Thermodynamics and Kinetics of Martensitic Transformation in Ni-Mn-based Magnetic Shape Memory Alloys

Xiao Xu1, Ryosuke Kainuma1,a, Takumi Kihara2,4, Wataru Ito3, Masashi Tokunaga4, and Takeshi Kanomata5

1 Department of Materials Science, Tohoku University, Sendai 980-8579, Japan
2 Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
3 Department of Materials and Environmental Engineering, Sendai National College of Technology, Natori 981-1239, Japan
4International MegaGauss Science Laboratory, Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan
5 Research Institute for Engineering and Technology, Tohoku Gakuin University, Tagajo 985-8537, Japan

Abstract. We herein present a review of recent thermodynamic and kinetic studies on Ni-Mn-based magnetic shape memory alloys along with some new data supporting the kinetic discussion. Magnetic phase diagrams and Clausius-Clapeyron relationships are mainly discussed for Ni-Mn-Ga and Ni-Mn-In systems. For the kinetics, a phenomenological model based on Seeger’s model is used to describe the temperature dependence of magnetic field hysteresis, as well as the change of hysteresis under different sweeping rates of magnetic fields.

1 Introduction

Research on Ni-Mn-based magnetic shape memory alloys dates back to 1984 when Webster et al. investigated the ferromagnetic Ni50Mn50Ga Heusler alloys showing martensitic transformation [1]. In 1996, Ullakko et al. reported a 0.2% magnetic field-induced strain (MFIS) in a Ni50Mn50Ga Heusler alloy [2]. Since then alloys showing variant rearrangement under a magnetic field in their martensite phase have been categorized as ferromagnetic shape memory alloys (FMSMA) and this field of research has received much attention. Other FMSMAs, such as Fe-Pd [3], Fe-Pt [4], Ni-Mn-Al [5], Ni-Co-Ga [6], Ni-Co-Al [7] and Ni-Fe-Ga [8], have successively been reported. In Ni-Mn-Ga systems, a huge MFIS of about 9.4% has been reported in 14M [9] and about 12% in non-modulated [10] martensites, despite the fact that the output stress is limited to several MPa [11, 12].

On the contrary, as first reported by Sutou et al., Ni-Mn-X (X = In, Sn, and Sb) alloys generally show a large difference in magnetization between the parent and martensite phases (AM) [13]. In the Ni-Co-Mn-In alloy, magnetic field-induced transformation (MFIT) has been realized by reverse martensitic transformation [14]. This group of alloys are called metamagnetic shape memory alloys (MMSMA). Substitutional Ni-Mn-based alloy systems such as Ni-Co-Mn-Sn [15], Ni-Co-Mn-Ga [16] and Ni-Co-Mn-Al [17], ferrous systems such as Fe-Mn-Al [18], Fe-Mn-Ga [19] and Fe-Mn-Al-Ni [20], as well as cobalt based Co-Cr-Ga-Si alloys [21] have been reported. In these alloys, there is a strong output stress during the MFIT [22–24] though a strong magnetic field is needed for the realization of MMSMA.

In this article, we review some representative experimental studies on Ni-Mn-based alloys. In the first section, magnetic phase diagrams as well as Clausius-Clapeyron relationships are discussed with a focus on thermodynamic analysis. In the second part, some kinetic studies on Ni-Mn-based alloys are reviewed along with some new data supporting the discussion.

2 Thermodynamics of Ni-Mn-based Magnetic Shape Memory Alloys

2.1 Ni-Mn-Ga- and Ni-Mn-In-typed Phase Diagrams

Figure 1 shows the experimental phase diagrams of Ni50Mn50−xGa x and Ni50Mn50−xIn x alloy systems. These two systems are chosen here because Ni-Mn-Ga and Ni-Mn-In alloys are representative alloys for FMSMA and MMSMA, respectively. This figure is based on experimental data for Ni50Mn50−xGa x [26] and Ni50Mn50−xIn x [25]. Reference to other consistent reports on the phase diagrams for Ni50Mn50−xIn x [13, 27] and Ni50Mn50−xGa x [28] should be made. Both the phase diagram of Ni50Mn50−xGa x and that of Ni50Mn50−xIn x can be divided into four major phase regions, which are as follows:

(I) the paramagnetic parent phase region,

(II) the ferromagnetic parent phase region,

(III) the paramagnetic martensite phase region, and

(IV) the ferromagnetic martensite phase region,

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where \( x_{CM} (i = P \text{ or } M) \) indicates the intersection composition for \( T_M \) and \( T_C \).

For the Ni_{50}Mn_{50-x}In \(_x\) system, region IV is wide and covers the stoichiometric Ni_{2}MnGa composition [1, 29]. Moreover, the Curie temperature of the martensite phase (\( T_{CM} \)) is slightly higher or almost equal to the Curie temperature of the parent phase (\( T_{CP} \)), and the \( \Delta M \) in the vicinity of martensitic transformation temperature (\( T_M \)) is very small. Similar phase diagrams can be found for Ni-Mn-Ga systems such as in Ni_{2}Mn_{1+y}Ga \([30–32]\) and other sections \([33, 34]\). Moreover, some substitutional quaternary systems such as (Ni_{52,5}Mn_{23,5}Ga_{24})_{100-x}Co \(_x\) \([35]\), Ni_{2}MnGa\(_{1-y}\)Co \(_y\) \([36]\), Ni-Mn-Ga-Cu \([37–39]\), and Ni-Mn-Ga-Fe \([40, 41]\) systems also show similar behaviors, and a magnetically coupled structural transition, i.e., a direct transition from region I to region IV, can be found in a wide range of compositions.

On the contrary, for the Ni_{50}Mn_{50-x}In \(_x\) system, region IV is narrow and disappears far from the stoichiometric Ni_{2}MnIn composition. Another major difference is that the \( T_{CP} \) is generally higher than \( T_{CM} \) and transition from region II to region III is possible where a ferromagnetic-parent-to-paramagnetic-martensite transformation occurs. However, it is of interest that, as reported by Yu et al. \([16]\), this Ni-Mn-In type transition can also be realized with a proper substitution of Co into Ni-Mn-Ga \([16]\). A clear phase diagram showing this evolution has been reported by Wang et al. \([42]\). Besides, except for Ga, the phase diagrams for other ternary alloy systems generally show a \( T_{CP} \) much higher than \( T_{CM} \), as shown by Sutou et al. \([13]\). This can also be found in other ternary Ni_{93–x}Mn_{11}In \(_x\) \([43]\) and quaternary Ni_{90-x}Co_{x}Mn_{50–y}In_{y} \([25]\), Ni_{2}Mn_{48–x}Ga_{x}Sn_{52} \([44]\), Ni_{90–x}Co_{x}Mn_{50–y}Al_{y} \([45–47]\) and Ni_{90–x}Co_{x}Mo_{50–y}Sn_{y} \([48]\) systems, where a region II to region III transition can be easily found.

A further comparison between the magnetic phase diagrams of Ni_{50}Mn_{50-x}Ga \(_x\) and Ni_{50}Mn_{50-x}In \(_x\) in Fig. 1 reveals that the two systems have a similar behavior for the composition dependence of magnetic transition temperatures (\( T_{CP} \) and \( T_{CM} \)). Moreover, if an extrapolation of \( T_{CP} \) and \( T_{CM} \) were possible, with the change of composition \( Z, Ni_{50}Mn_{50−x}Ga \(_x\) might also show \( T_{CP} > T_{CM} \) at about 15% Ga, and Ni_{50}Mn_{50−x}In \(_x\) might also show \( T_{CM} > T_{CP} \) at about 20% In compositions. Nevertheless, the \( T_M \) of the two series systematically differs by about 5% in \( Z \) composition. Specifically, with the increase of Ga or In composition, the martensite phase of Ni_{50}Mn_{50−x}Ga \(_x\) disappears whereas the martensite phase of Ni_{50}Mn_{50−x}In \(_x\) remains stable until stoichiometry, which can be considered as the biggest difference between Ni_{50}Mn_{50−x}Ga \(_x\) and Ni_{50}Mn_{50−x}In \(_x\) systems.

2.2 Entropy Change during Martensitic Transformation

Along with the determination of phase diagrams, which gives information on the change of thermodynamic equilibrium states with variation of composition, investigation of entropy change during first-order martensitic transformation (\( \Delta S \)) is also of great importance, as it reveals the Gibbs energy near the equilibrium state when the temperature is subjected to change.

The simplest direct way of obtaining \( \Delta S \) is by use of

\[
\Delta S = \frac{\Delta L}{T}
\]  

from thermoanalysis, where \( \Delta L \) is the latent heat or the enthalpy change (\( \Delta H \)) during the martensitic transformation. A graphical meaning of \( \Delta S \) is shown in Fig. 3(a). Other ways to determine \( \Delta S \) by use of Clausius-Clapeyron equations are discussed in Sec. 2.3.

Figure 2 shows \( \Delta S \) for Ni_{50}Mn_{50-x}Ga \(_x\) \([49]\) and Ni_{50}Mn_{50-x}In \(_x\) \([25]\) systems. Systematic studies on \( \Delta S \) in the Ni-Mn-Ga systems have been intensively performed \([50–52]\) due to its wide interest. For the Ni_{50}Mn_{50-x}Ga \(_x\) section, with increasing Ga content, the \( \Delta S \) increases near \( x_{CM} \) and decreases over \( x_{CP} \), as shown in Fig. 2. The composition where \( \Delta S \) starts to increase, which is indicated by a small triangle in Fig. 2, does not coincide with \( x_{CM} \), which is considered to be the result of short-range
ordering of the ferromagnetic martensite phase above its $T_{CM}$. Refer to [49] for a detailed discussion. For the Ni$_{30}$Mn$_{30}$In$_x$ system, the most important characteristic is that the $\Delta S$ to the left of $x_{CP}$ shows little change, whereas it abruptly decreases to the right of $x_{CP}$. Reports of a similar tendency of $\Delta S$ can be found in other ternary Ni-Mn-In alloys [53, 54]. The decrease of $\Delta S$ below $T_{CP}$ by direct measurements can also be found in Sb-doped [55] and Co-doped [56] quaternary systems, as well as in the Ni$_{30-x}$Co$_x$Mn$_{30-y}$Al$_y$ system [57]. This common tendency is considered to be the thermodynamic cause of the “thermal transformation arrest phenomenon” [58, 59], where the martensitic transformation is interrupted at a certain temperature during the cooling process.

### 2.3 Clausius-Clapeyron Equations

On the other hand, the Clausius-Clapeyron equations are widely used as they are convenient approaches for indirect measurements of $\Delta S$ due to the first-order nature of the martensitic transformation. By writing the total derivative of Gibbs energy $G$ as

$$dG = -SdT + Vdp + MdH + ldf + \sum \mu_i dx_i,$$  \hspace{1cm} (2)

where $V$ is the molar volume, $p$ is the hydrostatic pressure, $H$ is the magnetic field, $l$ is the length of the sample, $F$ is the uniaxial force, and $\mu_i$ is the chemical potential of component $i$. Assuming that $S$, $V$, $M$, $l$ and $\mu_i$ show little change in the parent and martensite phases, this deduces the Clausius-Clapeyron equations as [60]

$$\frac{d\tau_0}{dT} = -\frac{\Delta S}{eV},$$  \hspace{1cm} (3)

$$\frac{dp_0}{dT} = -\frac{\Delta S}{\Delta V},$$  \hspace{1cm} (4)

$$\frac{dH_0}{dT} = -\frac{\Delta S}{\Delta M},$$  \hspace{1cm} (5)

where $\tau$ is the martensitic transformation strain, $\sigma$ is the uniaxial stress, and the quantities with zero in subscript correspond to their thermodynamic equilibrium states.

Equation 3 is the most commonly used relationship for the investigations of conventional shape memory alloys, as reported for Ni-Ti alloys [61]. Since the martensite phase is uniaxial stress-favored, the application of uniaxial stress usually induces the martensite phase, which is illustrated in Fig. 3(b). In Ni-Mn-based alloy systems, research studies have been done for Ni-Mn-Ga [62], Ni-Co-Mn-In [14, 63–67] single crystals and Ni-Co-Mn-In [68] and Ni-Co-Mn-Al [69] polycrystals. On the other hand, this is the phenomenon attributable to the elastocaloric effect [70–72], which is of practical importance.

Equation 4 is effective for the investigation of $\Delta S$ since the samples can be small and polycrystalline, and it is applicable to brittle alloys. Note that hydrostatic pressure stabilizes the phase which has a smaller molar volume. A review article can be found in Ref. [73] and this phenomenon is also utilized in the barocaloric effect [74].

In Ni-Mn-Ga systems, the molar volume change during martensitic transformation is so small that reports for both a decrease [75, 76] and an increase [77–79] of $T_{CM}$ with increasing pressure can be found. In other systems such as Ni-Mn-In [80, 81], Ni-Co-Mn-Ga [82] and Ni-Mn-Fe-Ga [83], positive relationships of $dT_{CM}/dp$ have been reported by many groups, which is the cause of greater molar volume of the parent phase.

Equation 5 can be found in many reports in the field of Ni-Mn-based alloys both because of the easy access of moderately strong magnetic fields as well as interest in the magnetocaloric effect [84–86]. For Ni-Mn-Ga ternary alloys, the magnetization of martensite phase is greater than that of the parent phase [87], and therefore a strong magnetic field generally raises the $T_{CM}$ [88–90]. However, due to the large magnetic anisotropy in Ni-Mn-Ga alloys [2, 91], a low magnetic field results in a small decrease of $T_{CM}$ [88, 89]. Nevertheless, for Ni-Mn-In alloys, the magnetization of the parent phase is much greater than that of martensite phase, and thus magnetic fields will effectively decrease the $T_{CM}$ [23, 92–96], as is schematically shown in Fig. 2.3(c). In quaternary systems such as Ni-Co-Mn-In [58, 65, 66, 97–101], Ni-Co-Mn-Sn [15, 101, 102], Ni-Co-Mn-Sb, [101, 103, 104], Ni-Co-Mn-Al [17, 46, 105–107] and Ni-Co-Mn-Ga [16, 108–110], the same relationship of $\Delta M$ as well as MFIT have been found. It should be noted that in most of the above cited studies, magnetization was monitored for the detection of MFIT. Other methods, such as monitoring the electric resistance [99], the variation of sample temperature [100] or the variation of strain [65], have been used. In situ observation of optical microstructure [98, 107, 111] as well as X-ray diffraction patterns.
Δ from Refs. [25–27, 49] were used as in Eq. 6 for the calculation of Δμ.

Z

Simplicity. It can be seen that Ni50Mn50 and NiMn being the chemical potential change for the end-member NiZ and NiMn phases, respectively. Therefore, Δμ = ΔμNiZ - ΔμNiMn can be calculated for Ni50Mn50...Inx and Ni50Mn50...Ga1-x. The curves shown in Figs. 1 and 2 were traced for the calculation of Δμ and the results are shown in Fig. 4. Note that in Fig. 1 the composition at which T M occurs was used, therefore dxNiZ/dT was used instead of dxNiMn/dT for simplicity. It can be seen that Ni50Mn50...In1 generally has a greater absolute value of Δμ compared with that of Ni50Mn50...Ga1, Δμ also changes at magnetic transitions, as indicated by T C.P and T C.M in Fig. 4. Table 1 shows a comparison of Δμ for three alloy systems. The data at around 400 K, which is above the magnetic transitions, are summarized. One can see that Ni-Ti has the largest Δμ among the three series because of the large composition dependence of T M, as well as the large ΔS. Ni-Mn-Ga and Ni-Mn-In have comparable values of dT/dxNiZ, whereas Ni-Mn-In has a larger value of Δμ because of its larger ΔS at the martensitic transformation. However, an in-depth discussion on Δμ, especially for situations near the magnetic transitions, is avoided in this study, though the bending behavior of Δμ on crossing xC.P is consistent with the second-order nature of magnetic transitions, as indicated by the small triangle and xC.P in Fig. 4. Since ΔS → 0 and dT/dxNiZ → ∞ especially for the case of T C.P, an experimental determination of Δμ near T C.P is difficult and a theoretical background is needed for greater understanding.

2.4 Chemical Potential Change during the Martensitic Transformation

Figure 3(d) shows another section of the Gibbs energy curves, which are against the composition axis. Following Niitsu et al. [113], from Eq. 2 we have

\[
\frac{dx_0^C}{dT} = -\frac{\Delta S}{\Delta \mu_{NiZ} - \Delta \mu_{NiMn}}, \tag{6}
\]

where a pseudo-binary system of NiMn-NiZ (Z=In, Ga) under equilibrium is considered, with x0C being the equilibrium composition and ΔμNiZ and ΔμNiMn being the chemical potential change for the end-member NiZ and NiMn phases, respectively. The curves shown in Figs. 1 and 2 were traced for the calculation of Δμ and the results are shown in Fig. 4. Note that in Fig. 1 the composition at which T M occurs was used, therefore dxNiZ/dT was used instead of dxNiMn/dT for simplicity. It can be seen that Ni50Mn50...In1 generally has a greater absolute value of Δμ compared with that of Ni50Mn50...Ga1. Δμ also changes at magnetic transitions, as indicated by T C.P and T C.M in Fig. 4. Table 1 shows a comparison of Δμ for three alloy systems. The data at around 400 K, which is above the magnetic transitions, are summarized. One can see that Ni-Ti has the largest Δμ among the three series because of the large composition dependence of T M, as well as the large ΔS. Ni-Mn-Ga and Ni-Mn-In have comparable values of dT/dxNiZ, whereas Ni-Mn-In has a larger value of Δμ because of its larger ΔS at the martensitic transformation. However, an in-depth discussion on Δμ, especially for situations near the magnetic transitions, is avoided in this study, though the bending behavior of Δμ on crossing xC.P is consistent with the second-order nature of magnetic transitions, as indicated by the small triangle and xC.P in Fig. 4. Since ΔS → 0 and dT/dxNiZ → ∞ especially for the case of T C.P, an experimental determination of Δμ near T C.P is difficult and a theoretical background is needed for greater understanding.

3 Kinetics of Ni-Mn-based Magnetic Shape Memory Alloys

The kinetics of the martensitic transformation in Ni-Mn-based alloys have been paid less attention than thermodynamic phenomena, whereas different phenomenological approaches from several groups have been developed.

Sharma et al. first investigated the relaxation process during martensitic transformation in a Ni-Mn-In alloy [114]. Afterwards, in Ni-Mn-Ga [115], Ni-Co-Mn-In [116–119], Ni-Co-Mn-Sn [120] and Ni-Co-Mn-Sb [121] systems, isothermal behavior has been found for both the forward and reverse martensitic transformations.

As interpretations of the kinetic phenomena, Kustov et al. introduced equations from the magnetic aftereffect [122], within the framework of which the magnetic viscosity coefficient shows a local minimum at the temperature where the fastest transformation can be observed [117, 123]. On the other hand, based on the nucleation model [124], Fukuda et al. have shown that their experimental observations of time-temperature-transformation (TTT) diagrams can be well explained [125]. Recently, our group also proposed the use of a model based on Seeger’s model [126, 127]. The original model had been used for a phenomenological understanding of the critical resolved shear stress (CRSS), which has also proved valid for the application to diffusionless martensitic transformations [128, 129] as well as the case of stress hysteresis in stress-induced martensitic transformation [130]. The following discussions are based on this model.

For the case of MFIT, as in Ni-Mn-In type alloys, the applied magnetic field, H app, which is half of the magnetic field hysteresis H _SS = H Hys - H HLM, is thought to be divided into two parts: the thermally activated term H TA(T) and the athermal term H q [99]. This is written as

\[
H_{\text{app}}(T) = H_{\mu} + H_{\text{TA}}(T) = H_{\mu} + H_{\text{TA}}(0)[1 - \left(\frac{m k_B T}{Q_{0K}}\right)^{1/q}]^{1/p}, \tag{7}
\]

with H TA(0) being the value of H TA(T) at 0 K, Q0K being the activation energy, k_B being the Boltzmann constant, and m being the kinetic coefficient. p and q are the shape parameters describing the activation barrier, which have

\begin{table}[h]
\centering
\caption{Comparison of the chemical potential (\(\Delta \mu\)) at 400 K for Ni-Mn-Ga [57], Ni-Mn-In [25] and Ni-Ti [113] alloys.}
\begin{tabular}{|c|c|c|c|c|}
\hline
Alloy system & dT/dxNiZ \(^{\text{c}}/K\) & \(\Delta S\) \(\text{(kJ/mol-K)}\) & \(\Delta \mu\) \(\text{(kJ/mol)}\) & Ref.
\hline
Ni50Mn50...Ga1 & 4.3 & 1.6 & 7 & [57]
Ni50Mn50...In1 & 4.4 & 3.0 & 13 & [25]
Ni1/2Ti1/2 & 10.6 & 4.5 & 48 & [113]
\hline
\end{tabular}
\end{table}
Figure 5. Results for magnetization measurements of a Ni_{45}Co_{5}Mn_{36.7}In_{13.3} sample under pulsed magnetic fields. Results for 4.2, 75, 150 and 210 K are shown. Critical magnetic fields, for example, the martensitic transformation starting magnetic field $H_{Ms}$ and the reverse martensitic finishing magnetic field $H_{Af}$ were determined by extrapolation.

Figure 6. Critical magnetic fields $H_{Ms}$, $H_{Af}$ and $H_0$ under pulsed magnetic fields for Ni_{45}Co_{5}Mn_{36.7}In_{13.3} alloy determined in Fig. 5 are plotted against the corresponding temperatures. Critical magnetic fields obtained under steady magnetic fields are shown as dashed lines [58].

been obtained as $p = 1/2, q = 3/2$ for the case of magnetic field-induced martensitic transformation [99]. $m$ is expressed as

$$m = \ln(H_0/H),$$  

where $H = dH/dt$, which is the sweeping rate of the magnetic field, and $H_0$ is a constant. In this article, some new results supporting this model are shown.

A Ni_{45}Co_{5}Mn_{36.7}In_{13.3} sample [58] was subjected to magnetization ($MH$) measurements, where a condenser bank-powered magnet [131] was used. Figure 5 shows some $MH$ curves under different temperatures. The critical magnetic fields $H_{Ms}$ and $H_{Af}$ were obtained by extrapolation, as shown in the figure.

$H_{Ms}$ and $H_{Af}$ are plotted against temperature in Fig. 6 as filled circles. The dashed lines represent the critical fields determined under a steady magnetic field [58] whose sweeping rate was about 0.005 T/s. $H_0 = (H_{Ms} + H_{Af})/2$,

which is thought to be the thermodynamic equilibrium magnetic field [132] in Eq. 5, is also plotted. It can be seen that $H_0$ has almost the same values while $H_{Ms}$ and $H_{Af}$ show deviation under different sweeping rates.

In Fig. 7, the $H_{app}$ is plotted against the temperature for both steady [58] and pulsed magnetic fields. For $H_{app}$ under steady fields, a fitting against Eq. 7 was conducted. Here, $Q_{0K}$ was set to be 0.7 eV [133] because they have very close heat treatment conditions. $H_p$ and $H_{TA}(0)$ were obtained to be 0.9 T and 6.4 T, respectively, and $m$ was found to be 35.9 for the steady field. Here, if Eq. 7 is valid, one can estimate the value of $H_0$ to be 1.9 $\times$ 10^{13} T/s from Eq. 8 and expect a calculated temperature dependence of $H_{app}$ for the pulsed field to be consistent with the experimental data by only changing the value of $m$. Therefore $m = 23.2$ was calculated using Eq. 8 where $H = 1500$ T/s was used, which is a typical sweeping rate for pulsed magnetic fields. This is plotted as the red solid line in Fig. 7 and well reproduces the results of experimental $H_{app}$ under pulsed fields. Therefore Eq. 7 is considered to be a successful phenomenological model which is valid for the interpretation of kinetic phenomena in the current alloy systems. On the other hand, Fig. 7 also shows us that even at room temperature the $H_hys$ may increase under high sweeping rates of magnetic fields, thus attention should be given to MMSMAs when they are applied to devices where a high response rate is required.

4 Conclusion

In summary, a review of the thermodynamics and kinetics of Ni-Mn-based magnetic shape memory alloys was presented.

For thermodynamics:

1. The magnetic phase diagrams of Ni-Mn-Ga and Ni-Mn-In alloys were discussed, along with similar phase diagrams in other quaternary systems.
2. Some representative reports from the literature were reviewed, some of which focused on the direct measurement of entropy change during martensitic transformation, whereas others examined the martensitic transformation under a magnetic field, uniaxial stress and hydrostatic pressure.

3. The chemical potential change during martensitic transformation was deduced experimentally for Ni-Mn-Ga and Ni-Mn-In systems, where much smaller values than that of Ni-Ti alloys were found.

For kinetics:
1. A phenomenological model based on Seeger’s model was reviewed, which interprets the temperature dependence of magnetic field hysteresis ($H_{hys}$).

2. A comparison of $H_{hys}$ obtained under steady and pulsed magnetic fields was conducted over a wide temperature range. A large difference in the $H_{hys}$ was found under the condition that the supposed equilibrium magnetic field was consistent.

3. The equation based on Seeger’s model was used to fit the $H_{hys}$ under steady magnetic fields. By only substituting the actual magnetic field sweeping rate, the predicted $H_{hys}$ showed good agreement with experimental observations.

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