Thermal hysteresis and friction of phase boundary motion in ferromagnetic $Ni_{52}Mn_{23}Ga_{25}$ single crystals

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We calculated the energy consumed for phase boundary motion in a $Ni_{52}Mn_{23}Ga_{25}$ single-crystalline sample during martensitic transformation using a boundary friction phenomenological theory. It was found that the energy consumed for phase boundary motion is 13.14 J/mol, only a small part of the latent heat of martensitic transformation. Furthermore, the results of transformation loops measured by ac magnetic susceptibility proved that the thermal hysteresis of martensitic transformation is in direct proportion to the volume fraction of martensite. It was also indicated that the thermal hysteresis of martensitic transformation originates from the friction of phase boundary motion.

Ferromagnetic Heusler alloy Ni_2MnGa has been systematically investigated with regard to its structure,[1,2] premartensitic transition,[3–6] and magnetic properties[7,8] for years. The recent discovery of the large magnetic-field-induced strain (MFIS) and field-controllable shape memory behavior in this material has produced notable excitement for investigation in the field.[9–11] This achievement is extremely exciting as it opens a route in the search for ferromagnetic shape memory alloys. Therefore, recent attention has primarily focused on the improvement of MFIS and its mechanical properties to make this alloy more amenable to practical application.[12–15] However, comparatively few studies of thermodynamic transformation of this material are found in the literature, and studies on thermal hysteresis are still lacking. In this paper, based on a boundary friction phenomenological theory of thermoelastic martensitic transformation, we calculated the energy consumed for phase boundary motion of a $Ni_{52}Mn_{23}Ga_{25}$ single-crystalline sample during martensitic transformation. It was found that the energy consumed for phase boundary friction is 13.14 J/mol, only a small part of the latent heat of martensitic transformation. Furthermore, the transformation loops measured by an ac susceptometer give direct experimental evidence that the thermal hysteresis is in direct proportion to the volume fraction of martensite.

The composition of $Ni_{52}Mn_{23}Ga_{25}$ was slightly deviated from a stoichiometric Heusler alloy, Ni_2MnGa, in order to raise the martensitic transformation temperature to room temperature. The single crystals were grown in the [001] direction according to the cubic parent phase by a MCGS-3 CZ (Czochralski) instrument with a cold crucible system. Growth rates of 12–15 mm/h and the rotation rate of 30 rpm were adopted. A two-step postgrowth treatment was adopted: as-grown crystals were annealed at about 1123 K for 24 h for high chemical ordering, then cooled to 773 K quickly by compressed air, and annealed at this temperature again for 24 h to eliminate disordering residual stress caused by the quick cooling. Samples for the measurement of ac magnetic susceptibility and for thermal analysis by a differential scanning calorimeter (DSC) were spark-cut from the as-treated single-crystal rod. The magnetic-susceptibility measurement was performed by a susceptometer with an ac magnetic field of 5 Oe and a frequency of 77 Hz over a temperature range of 77 to 400 K. The temperature, alternating between cooling and heating, was varied at about 0.2 K/min.

Generally, the Gibbs free-energy change of a system upon martensitic transformation may be written as[16]

$$\Delta G = \Delta G_c + \Delta G_e + \Delta G_s, \tag{1}$$

where ΔG_c is a chemical energy term originating in the structural change from parent to martensite, ΔG_e is an elastic strain energy term around the martensite, and ΔG_s is a surface energy term between parent and martensite. It is generally accepted that for the thermoelastic martensitic transformation, the interface between parent and martensite is very mobile upon cooling and heating, and the transformation is crystallographically reversible in the sense that the martensite reverts to the parent phase in the original orientation. Pan and James[17] and Chopra *et al.*[18] have observed the growth and shrinkage of a martensite plate upon cooling and heating, respectively, in a Ni-Mn-Ga single crystal. A phenomenological theory[19] has shown that for a thermoelastic martensitic transformation, the slope of the transformation loop results mainly from elastic strain energy, however, its gap between the forward and reverse transformation segments, namely, the thermal hysteresis, comes from the friction of phase boundary motion. Based on this theory, we represent three types of thermoelastic martensitic transformation pictures as shown in Fig. 1. For example, in Fig. 1(a), straight line AB shows an absolute ideal case, i.e., during the transformation, there is no boundary friction and therefore no thermal hysteresis. Furthermore, there is no elastic strain energy and interfacial energy to resist the transformation, thus the forward transformation and reverse transformation occur at the same temperature. However, if there exists the elastic strain energy, then the transformation path would become an incline line CD. In Fig. 1(b), the loop of EFGH shows a transformation with both elastic strain energy and boundary friction. Obviously, due to the existence of boundary friction, the incline line CD separates and forms a transformation loop EFGH with thermal hysteresis.
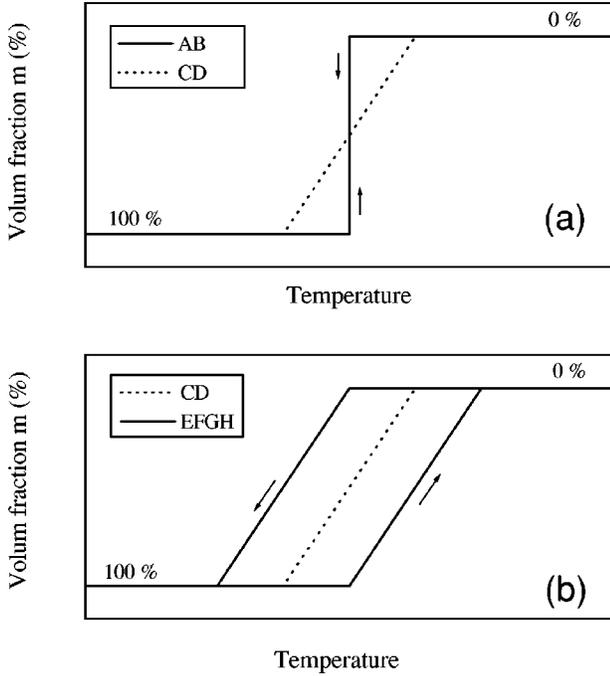
FIG. 1. Schematic representation of three types thermoelastic martensitic transformations: (a) solid line AB represents a transformation without friction and elastic energy and dotted line CD represents a transformation without friction but with elastic energy; (b) (EFGH) represents a transformation loop with both friction and elastic energy.

FIG. 2. (a) Temperature dependence of the ac magnetic susceptibility for a $Ni_{52}Mn_{23}Ga_{25}$ single crystal. Measurements have been conducted with an ac field of 5 Oe and a frequency of 100 Hz along the [001] direction. The solid line is a linear fit to the data; (b) cooling and heating DSC runs for a $Ni_{52}Mn_{23}Ga_{25}$ single-crystal sample.

Figure 2(a) shows the temperature dependence of ac magnetic susceptibility for a single crystal of $Ni_{52}Mn_{23}Ga_{25}$. One can see that the critical temperatures for martensitic transformation and reverse transformation M_s, M_f, A_s, and A_f marked in Fig. 2(a) are 308, 304, 314, and 318 K, respectively. It is clear that the Heusler alloy $Ni_{52}Mn_{23}Ga_{25}$ exhibits a narrow thermal hysteresis of 6 K ($\Delta T = A_s - M_s$), and belongs to thermoelastic martensitic transformation. Figure 2(b) shows the corresponding DSC curves for the single-crystal $Ni_{52}Mn_{23}Ga_{25}$ sample, which shows $\Delta T = 6$ K, in agreement with the susceptibility measurements. The transformation enthalpy of the martensitic transformation is calculated to be $\Delta H = -1615.40$ J/mol.

Based on the boundary friction phenomenological theory[19] as mentioned above, Deng and Ansell[20] set up a friction model of thermoelastic martensitic transformation, in which the order parameter is the volume fraction of martensite. In terms of this model, the free-energy function of a system has the following general form:

$$F = a + bm + cm^2, \qquad (2)$$

where m is the volume fraction of transformed martensite, and a, b, and c are independent of m, but can vary with temperature. The boundary motion friction can be expressed as a friction function,

$$F_r = H_r - T \cdot S_r, \qquad (3)$$

where H_r and S_r represent friction enthalpy and entropy, respectively. Moreover, the cooling and heating curves are
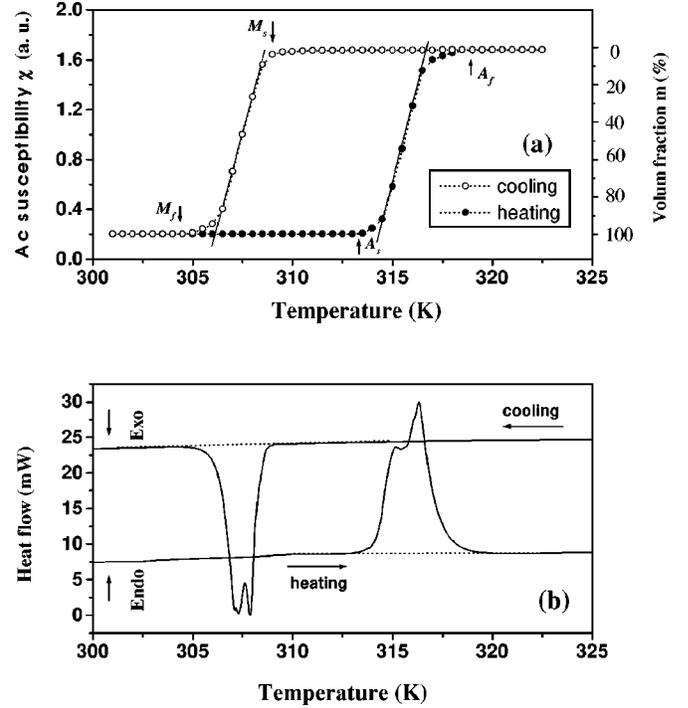
considered to be linear [see Fig. 1(b)], and can be described with the following equation of state,

$$L_c = m + j_c T + k_c = 0,$$

$$L_h = m + j_h T + k_h = 0, \qquad (4)$$

where the subscripts c and h refer to cooling and heating, and j_c, k_c, j_h, and k_h are coefficients. In Ref. 20, these coefficients were obtained through linear fitting the R-T curves. Here, in a similar method, we fit the cooling and heating linear parts of the χ-T curves in Fig. 2(a) to determine the four coefficients. Then we can obtain

$$L_c = m + 0.37T - 113.5 = 0,$$

$$L_h = m + 0.29T - 90.8 = 0. \qquad (5)$$

Here, the equilibrium state is defined as the state in which the system has minimum free energy, i.e., $\partial F/\partial m = 0$. When the system is not in equilibrium, its state has a tendency to change, and the driving force of the transformation would be $f_d = -\partial F/\partial m$. If the driving force f_d could overcome the resistance, the transformation would take place. This resistance originates from the friction during phase boundary motion, which can be expressed as $f_r = -\partial F_r/\partial m$. Therefore, the critical condition for forward martensite transformation is $f_d = f_r$, and the critical condition for reverse martensite transformation is $f_d = -f_r$. Then the equations

TABLE I. Comparative thermodynamic data: thermal hysteresis ΔT, transformation equilibrium temperature T_0, transformation entropy ΔS, transformation enthalpy ΔH, and F_r stands for the energy consumed for boundary friction in one transformation cycle.

Alloys	ΔT (K)	T_0 (K)	ΔH J/mol	ΔS J/mol·K	F_r J/mol
Cu29%Zn3%Al[a]	10	254	−416.2	−1.42	21.21
Cu14%Al2.5%Ni[b]	10	303	−515.0	−1.70	19.00
$Ni_{52}Mn_{23}Ga_{25}$[c]	6	311	−1617.2	−5.20	12.76

[a]Reference 19.
[b]Reference 22.
[c]This paper.

$$L_c = -\frac{\partial F}{\partial m} - \frac{\partial F_r}{\partial m} = 0,$$

$$L_h = \frac{\partial F}{\partial m} + \frac{\partial F_r}{\partial m} = 0 \qquad (6)$$

are equivalent to the first and second equation in Eq. (4), respectively, because they describe the same transformation process, i.e., martensite growth and shrinkage, respectively. From Eq. (6) we can write

$$\frac{\partial F}{\partial m} = \frac{1}{2}(L_c + L_h) = 0,$$

$$\frac{\partial F_r}{\partial m} = \frac{1}{2}(L_c - L_h) = 0. \qquad (7)$$

Thus, by putting Eqs. (5) into (7) and integrating over m, we obtained

$$F = (0.33T - 102.15)m + 0.5m^2 + C,$$

$$F_r = (0.04T - 11.35)m. \qquad (8)$$

Moreover, based on the Clausius-Clapeyron equation, the relationship between applied uniaxial stress and transformation temperature could be written as

$$\frac{d\sigma}{dT} = -\frac{\Delta S}{\varepsilon \cdot v} = -\frac{\Delta H}{\varepsilon \cdot T_0 \cdot v}, \qquad (9)$$

where σ is a uniaxial stress, ε is the transformation strain, v is mole volume, T_0 is the equilibrium transformation temperature, ΔS is the transformation entropy, and ΔH is the transformation enthalpy. For the Ni_2MnGa alloy, the left-hand side $(d\sigma/dT)$ of Eq. (9) has been obtained by Martynov and Kokorin[2] to be 2.5 MPa/K, and ε is calculated to be 0.06.[1] We measure v to be 32 cm^3/mol. Thus, from Eq. (9) we calculated the transformation entropy as $\Delta S = -5.20$ J/(mol K). Moreover, according to Tong and Wayman,[21] T_0 can be determined by $T_0 = 1/2(M_s + A_f)$. Our ac susceptibility curves show $M_s = 308$ K and $A_f = 314$ K, which subsequently gives $T_0 = 311$ K. Then the transformation enthalpy is $\Delta H = -1617.2$ J/mol. This result is in good agreement with that obtained from our DSC experiment. Moreover, based on Kaufman and Cohen,[16] for the one-mole material with $m\%$ transformed martensite, the free energy of

the system can be written as $G = G_0 + g_c m + g_e m + g_s m$, where G_0 is the free energy for 100% of the parent phase, and g_c, g_e, and g_s are chemical free-energy change, elastic energy, and interfacial energy for 100% martensite in the one-mole material. From the data of ΔS and ΔH obtained above, the chemical free energy of single-crystal $Ni_{52}Mn_{23}Ga_{25}$ is $g_c = \Delta H - T\Delta S = (-1617.2 + 5.2T)$ J/mol. Obviously, G and F are the same physical parameter, thus they must be equivalent to each other, i.e., $NF = G$, then

$$N[(0.33T - 102.15)m + 0.5m^2 + C]$$
$$= G_0 + (-1617.2 + 5.2T)m + (g_e + g_s)m, \qquad (10)$$

where N is a unit converting factor to convert F into an ordinary unit system. We now compare the term of (Tm) in both sides of Eq. (10), and obtain $N = 15.79$ J/mol. Thus, according to Eq. (3) the energy consumed for the boundary friction is $F_r = m(-0.63T - 185)$ J/mol. Here, T is the temperature in the middle point between the same m of the cooling and heating processes. We noticed that the linear relationship between m and T is in the range of 10%–90% in Fig. 2(a), hence it is easy to calculate the energy consumed for boundary friction in this linear range, which is $\Delta F_r = 9.98$ J/mol. Moreover, based on the assumption in Ref. 20 that the energy consumed is proportional to the area of the transformation loop, the total energy consumed for boundary friction during one transformation cycle can be obtained. First, the area of the linear part between 10% and 90% in Fig. 2(a) can be calculated as $A_r = 496\%$ K. Thus, the energy consumed per unit area is $\Delta F_A = \Delta F_r / A_r = 2 \times 10^{-2}$ (J/mol)/(% K). Then, the whole area of the transformation loop in Fig. 2(a) can be calculated as $A_r(100\%) = 638\%$ K. Therefore, the energy consumed for boundary friction in one transformation cycle is $F_r = \Delta F_A \times A_r(100\%) = 12.76$ J/mol. For comparison, Table I shows some thermodynamic data for different alloys having thermoelastic martensitic transformation obtained previously. It can be seen from these data that the value of F_r is only a small part of the latent heat of martensitic transformation.

Figure 3 shows the transformation loops for the $Ni_{52}Mn_{23}Ga_{25}$ single-crystalline sample carried out in the following sequence: during the second cycle, when the sample was cooled to 304 K, which lies between points M_s and M_f (at this temperature, the transformed martensite is 80%), we changed cooling into heating immediately. One
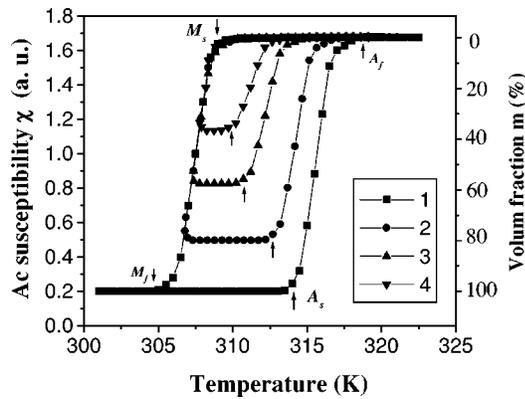
FIG. 3. The transformation loop for a $Ni_{52}Mn_{23}Ga_{25}$ single crystal. The arrows are guides to the eye.

FIG. 4. Thermal hysteresis ΔT as a function of the martensite percentage m. The inset shows the thermal hysteresis ΔT dependence on the normalized loop areas in the χ-T curve of Fig. 3. The solid line is a curve fit to the data.

can see that for this cycle the reverse transformation temperature A_s becomes 312.5 K, which is lower than that of the first cycle. When the transformation curve returned to the parent phase, similar to the second cycle, again the sample was cooled until m reduced to 40%. Heating from this point, the third loop was formed and a thermal hysteresis approximately two degrees smaller than the second cycle was obtained.

To look at the transformed martensite dependence of the thermal hysteresis more carefully, we plot the thermal hysteresis ΔT as a function of the volume fraction m, as shown in Fig. 4. Obviously, the thermal hysteresis ΔT decreases monotonically with the decrease of the volume fraction m, implying that ΔT is in direct proportion to m. It is interesting to note that if we carry out a curve fitting to the data and extrapolate ΔT to zero, the m is obtained to be zero. Moreover, if the normalized loop areas A_r in the χ-T curve of Fig. 3 are plotted against the thermal hysteresis ΔT, as shown in the inset of Fig. 4, one can easily see that ΔT decreases si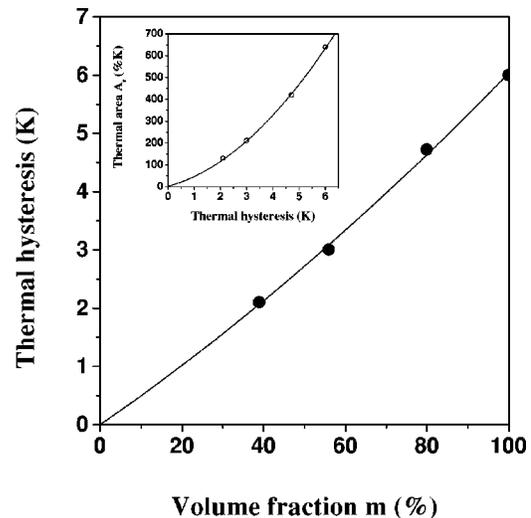gnificantly with the decrease of A_r, although a linear dependence of ΔT on A_r is not obeyed. The solid line is also a polynomial curve fitting to the data. Obviously, the extrapolated A_r corresponding to a zero ΔT is also zero. Therefore, it gives us direct evidence that the thermal hysteresis in our material results from the friction of phase boundary motion. On the other hand, it should be noted that the energy consumed for the twin boundary motion of self-accommodating martensite variants is not taken into account in our present work, due to the absence of both external stress and magnetic field. The effects of stress and bias field on the thermal hysteresis are topics of our ongoing research.

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