering [1-7]. We have demonstrated that a nanoscale atomic diffusion caused a significant change in their magnetic structure [8-11].

The technique of mechanical alloying has been used to introduce a large variety of nanoscale atomic concentration fluctuation in Ni-Mn alloys [8-11] and Fe-Ni alloys [12-14], and various magnetic structures have been introduced in these alloys. On the other hand, high hydrostatic pressure is a technique to change atomic distances without introducing any changes in atomic ordering. We combined these two techniques and looked for any new magnetic phases in Ni-rich Ni-Mn alloys.

2. Experimental
To synthesize mechanical alloy (MA) samples, 100-mesh size Ni and Mn powders were weighted and mixed, and then, put into two stainless containers. The purity of the elemental powders was 99.9%. They were mechanically alloyed by milling for 75 hours using a planetary ball mill in the same way as described in the references [12-14].

To compare the magnetic properties of the milled alloy with those shown in the literature [1-7], a standard bulk Ni-25at%Mn alloy was produced by using an arc-melting furnace. The bulk alloy was homogenized and powdered using the same procedure as mentioned in [12-14]. The homogenization
temperature was 1273 K and the annealing time was a week. The bulk sample was again homogenized at 1273 K for 3 hours. After the annealing procedure the bulk alloy sample was quenched to room temperature to keep the face centered cubic structure and the disordered state stable.

To obtain the Cu$_3$Au-type ordered state, the both MA and bulk alloys were annealed at 693 K for 1000 h. The crystal structure and the degree of order for MA and bulk alloy were confirmed by X-ray diffraction at room temperature. To investigate the magnetic properties for MA and bulk alloy at ambient pressure, magnetic field dependence and temperature variation of magnetization were observed by using a SQUID magnetometer.

To generate a hydrostatic pressure, a cubic anvil press system was operated by a 250-ton press. The cubic anvil press system was placed in a thermost bottle with which the temperature of the sample was varied from 4.2 to 400 K. AC-susceptibility measurements were performed under high pressures up to 7.7 GPa [8-10] by using a pick-up coil system which was wound around the sample. The intensity of the external AC-magnetic field for the susceptibility measurements was $5 \times 10^{-5}$ T.

3. Results

3.1. Mechanically alloyed Ni-25at%Mn

The magnetization values $M$ for the bulk and the MA samples observed at 1 T and 4.2 K under ambient pressure were plotted in figure 1 as a function of annealing time at 693 K.

![Figure 1](image)

*Figure 1. Annealing time variation of the magnetization during the ordering procedures observed at 4.2 K and 1 T for as milled MA, homogenized MA (annealed at 1273 K for 1 h) and the bulk Ni-25at%Mn alloy.*

It was shown that the annealing time of 1000 h at this temperature was enough to get almost complete atomic ordering [11]. The $M$ value in as milled MA was about 15% larger than that in the bulk alloy. However, after the homogenization (annealing at 1273 K for 1 h) treatment it almost reached to the bulk value. This fact proved that two alloys produced in different ways (mechanical alloying and conventional melting) had nearly the same concentration of Ni-25at%Mn. In this figure, it is seen that
the magnetization of the homogenized MA approaches to the value of the bulk alloy. The curves shown in this figure were calculated by solving the diffusion equation as explained in ref. [11].

The observed temperature dependences of the real part $\chi'$ and the imaginary part $\chi''$ of AC-susceptibility in Ni-25at%Mn as milled MA under various pressures are shown in Figure 2 (a) and (b), respectively. In both figures ferromagnetic signals could be seen in a narrow temperature range about 65-120 K. A reentrant spin glass (RSG) state could be seen in the curves up to 3.5 GPa below about 65 K. With further increasing pressure the ferromagnetic signal disappeared, and a spin glass (SG) state came to appear.

**Figure 2.** Observed temperature variation of magnetic susceptibility $\chi'$ (a) and $\chi''$ (b) for Ni-25at%Mn as milled MA under various pressures up to 7.7 GPa. In both figures, a ferromagnetic signal can be seen in a narrow temperature range around 65-120 K below 3.5 GPa.

From the observed AC-susceptibility curves shown in figure 2 (a) and (b) a magnetic phase diagram was drawn for Ni-25at%Mn as milled MA and shown in figure 3 (a). As pointed out by Tange et al. [6], there is a difficulty in determining the Curie temperature from AC-susceptibility-temperature curves due to the complicated magnetic interactions in Ni-Mn alloys. In this paper, we need only the relative shift of $T_C$ with pressure, and therefore, for convenience, $T_C$ was determined by using the same method described in work [9].

In figure 3 (a), $T_C$ is the Curie temperature, $T_{RG}$ is the transition temperature from RSG to FM state and $T_G$ from SG to paramagnetic state. The FM state disappeared at about 4.3 GPa, and with further increasing pressure a new SG phase came to appear. In figure 3 (b), the phase diagram determined for Ni-20at%Mn as milled MA [9] is also shown for comparison. The phase diagram (a) for Ni-25at%Mn MA was well fitted to the higher pressure region between 15 to 23 GPa (hatched area) in the phase diagram (b) for Ni-20at%Mn MA. From this result, we could estimate the chemical pressure acting on the disordered Ni-25at%Mn MA to be 15 GPa.
Figure 3. (a) The magnetic P-T phase diagram for Ni-25at%Mn as milled MA determined from the present experiment. This phase diagram corresponds to the hatched area in the phase diagram (b) obtained in [9] for Ni-20at%Mn as milled MA.

3.2. Ni-25at%Mn bulk alloy produced by conventional melting
Observed $\chi'$-$T$ and $\chi''$-$T$ curves in Ni-25at%Mn disordered bulk alloy under various pressures are shown in figure 4 (a) and (b), respectively.

Figure 4. Observed temperature variation of magnetic susceptibility $\chi'$ (a) and $\chi''$ (b) for Ni-25at%Mn disordered bulk alloy produced by conventional melting under various pressures up to 7.5 GPa.

As seen in figure 4 (a), there are two shoulders in the curve for $P=0.5$ GPa, one is about 30 K (shown as $T_P$), and the other is about 80 K (shown as $T_G$). Below the transition temperature $T_P$, the susceptibility did not change mainly with temperature. Hence the low-temperature phase below 30 K seems ferromagnetic. However, it seems difficult to define the magnetic structure of this low-temperature
phase at this moment. This new magnetic phase persisted up to the maximum pressure of 7.5 GPa. Here, we refer to this phase as the high-pressure magnetic (HPM) phase.

To clarify the low-temperature magnetic structure, we performed squid-magnetization measurements at ambient pressure. The results are shown in figure 5 (a) and (b). In figure 5 (a) the magnetization at the very low field of $5 \times 10^{-5}$ T is plotted as a function of temperature. We set the intensity of this weak magnetic field equal to that of AC-susceptibility measurements. In figure 5 (a) no such transition as $T_P$ could be seen. Therefore we concluded that the appearance of the transition $T_P$ was due to the application of the pressure of 0.5 GPa. In figure 5 (b) the magnetization at the field of $1 \times 10^{-3}$ T is plotted against temperature. In this figure an existence of SG state is seen below 81 K. This SG state disappeared above 2 GPa.

![Figure 5](image-url)

**Figure 5.** Temperature dependence of the magnetization for Ni-25at%Mn disordered bulk alloy; (a) at the field of $5 \times 10^{-5}$ T and (b) at $1 \times 10^{-3}$ T at ambient pressure. In (b), an SG state can be seen below 81 K, where the full circles show on heating from 4.2 K for the first time, and the open circles show on cooling from 320 K to 4.2 K and then again heating for the second time.

From the observed AC-susceptibility curves shown in figure 4, a magnetic phase diagram was drawn for the Ni-25at%Mn disordered bulk alloy and shown in figure 6 (a). The SG state observed at ambient pressure disappeared above 2 GPa. On the other hand, a new high-pressure magnetic phase (HPM) appeared above 0.5 GPa below 30 K. The transition temperature from HPM to a paramagnetic state remained constant with pressure up to 7.5 GPa. In this figure, $T_P$ denotes the transition point from the new HPM phase to SG or paramagnetic state and $T_G$ from SG to paramagnetic state.

In figure 6 (b) the phase diagram determined for Ni-20at%Mn disordered bulk alloy [9] is shown for comparison. The phase diagram (a) for Ni-25at%Mn bulk alloy corresponds well to the hatched area in the phase diagram (b) for Ni-20at%Mn bulk alloy. From this result we estimated the chemical pressure acting on the Ni-25at%Mn disordered bulk alloy to be 15 GPa. This value agrees well with the case of the Ni-25at%Mn disordered MA.
Figure 6. (a) Magnetic $P$-$T$ phase diagram for Ni-$25\text{at}\%$Mn disordered bulk alloy determined from the present experiment; (b) the phase diagram established in ref. [9] for Ni-$20\text{at}\%$Mn disordered bulk alloy. The area to be compared with the present study is shown with the hatched square.

4. Discussion

It is well known that Ni-$25\text{at}\%$Mn disordered bulk alloy made by conventional melting has no FM state, but has an SG state in the low-temperature range below 80 K [15]. On the other hand, an FM state was found in Ni-$25\text{at}\%$Mn disordered MA in the low-temperature range between 58 K and 120 K. Furthermore, below 58 K, an RSG state was observed from the present study.

To understand the difference of the magnetic behavior between the two alloys, as milled MA and the bulk alloy, we may assume a broad distribution of concentration fluctuation of the constituent atoms in as milled MA [9]. The distribution function is expressed as,

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-x_0)^2}{2\sigma^2}},$$

(1)

with the value of the standard deviation $\sigma=10$ for as milled MA [9]. The existence of the ferromagnetic state can be explained by considering the large concentration fluctuation introduced in the alloy by mechanical alloying [9]. By studying the well-defined phase diagram for Ni-Mn alloys [15], it is clear that Ni-rich nanoscale grains or particles in MA contribute to the appearance of ferromagnetism.

In Ni-$25\text{at}\%$Mn disordered as milled MA the Curie temperature decreased with pressure at the rate of 12 K/GPa, while the RSG range increased, and both the RSG and FM phases disappeared at 4.3 GPa to merge into an SG state. From the present study, it was found that the $P$-$T$ phase diagram determined for Ni-$25\text{at}\%$Mn MA was well fitted to the phase diagram for Ni-$20\text{at}\%$Mn MA in the pressure range between 15 and 23 GPa. From this fact we estimated the chemical pressure acting on the disordered Ni-$25\text{at}\%$Mn MA to be 15 GPa. Here, we set the reference of the chemical pressure at the Ni-$20\text{at}\%$Mn disordered MA. This chemical pressure, however, is too large and in the opposite sense as usually estimated from the difference of the lattice parameters between the two alloys [16]. This disagreement may come from the simple idea that magnetic properties depend only upon the lattice parameter. In Ni-Mn alloys, the magnetic properties depend more strongly upon the atomic configuration and the band structure [17]. The present result shows that change in the atomic configuration and the band structure
with increasing the Mn-concentration by 5 % exceeds the effect of a simple change in the lattice parameter.

As to the Ni-20at%Mn disordered bulk alloy, we predicted in our previous study by merely extrapolating the phase diagram determined below 7.5 GPa that the FM phase disappears around 15 GPa and an SG state would come out [9]. In figure 6 (b) it is seen that the high-pressure region above 15 GPa fits almost exactly to that of Ni-25at%Mn disordered bulk alloy. Thus, the same value of the effective chemical pressure of 15 GPa was also confirmed in the Ni-25 at%Mn disordered bulk alloy.

5. Conclusions

P-T magnetic phase diagrams were determined for Ni-25at%Mn disordered as milled MA and bulk alloys. An FM state was found in MA in the low-temperature range between 58 and 120 K. Below 58 K, an RSG state was observed. It was found that the Curie temperature decreased with pressure, while the transition temperature from RSG to FM state increased gradually with pressure up to 4.3 GPa, where the FM state disappeared. Above 4.3 GPa a new spin glass state came to appear. The transition temperature from SG to paramagnetic state remained almost constant up to 7.7 GPa. The P-T phase diagram determined for Ni-25at%Mn MA was well fitted to that for Ni-20at%Mn MA in the pressure range between 15 and 23 GPa.

In Ni-25at%Mn disordered bulk alloy, the SG state observed at ambient pressure disappeared at 2 GPa. A new HPM phase appeared above 0.5 GPa below 30 K. The transition temperature from HPM to paramagnetic state remained constant with pressure up to 7.5 GPa. In Ni-25at%Mn disordered bulk alloy the P-T phase diagram could also be well fitted to that of Ni-20at%Mn disordered bulk alloy by shifting the P-axis to 15 GPa. The effective chemical pressures acting on both Ni-25at%Mn disordered MA and bulk alloys were estimated to be 15 GPa.

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