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Atomic diffusion in Ni–Mn mechanical alloys around Ni_3Mn composition proved from magnetic measurements

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ABSTRACT

The character of thermal diffusion of magnetic atoms has been investigated in Ni–Mn mechanical alloys around Ni_3Mn composition by monitoring magnetic properties during the atomic ordering process. Observed susceptibility versus temperature curve after annealed at the ordering temperature of 693 K for 50 h shows at least four steps. Those multi steps came into two at the final stage of annealing for 1000 h. The step at the highest temperature corresponds to the Curie temperature T_C of Ni_3Mn. The observed variation of T_C with annealed time was explained by solving a diffusion equation, and the range of the concentration fluctuation was determined to be 4 nm.

1. Introduction

Ni-rich Ni–Mn alloys have a face centered cubic structure. Around the composition of Ni_3Mn, they have an ordered state of Cu_3Au type. Their magnetic structure is strongly dependent upon the degree of atomic ordering, and hence, many studies for these alloys have been concentrated in order–disorder problems [1,2]. Alloy samples in those studies were prepared using a conventional technique of melting the metal elements in a furnace.

A technique of quick measurements of magnetic susceptibility-temperature curves have been developed by the present authors group and applied for investigating thermally meta-stable magnetic states. By using this technique it becomes possible to observe rapidly changing magnetic character of mechanical alloys during various heat treatments [3–9].

In the present study this technique has been applied to investigate the character of thermal diffusion of magnetic atoms in Ni–Mn mechanical alloys during the heat treatment for atomic ordering.

2. Experimental

Ni and Mn powders of the particle size of 100 mesh and the purity of 99.9% were mixed to the composition of 75 and 80 at.%Ni–Mn alloys, and milled for 75 h in a planetary ball mill in argon atmosphere using stainless steel balls and containers [3–9]. The product was annealed at the ordering temperature of 693 K for 50, 200, 500 and 1000 h to obtain partially and fully ordered states.

The crystal structure of as milled and annealed mechanical alloys were examined by X-ray diffraction at room temperature. For low temperature magnetic measurements below room temperature a SQUID magnetometer was used, and magnetization curves and susceptibility versus temperature curves were investigated. For high temperature susceptibility measurements, a quick measuring system has been applied to investigate the character of thermal diffusion of magnetic atoms. The magnetic measurements have been made during the heat treatment for atomic ordering by keeping the specimens at the ordering temperature of 693 K for up to 1000 h.

3. Experimental results

X-ray diffraction patterns observed for as milled and annealed mechanical alloys (MA) shown in Fig. 1 indicate that those alloys are all in fcc phase. The peak

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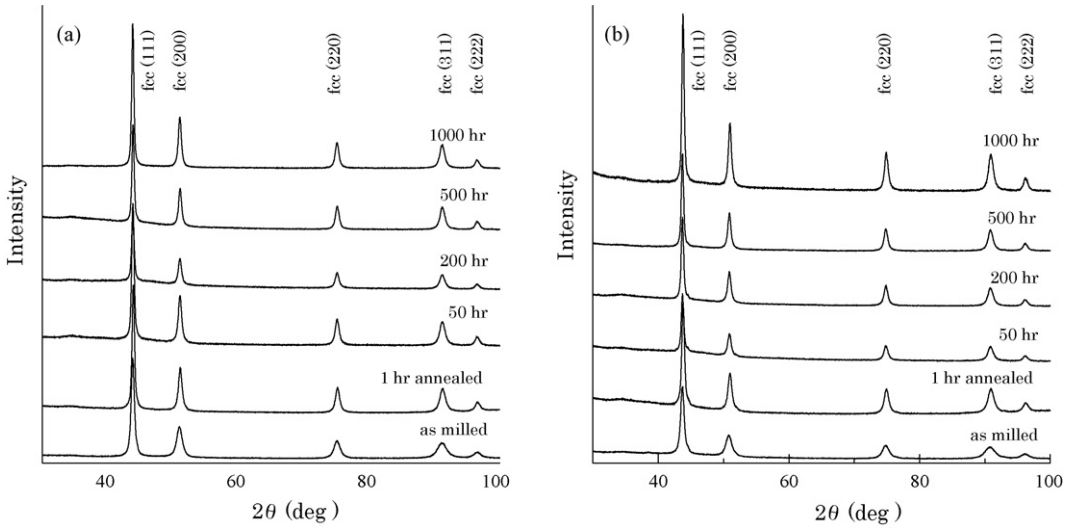

Fig. 1. X-ray diffraction patterns of Ni–Mn mechanical alloys for as milled and after annealed at 693 K for various hours: (a) 80 at.%Ni–Mn and (b) 75 at.%Ni–Mn.

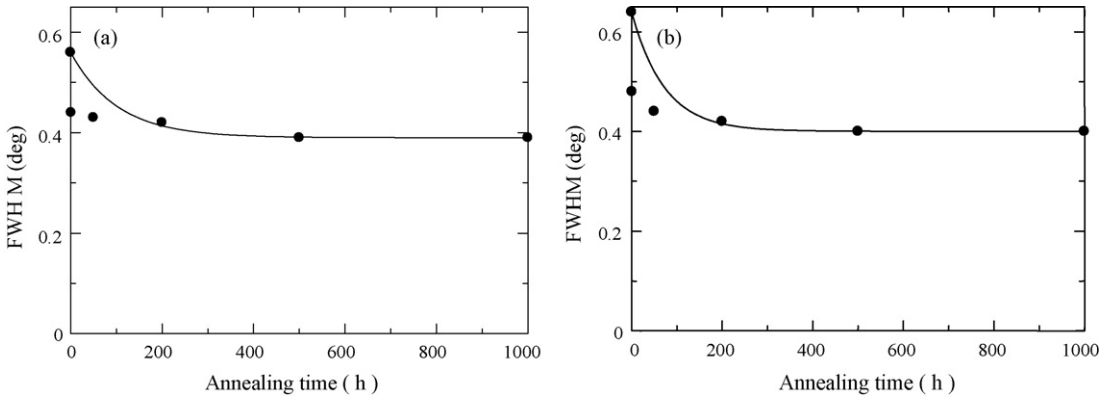

Fig. 2. Annealed time-variation of the FWHM of X-ray peaks: (a) 80 at.%Ni–Mn and (b) 75 at.%Ni–Mn. The solid curves are calculated from Eq. (3) using the magnetic data for 80 at.%Ni–Mn alloy.

widths of the as milled MA are wider and the intensities are weaker than those of the alloys made by conventional method of furnace melting. The peak intensities and the widths did not change much after long-time annealing as seen in Fig. 2.

Saturation magnetization versus annealed time curves observed at 4.2 K for 80 and 75 at.%Ni–Mn mechanical alloys were shown in Fig. 3(a) and (b), respectively. For 80 at.%Ni–Mn mechanical alloy M_S was about 53 Am^2/kg in the as milled state, and increased largely to about 103 Am^2/kg after annealed at 693 K for 1000 h.

Observed susceptibility versus temperature curves for 80 and 85 at.%Ni–Mn MA as milled and annealed at 693 K for various hours are shown in Fig. 4(a) and (b), respectively. The variations of T_C for 80 and 75 at.%Ni–Mn mechanical alloys with annealed time were illustrated in Fig. 5(a) and (b), respectively. As seen in Fig. 4(a) in the curve of 80 at.%Ni–Mn alloy annealed for 50 h there are at least four steps. Those multi steps came into two at the final stage. The step at the lower temperature side corresponds to the Curie temperature of 85 at.%Ni–Mn ordered alloy and the higher temperature side corresponds to that of Ni_3Mn. On the other hand, as seen in Figs. 4(b) and 5(b), no such trend of phase separation was observed in 75 at.%Ni–Mn MA.

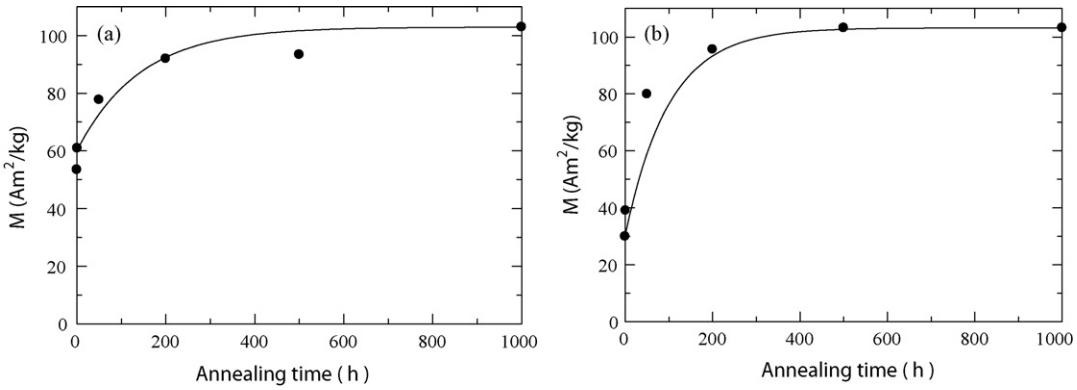

Fig. 3. Annealed time variation of the saturation magnetization observed at 4.2 K at 1 T for (a) 80 at.%Ni–Mn and (b) 75 at.%Ni–Mn mechanical alloys. The solid curves are calculated from Eq. (3).

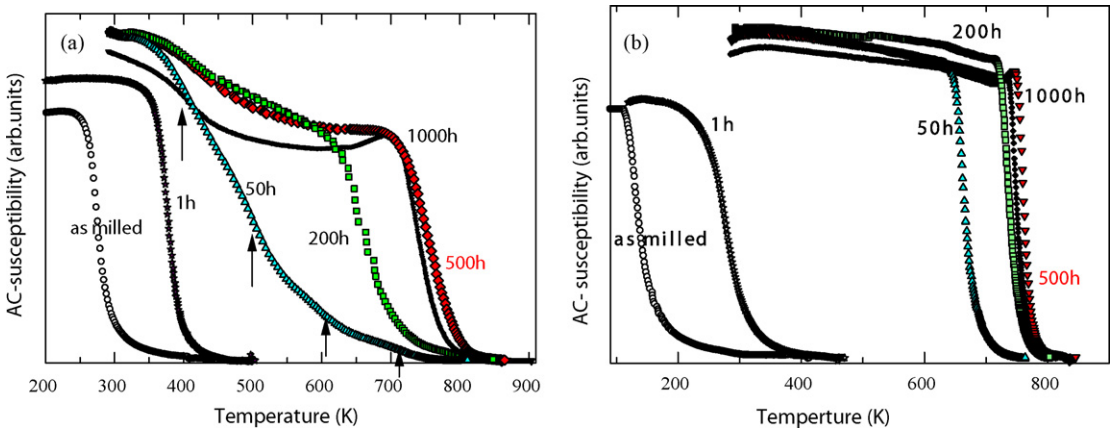

Fig. 4. AC-susceptibility versus temperature curves observed for (a) 80 at.%Ni–Mn and (b) 75 at.%Ni–Mn mechanical alloys at various stages of atomic ordering. The arrows in (a) indicate the four steps observed for 50 h-annealed alloy.

4. Discussion

From the present experimental results described above, it was shown that in 80 at.%Ni–Mn MA, Ni and Mn atoms migrate to reduce Ni-concentration to 75 at.% to form an ordered state of Ni_3Mn. As a result, the remaining part increases its Ni-concentration to 85 at.% after long-time annealing at the ordering temperature of 693 K. This situation can be described by a diffusion theory.

The transient process of atomic diffusion during the heat treatment can be expressed by solving the diffusion equation [10],

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{1}$$

where D is the diffusion constant and c the density of the flowing atoms along the x-direction. Here, we set the direction of migration of magnetic atoms as x-direction. The simplest form of the solution c for a system slowly approaching to saturation can be expressed in the form, $c = C(x)F(t)$. Then, the Eq. (1) is separated into two independent equations using a common constant $-\lambda^2$, as

$$\frac{1}{DF}\frac{dF}{dt} = \frac{1}{C}\frac{d^2C}{dx^2} = -\lambda^2. \tag{2}$$

The solution of the time-dependent term is expressed as

$$F(t) = F_0 \ \exp(-\lambda^2 Dt) \tag{3}$$

and the space-dependent term can simply be written as

$$C(x) = C_0 \ \sin \lambda x.$$

The coefficient, $\lambda^2 D$ of the time-dependent term is estimated by fitting Eq. (3) to the observed M_S versus annealed time curve as shown in Fig. 3(a), and $\lambda^2 D = 2.0 \times 10^{-6}\ s^{-1}$ is obtained.

To determine λ, it is necessary to know the value of the diffusion constant D at 693 K. However, we could not find any available data. Therefore, we adopted the expression

$$D = D_0 \ \exp\left(-\frac{Q}{kT}\right) \tag{4}$$

where Q is the activation energy and k the Boltzmann constant. By substituting available values, $D_0 = 1.30\ cm^2/s$ for self-diffusion of Ni [11] and $D = 1.9 \times 10^{-9}$ at $T = 1600$ K [12] into Eq. (4), the diffusion constant for Ni and Mn atoms at $T = 693$ K can be estimated to be $D = 10^{-20}\ cm^2/s$. By using this value, $\lambda = 1.4 \times 10^9\ m^{-1}$ was obtained. Then, the width of the fluctuation of the atomic potential is estimated to be

$$L = \frac{2\pi}{\lambda} = 4 \times 10^{-9}(\text{m}).$$

This magnitude is in good agreement with the width of the concentration fluctuation, 6 nm, estimated by Kachi et al. [13] in Fe–Ni invar alloys.

The solution of the time-dependent term was compared in Fig. 6 in a scaled form with the experimental data of annealed time-dependences of M_S, T_C and the full width at half maximum (FWHM) of the X-ray peaks for 75 at.%Ni–Mn mechanical alloy. In this figure it is seen that the observed variation of the magnetic quantities can be explained by the present analysis of the diffusion theory.

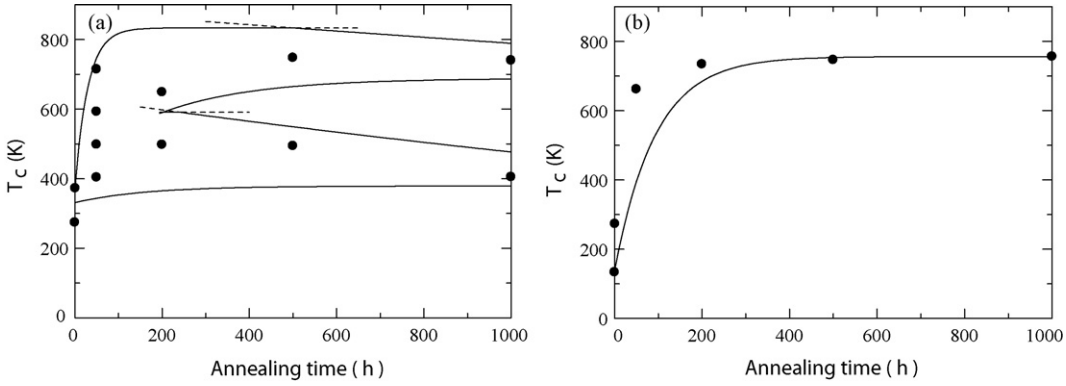

Fig. 5. Observed Curie temperatures (steps in the susceptibility-temperature curves) plotted as a function of annealed time at 693 K for (a) 80 at.%Ni–Mn and (b) 75 at.%Ni–Mn mechanical alloys. All the solid curves shown are calculated from Eq. (3) using the common constant of $\lambda^2 D$ determined in the text.

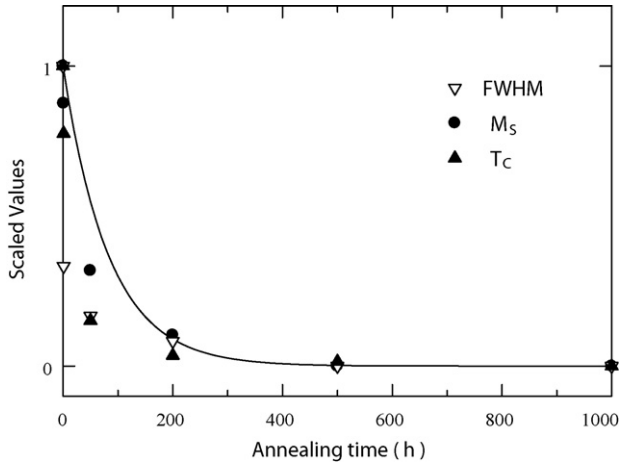

Fig. 6. Annealed time variation of the X-ray peak width, the saturation magnetization and the Curie temperature for 75 at.%Ni–Mn mechanical alloys plotted in a scaled form. The solid curve is calculated from Eq. (3).

On the other hand, observed annealed time variation of the X-ray peak width came to saturate much earlier than the magnetic quantities. This tendency can be explained by considering the fact that the X-ray peak width is sensitive to lattice distortion which was inserted into the specimen during the mechanical alloying and which relaxes much earlier than atomic diffusion.

5. Conclusions

From the present analysis by solving the diffusion equation, it is concluded that the annealed time dependence of the spontaneous magnetization in Ni–Mn mechanical alloys around the Ni_3Mn concentration is well expressed with an exponential function. Observed annealed time dependence of the Curie temperature is also expressed with the same exponential function. By solving the space-dependent equation, the range of the potential fluctuation was estimated to be 4 nm. This result indicates that the distance of diffusion for a migrating atom to make appreciable changes in magnetization is 4 nm.

On the other hand, it was found that annealed time dependence of the half width of the X-ray peaks came to saturate earlier than the magnetic quantities. This tendency could be explained by considering the fact that the X-ray peak width is sensitive to lattice distortion which relaxes much earlier than atomic diffusion.

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