Tunable elastic modulus in Mn-based antiferromagnetic shape memory alloys

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Abstract

Compared with the normal relation between temperature (T) and elastic modulus (E) in most materials, martensitic transformation (MT) and magnetic transition could result in the softening of elastic modulus (dE/dT > 0) within a narrow range of T (<100 °C). It becomes possible in MnFeCu alloys to tune this range and broaden it to about 200 °C through combining MT and paramagnetic-antiferromagnetic (P-A) transition. The alloying elements and their contents play a key role in making MT separate from P-A transition, in which first-order MT made a greater contribution to this maximum value than second-order P-A transition. The intrinsic mechanism is that MT can continue causing the modulus to soften even after the P-A transition ends. This wide range keeps stable under different cooling/heating rates. An expression for dE/dT is deduced based on the proposed free energy model and the corresponding theoretical curve (dE/dT-T) gives a reasonable explanation on the experimental results in MnFeCu alloys. A modulus–temperature–composition phase diagram is obtained to describe such critical behaviors and it is found that there exists a specific triangle zone in which dE/dT > 0. The present results may enrich approaches to designing new functional materials, e.g. the elastic and Elinvar alloys.

1. Introduction

Elastic modulus (E) is one of the important mechanical properties for some new materials such as graphene [1], spider silks [2], transforming metal nanocomposite [3] and metallic glass [4]. In most metals and alloys, E usually decreases with increasing temperature (T), i.e. dE/dT < 0. On the other hand, phase transitions, such as martensitic transformation (MT) [5], magnetic transition [6], or order-disorder transition [7], can also cause the softening of E during cooling and lead to the result of dE/dT > 0. However, the range of T for dE/dT > 0 owing to such a phase transition is quite narrow (e.g. smaller than 100 °C [5–7]), which limits its industrial application in functional materials. Therefore, an interesting question arises: whether it is possible to broaden the range of T (in which dE/dT > 0) through coupling two types of phase transitions so as to break this traditional limitation in some magnetic martensitic alloys.

Mn-based antiferromagnetic alloys might be an excellent candidate because both fcc-fct MT and paramagnetic-antiferromagnetic (P-A) transition could occur in some high-Mn content alloys [8]. It seems very promising to tune the range of T for dE/dT > 0 and realize the wide range of T (>100 °C) through controlling MT and magnetic transition in this kind of alloys. Besides high damping property [9], Mn-based alloys have one-way [10], two-way [11] and magnetic field controlling shape memory effects [12] and deserve to be deeply explored as functional devices in future. However, there has no investigation focused on the dE/dT as a function of T during phase transition in martensitic alloys. The modulus loss (ΔE) related to phase transition was studied and found to be related to chemical composition, magnetic moment and the stability of FCC lattice [13]. The alloying elements play a key role in affecting both Mₙ (MT starting temperature) and Tₙ (P-A transition temperature) and only little work has been done on the variation of dE/dT with chemical composition. Besides,
the cooling or heating rates also enhance the softening of modulus in Mn-based [14] and NiMnGa alloys [15] due to the change of kinetic process of MT [16]. Planes et al [16] studied the influence of cooling rate on the first-order phase transition in Cu–Zn–Al and Cu–Al–Ni alloys within a general framework (power-law) of competing time scales of avalanche relaxation, driving rate and thermal fluctuations. It is reasonable that the type of phase transition could influence \( \frac{dE}{dT} \), but it is still unclear how this dynamic process of phase transition affects the range of \( T \) for \( \frac{dE}{dT} > 0 \).

In this study MnFeCu alloys will be chosen to study the dependence of \( \frac{dE}{dT} \) on chemical composition and cooling/heating rate; the main purpose is to tune the range of \( T \) for \( \frac{dE}{dT} > 0 \) (50 ~ 200 °C) through controlling the gap between MT and magnetic transition. A Landau free model related to both phase transitions will be presented to deduce an expression for \( \frac{dE}{dT} \) so as to describe the contribution of each phase transition to the origin of \( \frac{dE}{dT} > 0 \). The intrinsic mechanism involved would be useful in designing new kinds of functional materials such as elastic and Elinvar alloys [17].

2. Experimental

MnFeCu alloys were melted in high vacuum induction furnace and the as-cast ingots kept under high vacuum for 11 h, then cooled to room temperature in water. The raw materials were industrial pure Fe (99.9 wt %), electrolytic Mn (99.99 wt %) and industrial pure Cu plate (99.9 wt %). Three compositions—\( \text{Mn}_{100-x} \text{Fe}_x \text{Cu}_5 \) \( x = 20, 30, 40 \)—were chosen and the alloys named as A1, A2 and A3 respectively. The modulus and internal friction change related to martensitic transformation (MT) and magnetic transition in MnFeCu alloys could be measured by using dynamic mechanism analyzer (DMA 800) within the temperature range of −150 °C and 300 °C. Different cooling/heating rates (2, 4 and 6 °C min\(^{-1}\)) and various frequencies (1, 2, 4, 10 and 20 Hz) were set to study the stability of temperature-dependence modulus. The dimensions of the specimens for DMA were 30 × 5 × 1 mm (length × width × thickness). The surface relief associated with MT at different temperatures (room temperature, 300 °C, −70 °C) was scanned by means of in situ atomic force microscopy (AFM) (SII Nanonavi E-Sweep) for which the specimen size was 10 × 10 × 1 mm. The thermal flow related with magnetic transition was measured by means of DSC (DSC-204-F1) at different cooling and heating rates (5, 10, 15, 20 and 30 °C min\(^{-1}\)) using specimens of dimension 3 × 3 × 1 mm. X-ray diffraction (XRD) (D/MAX2550V/84) was used to characterize the crystal structure at room temperature (specimen size of 10 × 10 × 1 mm) and thermal expansion measurement (DIL402PC) was employed to detect the P–A magnetic transition during heating and cooling through the length change of specimens of 5 × 5 × 20 mm.

3. Results

3.1. Variation of \( E \) and \( \frac{dE}{dT} \) with \( T \)

Figure 1 shows the DMA results for the temperature dependences of modulus \( (E) \) and internal friction (\( \tan \delta \)) in alloys A1, A2 and A3. For alloy A1, an obvious softening of modulus during heating occurred because of the strong coupling between MT and magnetic transition and two peaks of internal friction were related to MT and martensitic twin boundary. For alloy A2, there was only magnetic transition corresponding to the weakly abnormal modulus and no peak of internal friction was observed for this transition. For alloy A3, the variation of the modulus with \( T \) was nonlinear during the softening process and its MT occurred far below magnetic transition, which was much different from that in the A1 or A2 alloys. In figures 1 (a)–(c), each \( E-T \) curve can be divided into three zones designated as A, B and C. The first zone represented normal, abnormal, normal states of modulus respectively. It was easy to find that the range of \( T \) spanning zone B in A2 alloy was almost 200 °C—much wider than that in A1 or A3 alloys and even than that in other materials with only one type of phase transition [5–7].

Normally, the elastic modulus increases with the decrease of interatomic distance when being cooled or under high pressure. However, at least one previous study has shown that high pressure caused softening in CrN owing to a strong competition between different types of chemical bond [18]. The related mechanism in CrN was proposed at a constant \( T \) and could not be used to explain the character of \( E-T \) curve in A2 alloy.

Based on experimental data of \( E \) varying with \( T \), the corresponding \( \frac{dE}{dT} \) could be deduced and the \( \frac{dE}{dT} \sim T \) curves could be drawn as in figure 2. It seems clear that A, B and C zones in figure 1 are referred to \( \frac{dE}{dT} < 0, \frac{dE}{dT} > 0 \) and \( \frac{dE}{dT} < 0 \) respectively; it is interesting to see that \( \frac{dE}{dT} \) does not keep stable though the heating or cooling rate is set as a constant value. For A1 or A3 alloy, there is only one peak in the \( \frac{dE}{dT} \sim T \) curve and the range of \( T \) for \( \frac{dE}{dT} > 0 \) is about 50 °C, indicating that it is difficult to extend the range of \( T \) for abnormal modulus if there is a strong coupling between MT and magnetic transition as in A1 alloy or there is only one magnetic transition as in A3 alloy. However, for A2 alloy, there are two peaks, originating from MT and magnetic transition. Moreover, MT as a first-order transition in A2 alloy made a great contribution (about 150 °C) to the range of \( T \) for \( \frac{dE}{dT} > 0 \), while the second-order magnetic transition contributed about 50 °C.
Figure 1. Modulus varying with temperature in A1 (a), A2 (b) and A3 (c) alloys, and the related internal friction varying with temperature in A1 (d), A2 (e) and A3 (f) alloys.

Figure 2. $dE/dT$ varying with $T$ during heating and cooling in A1 (a), A2 (b) and A3 (c) alloys.
Comparing the $dE/dT$ during heating and cooling (in figure 2), the ranges of $T$ for $dE/dT > 0$ have no obvious difference and exhibit good reversibility for all three alloys.

3.2. Effect of frequency on $E$ and $dE/dT$

In order to further confirm the types of phase transition, the variation of modulus and internal friction with $T$ under different frequencies from 0.1 to 20 Hz were measured in A1, A2 and A3 alloys, as shown in figure 3. For both cooling and heating processes with rate of 2 K min$^{-1}$, the frequency has only a little influence on $E$, which also proves that $dE/dT$ does not change with the frequency during MT and magnetic transition. This is different from a strain glass, in which the modulus during the glassic transition has an apparent change with the external frequency [19] and, therefore, it seems impossible that there exist glass states in the present A1 and A2 alloys. In particular, the wide range of $T$ for $dE/dT > 0$ in A2 alloy does not originate from the strain glass or other glass states. However, the internal friction is influenced by different frequencies. The peak value of internal friction associated with MT in A2 alloy increases with the frequency while the corresponding $T$ could not move, as shown in figure 3(a). The emigration of twin boundary could also cause the internal friction accompanying with a characteristic peak located at about $-50$ °C, which could shift to the side of high temperature with the increase of frequency, as shown in figures 3(a) and (b). There are two peaks of internal friction corresponding to martensite/parent interface and twin boundary in A1 alloy, while in A2 alloy there is only one peak due to the movement of martensite twin boundary which indicates that MT occurs and its $M_s$ is far below $T_N$. The peak of internal friction associated with MT in A2 alloy is merged into the twin peak, which is of frequency-dependence. Considered no change of modulus with frequency during the magnetic transition in A2 alloy, the glass state or spin glass could not form between $M_s$ and $T_N$ and only MT and magnetic transition contribute to the range of $T$ for $dE/dT > 0$. 

Figure 3. Modulus and internal friction varying with the frequency in A1(a), A2(b) and A3(c) alloys.(Cooling or heating rate is 2 °C/min.)
3.3. Effect of cooling and heating rate on $E$ and $dE/dT$

The kinetic processes of both MT and magnetic transition are influenced by the cooling and heating rates and the velocity of MT could increase with the increase of driving rate through increasing the nucleation probability of MT measured by using ultrasonic method [16]. It may be possible that the probability of modulus softening during MT and magnetic transition would also increase as the rate increases. Figure 4 shows the modulus in A1, A2, and A3 alloys varying with the different rates ($2 \degree C/\text{min}$ and $6 \degree C/\text{min}$). It is found that the modulus softening and the modulus loss ($\Delta E$) increase with the increase of driving rate in three alloys, which is in accordance with that in MnCu [14] and NiMnGa [15] alloys. However, the driving rate has little influence on the $M_s$ and $T_N$ temperatures, as seen in the fact that the temperature corresponding to $dE/dT = 0$ does not change with the increase of driving rates. The effect of driving rate on the range of $T$ for $dE/dT > 0$ could be compared in figure 5. It is clear that the larger driving rate could strengthen the peak of $dE/dT \sim T$ curve but has little effect on broadening the anomalous zone of modulus. This also presents a good stability of $dE/dT$ varying with $T$ under different driving rates in the present alloys.

3.4. fcc-fct martensitic transformation

The experimental results of internal friction (figures 1(d), (e)) and 3(a), (b)) had indicated that MT occurred in A1 and A2 alloys. In order to verify the shearing character of fcc-fct MT, $in situ$ AFM was used to scan the surface relief associated with MT. The $M_s$ temperatures of A1 and A2 alloys are above and below RT respectively and, thus, the fct martensite could be found in A1 specimen but not in A2 alloy from their XRD spectra at RT shown in figure 6. The surface relief associated with its reverse transformation in A1 alloy was observed at 300 $\degree C$, shown in figure 7(b). For A1 alloy, its MT occurred below RT and the surface relief related to MT was observed at $-70 \degree C$ shown in figure 7(d). The shearing associated with fcc-fct MT was detected and verified in figures 8(b) and (d). The angle of surface relief was measured, showing that it varies from 0.1$\degree$ to 1.2$\degree$ in A1 alloy, while this angle is less than 0.2$\degree$ in A2 alloy. Based on the above experimental results, it was believed that MT and magnetic transition strongly coupled with each other and had made an apparent modulus softening which led to a big

![Figure 4. Modulus varying with T under different driving rates in A1(a), A2(b) and A3(c) alloys.](image-url)
Figure 5. \( \frac{dE}{dT} \sim T \) curves affected with different driving rates in A1 (a), A2 (b) and A3 (c) alloys.

Figure 6. XRD at RT in A1, A2 and A3 alloys.
shearing in A1 alloy, compared with the small shearing strain because of the little correlation between the two transitions in A2 alloy. This kind of shearing due to MT is in accordance with that in FeMnSi alloys [20].

Paramagnetic-antiferromagnetic (P-A) transition as a second-order one could not cause the surface relief because of its very small lattice distortion (~10^{-6}). Therefore, the strong coupling between two transitions could decrease the range of T between Ms and TN and result in a small range of T (~50 °C) for dE/dT > 0 in A1 alloy. When Ms is far below TN in A2 alloy, the effect of this correlation between MT and magnetic transition is weakened and MT could continue contributing to the modulus softening after the P-A transition has ended so as to extend the range of T for dE/dT > 0.

3.5. Paramagnetic-antiferromagnetic (P-A) transition

The abnormal modulus associated with magnetic transition could be detected via the latent heat measured by using DSC experiments. However, in Mn-based alloys with high-Mn content such as A1 alloy, magnetic transition occurs before MT and may affect MT if both transitions are strongly coupled with each other or Ms is very close to TN. P-A transition also causes an increasing latent heat with the increase of driving rate as MT does in A2 and A3 alloys as shown in figures 9(b) and (c). It is seen that the coupling between MT and P-A transitions in A1 alloy gives rise to a greater contribution to thermal flow change during heating and cooling than that in A2 and A3 alloys. This kind of coupling in A1 alloy could also be verified from the transition strain [21] and the strain of the order of 10^{-6} related to magnetic transition is rather less than 10^{-2}, the order of strain of MT. Thermal expansion measurement was used to directly measure the strain originating from phase transition in A1 and A2 alloys as shown in figure 10. There exists a clear change in the specimen length of A1 due to the strong coupling between MT and magnetic transition, while no such variation was found during P-A transition in A2 alloy.

With the increase of driving rate, the peak value of thermal flow during heating and cooling apparently increased and this transition was seen to be second-order-like from the character of these peaks, even in A1 alloy. For MT and magnetic transition, greater latent heat could lead to greater increase of local temperature within the specimen and, thus, cause a greater softening of local modulus with the increase of driving rate. Another
important result is that the temperatures corresponding to these peaks in A1 alloy vary much more than that in A2 and A3 alloys, because the coupled MT delivers another part of latent heat to the thermal flow besides the P-A phase transition.

4. Discussions

4.1. Theoretical model
Based on the above experimental observation and analyses, it is reasonable to suppose that MT and magnetic transition could be an effective way to widen the range of $T$ for $\frac{dE}{dT} > 0$. In order to quantitatively study this
Figure 9. Heat flow associated with phase transition under different driving rates in A1 (a), A2 (b) and A3 (c) alloys.

Figure 10. Thermal expansion related to phase transition in A1 and A2 alloy.
abnormal effect originating from MT and magnetic transition, a Landau free energy model connected with both phase transitions is presented and the expression of $dE/dT$ could be deduced. A sub-lattice model was used to describe the antiferromagnetic phase in Mn-based alloys [22]. The total Landau free energy ($F$) of system is the sum of nonmagnetic free energy ($F_{PA}$), magnetic free energy ($F_{MA}$), strain energy ($F_{ST}$) and their interaction ($F_{INT}$):

\[ F = F_{PA} + F_{MA} + F_{ST} + F_{INT} \]  
(1)

\[ F_{PA} = F_{0}^{b} + d_{0}(T - M_{i})\eta_{i}^{2} + d_{1}\eta_{i}^{4} + d_{2}\eta_{i}^{4} \]  
(1a)

\[ F_{MA} = F_{MA}^{A} + F_{MA}^{B} = [a_{A}(T - T_{A}) \cdot M_{A}^{2} + b_{A}M_{A}^{4}] + [a_{B}(T - T_{B}) \cdot M_{B}^{2} + b_{B}M_{B}^{4}] + k_{AB}M_{A}^{2} \cdot M_{B}^{2} \]  
(1b)

\[ F_{ST} = F_{ST}^{A} + c_{1}\varepsilon^{2} + c_{2}\varepsilon^{3} \]  
(1c)

\[ F_{INT} = (\lambda_{1}M_{A}^{2} + \lambda_{2}M_{B}^{2})\varepsilon^{2} + (\lambda_{3}M_{A}^{2} + \lambda_{4}M_{B}^{2})\eta^{2} + \lambda_{5}\varepsilon^{2}\eta^{2} \]  
(1d)

in which $\eta$ and $\varepsilon$ are the order parameter of martensite and strain of phase transition respectively. In the antiferromagnetic system, $F_{MA}^{A}$, $F_{MA}^{B}$ are the magnetic free energies in which the atomic magnetic moments for the sub-lattice are $M_{A}$ and $M_{B}$, $F_{MA}^{AB}$ is the interaction energy between $A$ and $B$ magnetic lattice with the interaction constant $k_{AB}$. $F_{ST}^{A}$ and $F_{ST}^{B}$ are the initial energies of the system. $\lambda_{i}$ ($i = 1, ..., 5$) are the related coupling constants among the three order parameters of $\eta$, $M$, $\varepsilon$. $d_{0}$, $d_{1}$ and $d_{2}$ are the parameters of the martensitic system. $a_{A}$, $a_{B}$, $b_{A}$ and $b_{B}$ are the parameters of magnetic system. $c_{1}$ and $c_{2}$ are the elastic constants for the strain system. Based on the equation (1), the elastic strain energy ($E_{E}$) of the system can be expressed as

\[ E_{E} = E_{ST}^{A} + c_{1}\varepsilon^{2} + c_{2}\varepsilon^{3} + (\lambda_{1}M_{A}^{2} + \lambda_{2}M_{B}^{2})\varepsilon^{2} + \lambda_{5}\varepsilon^{2}\eta^{2} \]  
(2)

According to the equation: $E = \partial^{2}E_{E}/\partial\varepsilon^{2}$, the modulus ($E$) can be obtained:

\[ E(T) = 2c_{1} + 6c_{2}\varepsilon + 2(\lambda_{1}M_{A}^{2} + \lambda_{2}M_{B}^{2}) + 2\lambda_{5}\varepsilon^{2} \]  
(3)

As for the antiferromagnetic structure, it satisfies $M_{A} = -M_{B}$ under no magnetic field. Assuming $\lambda_{1} = \lambda_{2} = \lambda_{0}$, the above equation can be rewritten as

\[ E(T) = 2(\xi_{1} + 3c_{2}\varepsilon + 2\lambda_{0}M_{A}^{2} + \lambda_{5}\varepsilon^{2}). \]  
(4)

Considering that the total strain includes two parts: strain of MT ($\varepsilon_{PA}$) and strain of magnetic transition ($\varepsilon_{MT}$), the above strain is simplified as

\[ \varepsilon = \varepsilon_{PA} + \varepsilon_{MT} = \xi_{1}M_{A} + \xi_{2}\eta. \]  
(5)

Here, $\xi_{1}$ and $\xi_{2}$ are the linear parameters correlated to $M_{A}$ and $\eta$, which meets $\varepsilon_{PA} = \xi_{1}M_{A}$ and $\varepsilon_{MT} = \xi_{2}\eta$. So the following expression for the modulus could be obtained:

\[ E(T) = 2\xi_{1} + E_{M} + E_{\eta} \]  
(6)

in which

\[ E_{M} = 2(3c_{2}\xi_{1}M_{A} + 2\lambda_{0}M_{A}^{2}) \]  
(7a)

\[ E_{\eta} = 2(3c_{2}\xi_{2}\eta + \lambda_{5}\eta)^{2}. \]  
(7b)

Here, $E_{\eta}$ is the modulus related to MT and $E_{M}$ is the modulus related to magnetic transition. Then the modulus related to $T$ and its kinetics could be considered as following

\[ \frac{dE(T)}{dT} = 2\left[ (3c_{2}\xi_{1} + 4\lambda_{0}M_{A})\frac{dM_{A}}{dT} + (3c_{2}\xi_{2} + 2\lambda_{5}\eta)\frac{d\eta}{dT} \right]. \]  
(8)

From the above equation, the dynamics of modulus is related to kinetics of MT ($d\eta/dT$) and magnetic transition ($dM_{A}/dT$).

In order to study the effect of driving rate on $dE(T)/dT$, the equation of dynamic evolution of modulus as a non-conserved variable can be obtained from the variation principle and the principle of minimum energy,

\[ \frac{dE(T)}{dT} = -L_{\varepsilon} \frac{\partial F}{\partial E_{T}}. \]  
(9)

Because $dE(T)/dt = [dE(T)/dT] \cdot [dT/dt]$, the driving rate is expressed as $V_{T} = dT/dt$, the relationship between $dE(T)/dT$ and $V_{T}$ could be expressed as:

\[ \frac{dE(T)}{dT} = -V_{T}L_{\varepsilon} \frac{\partial F}{\partial E(T)}. \]  
(10)
The phase transition, which was persisted by the previous experimental results, is an equivalent equation between modulus and entropy. The change of entropy was nonlinear due to phase transition on $d_1$. Therefore, the modulus related to magnetic moment and the long range order parameter can be expressed as the function of $T$. From this equation, it is easy to compare the experimental results of $E_t/E_0$ for three alloys (A1, A2 and A3) with the theoretical results (L1, L2 and L3) as below.

\[
\left( \frac{dE(T)}{dT} \right)^2 = -V_tL_c \frac{\partial F}{\partial T}.
\]

(11)

From this equation, it is easy to find that the driving rate could enhance the softening of modulus during the phase transition, which was proved by the present experiments as well. The modulus could be divided into different stages during cooling ($T_1 \rightarrow T_s \rightarrow T_f \rightarrow T_2$)

\[
E(T) = -\int_{T_1}^{T_s} (-V_tL_cS)^2dT + \int_{T_s}^{T_f} (-V_tL_cS)^2dT - \int_{T_f}^{T_2} (-V_tL_cS)^2dT
\]

(14)

This is an equivalent equation between modulus and entropy. The change of entropy was nonlinear due to phase transition \[23\] and the $dE(T)/dT$ too, which were proved by the present experiments as well. The modulus could be obtained by numerical calculation and could be compared with the above experimental results. Figure 11 gives a comparison of experimental $E_t/E_0 \sim T$ with the theoretical results (labelled as L1, L2 and L3 respectively) for A1, A2 and A3 alloys. They seem very consistent. In order to study the different effects of MT and magnetic transition on $dE^*/dT^*$, the $dE^*/dT^* \sim T^*$ curve ($E^* = E_t/E_0$) is separated into two parts, one is related to MT and another is related to magnetic transition as shown in figure 12. If MT is strongly coupled to magnetic transition, the variation of the modulus with $T$ is expressed as $E^*$—shown in figure 12(a)—and it is found that the final abnormal modulus or $dE^*/dT^*$ is just the sum of the contributions from MT and magnetic transition, which is in accordance with the characters of modulus in A1 alloy (shown in figure 1(a) and figure 2(a)). It is important to note that the range of $T$ for $dE^*/dT^* > 0$ during MT is larger than that during magnetic transition and the final range of $T$ for $dE^*/dT^* > 0$ is between them. This indicates that $dE/dT$ is synthetically decided by both MT and magnetic transition instead of the simple sum of them. Some previous experiments showed that in high-Mn content alloys, MT would seriously interact with magnetic transition and exhibit the second-order character.

4.2. $dE/dT$ related to MT and magnetic transition

By using equations (1)–(16), most of the theoretical curves such as $E_t \sim T$ and $dE/dT \sim T$ could be obtained via numerical calculation and could be compared with the above experimental results. Figure 11 gives a comparison of experimental $E_t/E_0 \sim T$ with the theoretical results (labelled as L1, L2 and L3 respectively) for A1, A2 and A3 alloys. They seem very consistent. In order to study the different effects of MT and magnetic transition on $dE^*/dT^*$, the $dE^*/dT^* \sim T^*$ curve ($E^* = E_t/E_0$) is separated into two parts, one is related to MT and another is related to magnetic transition as shown in figure 12. If MT is strongly coupled to magnetic transition, the variation of the modulus with $T$ is expressed as $E^*$—shown in figure 12(a)—and it is found that the final abnormal modulus or $dE^*/dT^*$ is just the sum of the contributions from MT and magnetic transition, which is in accordance with the characters of modulus in A1 alloy (shown in figure 1(a) and figure 2(a)). It is important to note that the range of $T$ for $dE^*/dT^* > 0$ during MT is larger than that during magnetic transition and the final range of $T$ for $dE^*/dT^* > 0$ is between them. This indicates that $dE/dT$ is synthetically decided by both MT and magnetic transition instead of the simple sum of them. Some previous experiments showed that in high-Mn content alloys, MT would seriously interact with magnetic transition and exhibit the second-order character.
because MT is greatly affected by second-order magnetic transition and the range of $T$ for $\frac{dE}{dT} > 0$ due to MT would be narrowed by the magnetic transition. When MT occurs at a temperature far below that of magnetic transition (marked as $E^*$ in figure 12(b)), there are two separated independent peaks for the $\frac{dE^*}{dT^*} \sim T^*$ curve. It is seen that the range of $T^*$ for $\frac{dE^*}{dT^*} > 0$ due to magnetic transition is only half of that due to MT because of the difference between first-order and second-order transitions. Based on these considerations, MT in A$_2$ alloy is thought to make a great contribution to the extension of range of $T$ for $\frac{dE^*}{dT^*} > 0$ shown in figures 1(b) and 2(b).

4.3. Range of $T$ for $\frac{dE}{dT} > 0$

Figure 13 shows the modulus softening related to MT or magnetic transition without coupling of phase transitions, i.e. for A$_3$ alloy. In Fe–Pd–Pt alloy [26], anomalous modulus was observed during fcc-fct MT. In the present A$_3$ alloy, the paramagnetic-antiferromagnetic (P-A) transition is accompanied by the modulus softening, which was also found in antiferromagnetic Mn$_{69.4}$Ni$_{30.4}$ alloy [27]. In Mn-based alloy, $T_N$ is always above $M_s$ and the softening due to magnetic transition might occur before that of MT during cooling as shown in figures 1(a) and 2(a). When $M_s$ is very close to $T_N$, temperature, the $E-T$ curve cannot be divided into different stages, just like in A$_1$ alloy (shown in figures 1(a) and 2(a)). When $M_s$ is far below $T_N$, the $E-T$ curve obviously separates into several stages for the zone of anomalous modulus or $\frac{dE^*}{dT^*} > 0$, which is confirmed in A$_2$ alloy (shown in figures 1(b) and 2(b)). Although both $T_N$ and $M_s$ temperatures decrease with the decrease of Mn content [28], Mn has a much greater on the MT than magnetic transition, which means that the range of $T$ for


\textbf{4.4. Critical phenomenon of phase transition in Mn-based antiferromagnetic alloy}

Based on the temperature-composition phase diagram of MnFeCu alloys [28], mechanical properties (\(dE/dT\)) could be added into it, as shown in figure 14. The most important deduction is that, located in a special triangle zone (\(\Delta ABC\)) with certain ranges of temperature and composition, an alloy exhibits \(dE/dT > 0\) under antiferromagnetic state. The range of \(T\) for \(dE/dT > 0\) increases with increasing Fe-content from \(c_A\) to \(c_B\) owing to an increase of \(\Delta T = T_N - M_s\), which also indicates that MT plays a key role in causing the modulus to soften after magnetic transition ends in \(A_2\) alloy as shown in figure 1(b). When \(c_A > c_B\), the system exhibits the spin glass state as in MnCu alloys [29, 30]. In other words, the chemical composition of Mn-based alloys might play an important role in deciding the range of \(T\) for \(dE/dT > 0\) through combining MT and magnetic transition. Moreover, the elastic modulus varying along the lines of \(L_{AB}, L_{BC}\) and \(L_{AC}\) should meet the condition: \(dE/dT \neq 0\) on both sides of them has opposite signs while, on the lines, it remains at zero and shows the continuous condition of modulus. For the alloy with the composition of \(c_B\), \(dE/dT\) remains at zero in the range of \(T\) from \(T_C\) to \(T_B\), which was thought of as the Elinvar effect [31]. Hakaru \textit{et al} studied the Elinvar effect in MnFeCu and MnCu alloys [32, 33], but did not give rise to a reasonable explanation of this property and, thus, its intrinsic mechanism is still unclear. The Elinvar effect was also found in Mn\textsubscript{79.6}Ni\textsubscript{20.4} alloy within the range of 50 °C–150 °C [27] in accordance with the prediction from figure 14. Therefore, the present modulus–temperature–composition phase diagram seems to be helpful to design new Mn-based elastic alloys.

\textbf{5. Conclusions}

Elastic modulus as an important property usually increases with the decrease of temperature in metals and alloys (\(dE/dT < 0\)). Phase transitions such as MT and magnetic transition could cause it to be abnormal, i.e. the modulus to soften upon cooling (\(dE/dT > 0\)). The range of \(T\) for \(dE/dT > 0\) in MnFeCu antiferromagnetic alloys has been investigated and the effects of alloy composition and driving rate were carefully considered. A Landau free energy model was built to deduce the expression of \(dE/dT\) so as to explore the intrinsic mechanism and the related critical phenomenon associated with phase transition in MnFeCu alloys. The main results are the following:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{Modulus–temperature–composition phase diagram in MnFeCu alloys.}
\end{figure}
• The range of $T$ for $dE/dT > 0$ could be tuned through combining MT and magnetic transition. The maximum $T$ range could reach about 200 °C from the related $dE/dT \sim T$ curve in $A_2$ (Mn$_{70}$Fe$_{25}$Cu$_{5}$) alloy based on the DMA experimental results.

• The range of $T$ for $dE/dT > 0$ could remain rather stable under different cooling or heating rates. The content of alloying element Fe plays a key role in separating MT from magnetic transition in order to increase $\Delta T \ (\sim T_N - M_S)$. MT could continue softening the modulus after that due to magnetic transition.

• An expression for $dE/dT$ was deduced based on the proposed Landau free energy model. MT as a first-order transformation has a greater influence in extending the range of $T$ for $dE/dT > 0$ than the second-order magnetic transition. The calculated theoretical $dE/dT \sim T$ curve has given a reasonable explanation for the results observed in $A_1$, $A_2$, and $A_3$ alloys.

• A modulus–temperature–composition phase diagram was suggested to demonstrate the critical phenomenon in MnFeCu antiferromagnetic alloys and there existed a special triangle zone ($\Delta$ABC) in which the alloy meets $dE/dT > 0$. Elinvar effect could also be predicted within a certain range of temperature in some Mn-based alloys.

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