

Internal friction peak associated with the interface motion in the martensitic transformation of CuAlNiMnTi shape memory alloy

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Two internal friction peaks were observed in a CuAlNiMnTi polycrystalline shape memory alloy during the martensitic transformation through an incomplete phase transformation method, of which the high-temperature peak P_H is discussed in the present study. It has been found that the P_H peak is discernible only at relatively low frequencies and its maximum corresponds to the inflection point of the relative dynamic modulus rather than its minimum, i.e., this peak is related to a process without soft mode effect. An internal friction model is proposed to describe the P_H peak based on the theory of phase nucleation and growth in the thermoelastic martensitic transformation and is verified by the experimental results. © 2007 American Institute of Physics.

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I. INTRODUCTION

A single internal friction (IF) peak is usually observed during thermoelastic martensitic transformation (MT), as has been addressed by a number of authors over the past decades.^{1–6} This peak, however, is, in fact, composed of two peaks⁷ and they are different from those observed near the critical temperature in materials during second order or weak first order phase transformations.^{8–10} Study on the operative mechanisms of the two peaks will be certainly helpful for understanding the thermoelastic MT or even common MT.^{11–15} The double-peak phenomenon suggests that the thermoelastic MT should arise from multiple mechanisms, and they have to be experimentally separated to allow for studying and understanding the individual transformation process. This has been realized through an incomplete phase transformation method by the present authors. The two IF peaks found in the CuAlNiMnTi polycrystalline shape memory alloy (SMA) during nonisothermal measurements have been demonstrated to be associated with two different motions of phase interfaces in terms of the dependence of the peaks on the measuring frequency and the corresponding changes in the relative dynamic modulus (RDM). The high-temperature peak P_H appears at a fixed temperature independent of frequency and is caused by the normal motion of the phase interfaces due to the cooperative shear movement of atoms on the interfaces, while the low-temperature peak P_L occurring around 10 °C below the P_H peak is due to the viscous motion of atoms along the phase interfaces.⁷ The

mechanism of P_L peak has been theoretically analyzed in another study⁸ and the present work is focused on the origin of the P_H peak and both the experimental and theoretical results are presented.

II. EXPERIMENT

A CuAlNiMnTi SMA with the nominal composition of Cu–12Al–5Ni–2Mn–1Ti (wt %) was chosen as the studying material in consideration of its promising applications and relatively high transformation temperatures. The specimens used for IF measurements have a dimension of $1 \times 4 \times 70$ mm³. Before the IF measurements, the specimens were homogenized under an argon atmosphere at 850 °C for 60 min followed by water quenching, allowing the high-temperature phase β to be transformed into a single martensite structure, and then subjected to several hundreds of thermal cycles between –20 and 100 °C in a vacuum of 10^{-5} Torr to reach a sufficient structural stability. The quenched structure was characterized by x-ray diffraction to confirm its phase constituent.

The IF of the alloy is characterized by $\tan \varphi$, where φ is the phase difference between the oscillatory stress and strain,⁹ and measured simultaneously with the RDM by a computer-controlled automatic inverted torsion pendulum in vacuum through forced vibration. The apparatus basically consists of an inverted torsion pendulum, a temperature programmer, and a photoelectron transformer. A computer and an 8087 processor are used to control the whole measurement and allow the data to be processed in real time. The range of the maximum excitation torsion strain amplitude is

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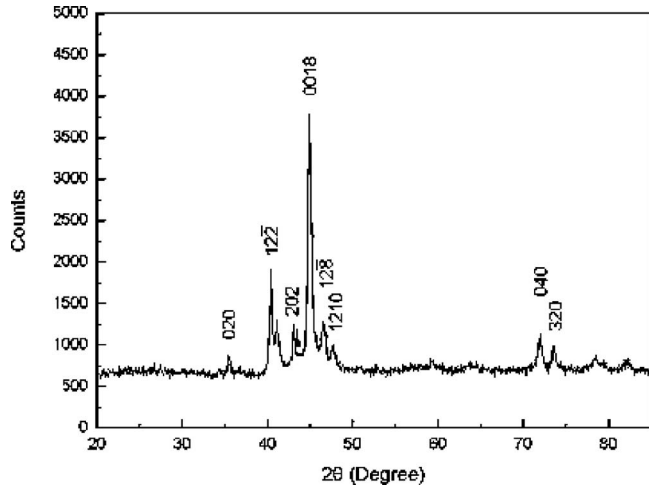


FIG. 1. X-ray diffraction spectrum of water-quenched CuAlNiMnTi alloy.

10^{-6} – 10^{-4} and the resolution in the IF measurements is 1×10^{-4} . The details of the apparatus and the measuring fundamentals were described in Ref. 16.

The incomplete transition measurements were performed in such a way that an incomplete transformation temperature T_s was determined in advance according to the complete transformation temperature range. The specimens were then heated to 100 °C for holding 60 min and then cooled to the selected incomplete transformation temperature T_s for holding 30 min to approach an equilibrium state, allowing only partial martensitic structure to be produced that was characterized under a metaloscope (MM6, Leitz, Germany) using polished specimens. The IF and RDM were finally measured upon heating from this T_s . It should be noted that the resolution of the IF measurements is at least 10^{-4} and the stability of the measuring system is high enough to ensure the reliability of the results.

III. RESULTS

Studies on CuAlNiMnTi shape memory alloys disclosed that the alloys underwent a transformation from DO₃ to M18R₁ structure when quenched.^{17,18} This is also demonstrated by the present study, as shown in Fig. 1, in which the

peaks of 0018, $12\bar{8}$, $12\bar{2}$, etc., are the most typical features of M18R₁ martensite.

Figure 2 gives the IF and corresponding RDM against temperature measured in a complete MT at a cooling rate of 1 °C/min. An IF peak is clearly seen; the maximum of which corresponds to the minimum of the RDM and increases with decreasing frequency. From the IF peak, it is known that the MT began at around 50 °C and finished at around 10 °C, and thus three incomplete transformation temperatures were selected, i.e., 36, 42, and 48 °C, and the IF behaviors of the alloy were reexamined by the incomplete transition method upon heating. It is shown that the IF peak in Fig. 2 is divided into two different peaks, as shown in Figs. 3(a) and 3(b). The low-temperature peak P_L appearing at around 64.5 °C is similar to the peak in Fig. 2, that is, its maximum corresponds to the minimum of the RDM, suggesting that it resulted from a viscous movement of the phase interfaces associated with soft mode effect. The high-temperature peak P_H appearing at about 78.6 °C is much sharper and higher than the P_L peak and its maximum corresponds to the inflection point of the RDM rather than its minimum. In comparison with Figs. 3(a) and 3(b), it is found that the P_H peak is only apparent at relatively low frequencies, e.g., below 0.125 Hz.

As the incomplete temperature decreases or the completeness of transformation increases, the two peaks tend to joint together to form only one peak, suggesting that the double-peak phenomenon can only be observed in the specimens with less martensites, as shown in Fig. 4. Figures 5(a) and 5(b) give the typical martensite structures when cooled to the incomplete transformation temperatures of 42 and 36 °C, respectively. There are only fewer and finer martensite plates when the incomplete transformation temperature is relatively high, while they become more and coarser when the incomplete transformation temperature is reduced.

In order to disclose the dependence of the P_H peak on frequency, a Lorentz-Gauss function was employed to separate the two peaks from the IF curves in Fig. 3(a), as displayed in Fig. 6. Obviously, the two peaks show completely different dependences on frequency. The P_L peak decreases while the P_H peak increases as the frequency is reduced.

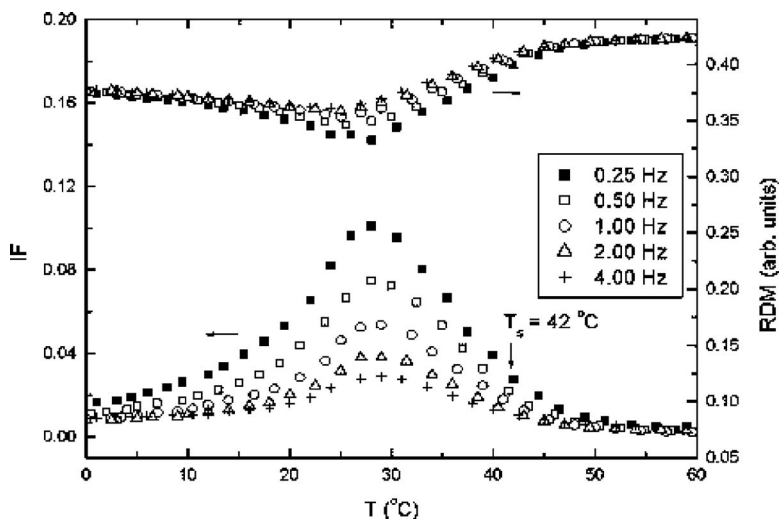


FIG. 2. The IF and RDM as functions of temperature during the complete MT upon cooling at varied frequencies.

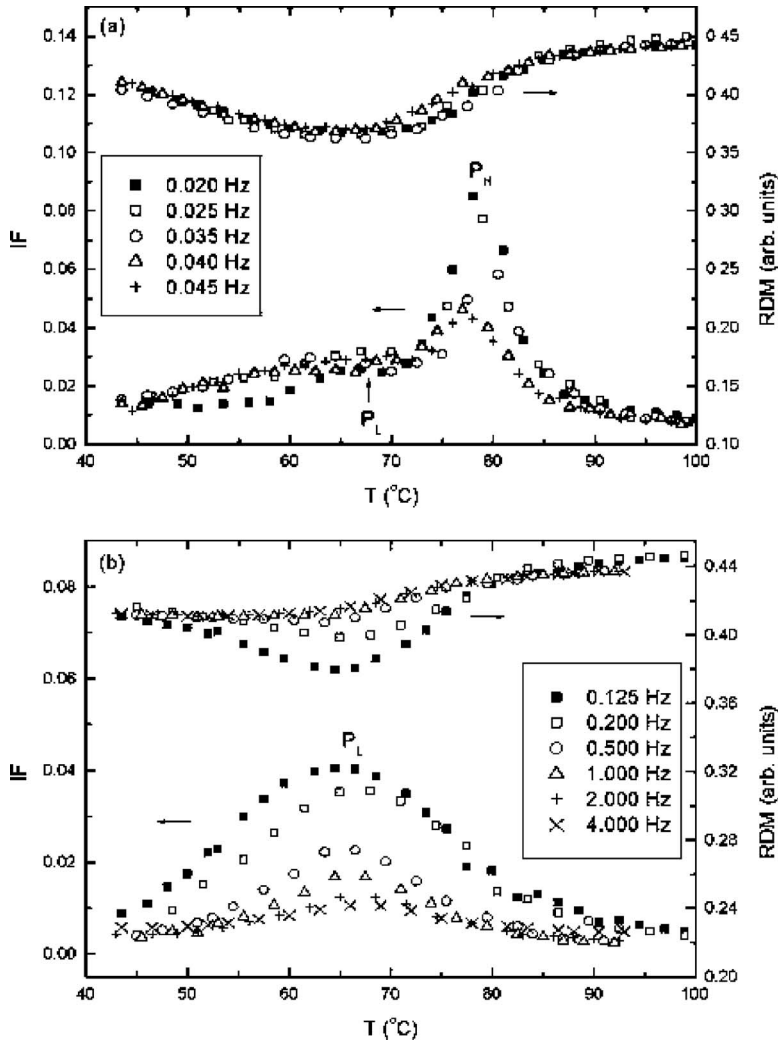


FIG. 3. The IF and RDM as functions of temperature upon heating with a heating rate of 1.5 °C/min for the partial reverse MT temperature $T_s=42$ °C at frequencies of (a) 0.02–0.045 Hz and (b) 0.125–4.000 Hz.

Making plots using the maximum values of the P_H peak against reciprocal frequency, as shown in Fig. 7, it is seen that the maximum IF value is inversely proportional to frequency in the present frequency range, being coincident with the prediction of Belko and Delorme models.^{10,11} The linear relation shows that during the MT the nucleation and growth of new phase are independent of time, or in other words, the two processes are driven only by temperature. If the nucleation in a MT is also considered to be a migration process of phase interfaces, the P_H peak should be attributed to the normal motion of the interfaces because of no soft mode effect arisen in this process.

IV. THE INTERNAL FRICTION THEORY WITHOUT SOFT MODE EFFECT IN A MT

Since Belko and Delorme models are based on the nucleation and growth of the new phase in a transformation, they would be most applicable for analyzing the IF phenomena associated with the first order phase transformation.^{10–15} However, these models only deal with volume change of the related phases during the transformation without considering the time effect that should be closely related to the motion of phase interfaces. Therefore, the following analysis is to take

the effect of time into account on the nucleation and correlated nonelastic strain, aimed to reveal the dynamic behavior of phase interfaces during the MT.

During a nonisothermal transformation, the number of nuclei (N) per unit material volume is a function of temperature (T), time (t), heating/cooling rate (\dot{T}), and applied stress (σ), in which only T and t are independent. When $\sigma=0$ and $\dot{T}=\text{const}$, the time derivative of the nucleus density $N(T, t, \sigma)=N(T, \dot{T}, \sigma)$ can be simplified to be

$$\dot{N}_0 = \dot{T} \left[\frac{\partial N_0(T, \dot{T})}{\partial T} \right]_{\dot{T}}, \quad (4.1)$$

where the subscript “0” means $\sigma=0$. In general, the nucleation rate \dot{N}_0 is a binary function of T and t (or \dot{T}).

The nucleation rate can also be defined by the following equations:

$$\dot{N}_0 = \frac{N_{0c}}{\tau_0}, \quad \dot{N} = \frac{N_c}{\tau}, \quad (4.2)$$

where N_{0c} and N_c are the critical nucleus densities at $\sigma=0$ and $\sigma \neq 0$, respectively, and τ_0 and τ are the relaxation times (nucleation time) at $\sigma=0$ and $\sigma \neq 0$, separately.

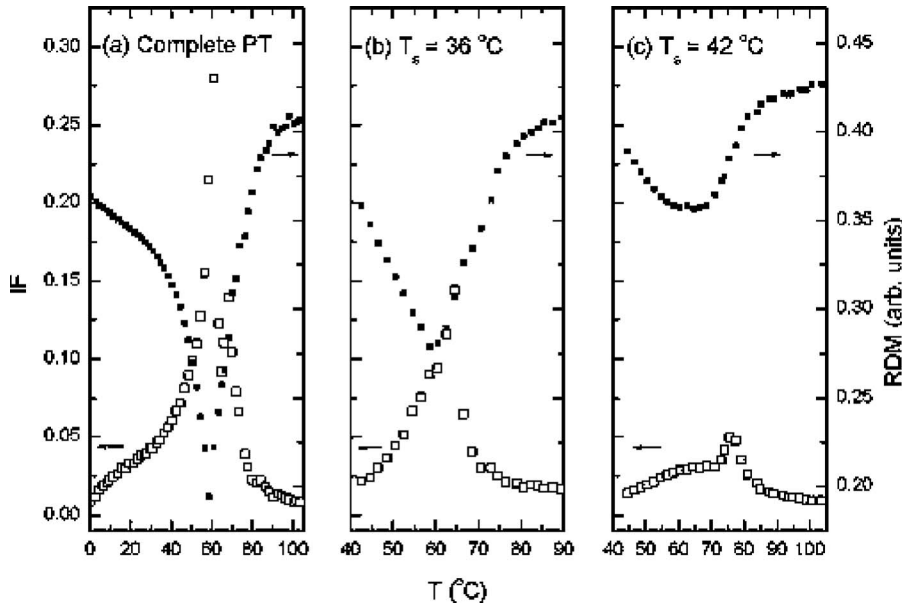


FIG. 4. The effect of MT temperatures on the IF peaks upon heating at the frequency of 0.015 Hz and the heating rate of 1 °C/min.

If σ enhances nucleation, then N_c will increase whereas τ will decrease so that there must be a unique exponent l that makes the following expression true:

$$N_{0c}\tau_0^l = N_c\tau^l = A, \quad (4.3)$$

where A is a constant. Let the critical volume of a nucleus be β , and the nonelastic strain in a nucleus induced by σ be a , then the work done by σ per unit volume is approximately equal to $a\sigma$.⁹ It is well known that the nucleation time in a MT meets Arrhenius relation with temperature, that is, $\tau_0 = B \exp(\Delta G/kT)$, where k is the Boltzmann constant and ΔG is the formation work of a nucleus. Supposing that σ only takes effect on the nucleation time, then from Eq. (4.2), the following equations hold:

$$\tau = \tau_0 \exp\left(\frac{-\eta\beta a\sigma}{kT}\right), \quad N_c = N_{0c} \exp\left[\frac{(1-\eta)\beta a\sigma}{kT}\right], \quad (4.4)$$

where η is a constant. By substituting (4.4) into (4.2), one gets

$$\delta\dot{N} = \frac{N_c}{\tau} - \frac{N_{0c}}{\tau_0} \approx \frac{\beta a\sigma}{kT} \dot{N}_0. \quad (4.5)$$

Equation (4.5) describes the effect of applied stress σ upon the nucleation rate although the N_{0c} is unknown.

The relation between l and η can be determined by Eq. (4.4) and when $l=(1-\eta)/\eta$, Eq. (4.4) becomes Eq. (4.3), which further demonstrates that the coefficient A in (4.3) is a constant independent of temperature.

It is seen from (4.4) that both l and η are important parameters describing the features of the first order transformation and also reflect the effect of σ upon τ and N_c , depending on both the characteristics of material and σ . When $\sigma \rightarrow 0$, $\tau \rightarrow \tau_0$ and $N_c \rightarrow N_{0c}$; thus $l \rightarrow l_0$ and $\eta \rightarrow \eta_0$, that is, they become the intrinsic parameters of material.

As is known, the kinetic equation of a first order transformation can be described as

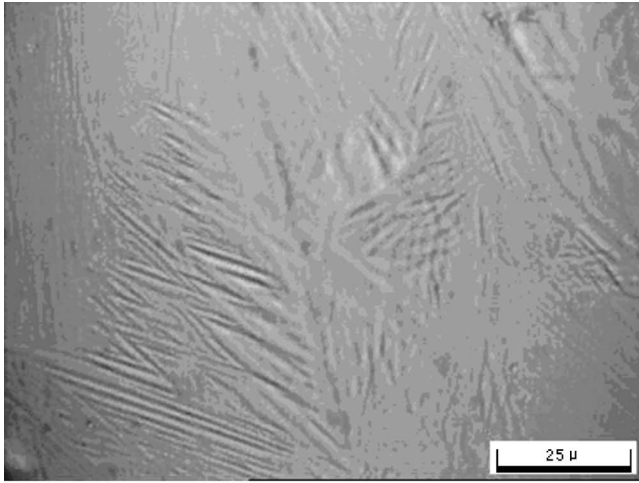
$$\frac{df}{dt} = \alpha \dot{N}, \quad (4.6)$$

where f is the transformed volume fraction and α the average volume of martensite plates formed during $t=0$ and a given time t . From (4.5) and (4.6), the changes in the volume fraction of the new phase, δf , induced by σ are given by

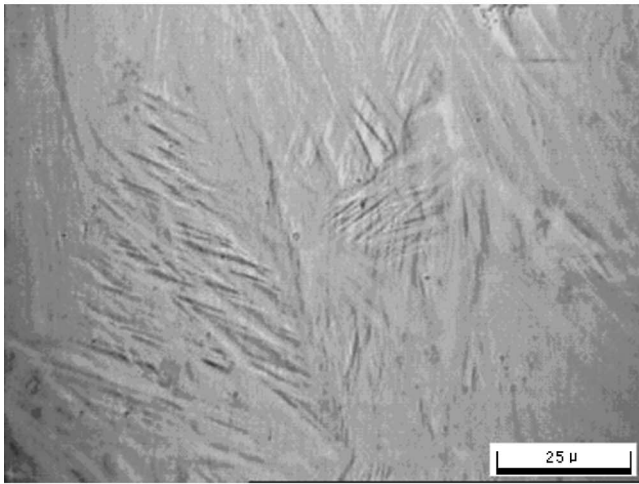
$$\delta f = f - f_0 = \alpha \delta N = \alpha \int \frac{\beta a\sigma}{kT} \dot{N}_0 dt. \quad (4.7)$$

In a nonisothermal transformation, if the above integration is conducted in the time range $0 \sim t$, corresponding to the temperature range from the beginning of the transformation to a given temperature T , the result represents the total volume change induced by σ within $0 \sim t$. It follows that the total volume change depends not only on time but also on continuous change of temperature. Nevertheless, the nonelastic strain at T induced by σ should be only related to the volume change, which actually includes not only the change due to the nucleation within the time interval but also the continuing growth of the grains formed before T . Accordingly, the nonelastic strain at T should be related to the volume change arisen at a very short time interval, i.e., from $t - \tau_0$ to t .

In principle, both τ_0 and \dot{N}_0 are time related variables distributed over the time interval from $t - \tau_0$ to t . In fact, the time increment τ_0 in the phase transformation can be treated as a most probable time independent of time change or the mean relaxation time. However, \dot{N}_0 must be dependent on time because it is impossible for the stable critical nuclei to instantaneously form at T without sufficient structure organization or in other words, a pregnant time τ_0 is needed before the nuclei become thermodynamically stable. Although the formation of these quasistable nuclei makes the chemical driving force decrease, it makes the elastic strain energy and thus the forming work of the nuclei decrease, too. From this analysis, a function describing the nucleation rate is introduced as follows:



(a)



(b)

FIG. 5. The typical martensite structures at the incomplete transformation temperatures of (a) 42 °C and (b) 36 °C.

$$\frac{d}{dt'} N_0(T, t' - t + \tau_0) = \frac{N_{0c}(T, t' - t + \tau_0)}{\tau_0}, \quad (4.8)$$

where t' is a time variable needed for the nucleation at $t - \tau_0 \leq t' \leq t$. It is known from the above analysis that when $t' \leq t - \tau_0$, $N_{0c}(T, t' - t + \tau_0) = 0$, and only when $t' = t$, the nuclei are stable and $\dot{N}_0(T, t) = \dot{N}_0(T, \tau_0) = N_{0c}(T, \tau_0) / \tau_0$, which represents the real nucleation rate at T . In comparison with the two expressions for nucleation rate, it is clear that $\dot{N}_0(T, t)$ is the variation of total nucleus density with time at T in $0 \sim t$, while $(d/dt') N_0(T, t' - t + \tau_0)$ denotes the change of critical nucleus density with time at T in $t - \tau_0 \leq t' \leq t$.

Replacing the \dot{N}_0 of Eq. (4.7) by (4.8), we obtain

$$\delta f = \frac{\alpha}{\tau_0} \int_{t-\tau_0}^t \frac{\beta \alpha \sigma}{kT} N_{0c}(T, t' - t + \tau_0) dt'. \quad (4.9)$$

In Eq. (4.9), a can be considered to be the mean nonelastic strain of the critical nuclei induced during $t - \tau_0 \sim t'$ by σ , and $\beta \alpha \sigma / kT$ and $(\beta \alpha \sigma / kT) N_{0c}$ to be the contributions of the work done by σ on a single nucleus and N_{0c} nuclei to δN ,

respectively, where the mean value of δN is taken in $t - \tau_0 \leq t' \leq t$.

If the applied alternative load in the IF measurements takes the form $\sigma = \sigma_0 \exp(i\omega t)$, where σ_0 is the stress amplitude and ω is the circular frequency of vibration, then the nonelastic strain a can be expressed as

$$a(\omega t) = a_1(\omega t) - i a_2(\omega t). \quad (4.10)$$

Here a complex form is used to characterize the nonelastic strain related to frequency because it is not only caused by thermally driven phase transformation but also by applied force. Therefore, there should be a constant term independent of ω in the real part $a_1(\omega t)$, representing the inherent nonelastic strain caused by the phase transformation itself. Inserting $\sigma = \sigma_0 \exp(i\omega t)$ and (4.10) into (4.9), integrating the two integrands by parts, and noting that if no abrupt change occurs when the formation of the quasistable nuclei begins at $t - \tau_0$ there exist left boundary conditions at $t - \tau_0 \leq t' \leq t$, i.e.,

$$N_{0c}^{(n)}(T, t' - t + \tau_0) \Big|_{t'=t-\tau_0} = N_{0c}^{(n)}(T, 0) = 0, \quad n = 0, 1, 2, \dots \quad (4.11)$$

We get the increment of new phase volume fraction induced by the stress

$$\begin{aligned} \delta f = & \frac{\alpha \beta \sigma_0 \exp(i\omega t)}{kT \tau_0 \omega} \left(\sum_{n=0}^{\infty} \left\{ \frac{(-1)^n}{\omega^{2n+1}} [N_{0c}(T, \tau_0) a_1(\omega \tau_0)]^{(2n+1)} \right. \right. \\ & \left. \left. - \frac{(-1)^n}{\omega^{2n}} [N_{0c}(T, \tau_0) a_2(\omega \tau_0)]^{(2n)} \right\} \right. \\ & \left. - i \sum_{n=0}^{\infty} \left\{ \frac{(-1)^n}{\omega^{2n}} [N_{0c}(T, \tau_0) a_1(\omega \tau_0)]^{(2n)} \right. \right. \\ & \left. \left. + \frac{(-1)^n}{\omega^{2n+1}} [N_{0c}(T, \tau_0) a_2(\omega \tau_0)]^{(2n+1)} \right\} \right), \quad (4.12) \end{aligned}$$

where all superscripts in parentheses represent the derivative values at $t' = t$.

The physical significance of Eq. (4.12) is giving a general relationship among the phase volume fraction, the intrinsic physical parameters of a material, and applied stress during a first order phase transformation. If the change of N_{0c} and a with time is known, δf and correlated IF can be easily obtained. The detailed deduction of the above equations can be seen in Ref. 8.

In the ideal condition, $N_{0c}(T, t' - t + \tau_0)$ is a constant independent of time. However, $N_{0c}(T, t' - t + \tau_0)$ is time dependent at the very beginning of a practical nucleation process, i.e., it rapidly increases up to a constant at a very short time $t' = t - \tau_0$ and thereafter keeps unchanged in $t - \tau_0 \leq t' \leq t$. It is noted that the quasistable critical nuclei formed in $t - \tau_0 \leq t' \leq t$ have different forming energies due to the differences in the crystalline orientation and the microstructure at the interfaces among the nuclei. By contrast, the change of nonelastic strain a with time is much slower than that of $N_{0c}(T, t' - t + \tau_0)$ because the occurrence of it is more dependent on time. Figures 8(a) and 8(b) schematically display the changes of N_{0c} and $a_1[\omega(t' - t + \tau_0)]$ with $t' - t + \tau_0$, respectively, in which curves (1), (2), and (3) represent the time

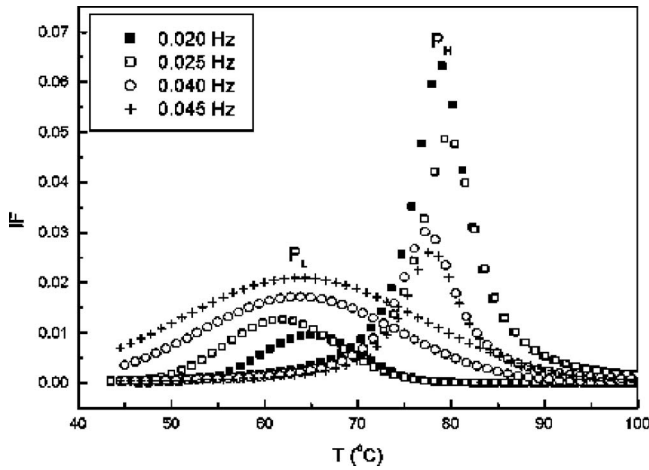


FIG. 6. The net P_L and P_H peaks as functions of temperature upon heating after the backgrounds were subtracted for the partial reverse MT temperature $T_s=42$ °C.

independent (ideal), less time independent, and time dependent conditions, respectively, and curve (2) in Fig. 8(a) and curve (3) in Fig. 8(b) are the cases mentioned above.

If a phase transformation does not cause soft mode effect like the present P_H peak, the real part in Eq. (4.12) is equal to zero, and thus through a simple calculation we get

$$[N_{0c}(T, \tau_0) a_1(\omega \tau_0)]^{(n)} = \omega [N_{0c}(T, \tau_0) a_2(\omega \tau_0)]^{(n-1)}, \quad n = 1, 2, 3, \dots \quad (4.13)$$

Accordingly, only the zero derivative term $N_{0c}(T, \tau_0) a_1(\omega \tau_0)$ is retained in the imaginary part of (4.12), i.e.,

$$\delta f = -i \frac{\alpha \beta \sigma N_{0c}(T, \tau_0) a_1(\omega \tau_0)}{kT \omega \tau_0}. \quad (4.14)$$

Although Eq. (4.14) has a similar form to Belko and Delorme models,^{10,11} the parameters have completely different meanings, e.g., the $N_{0c}(T, \tau_0)$ is a function of τ_0 dependent upon temperature, and $a_1(\omega \tau_0)$ is a function of $\omega \tau_0$ rather than a constant.

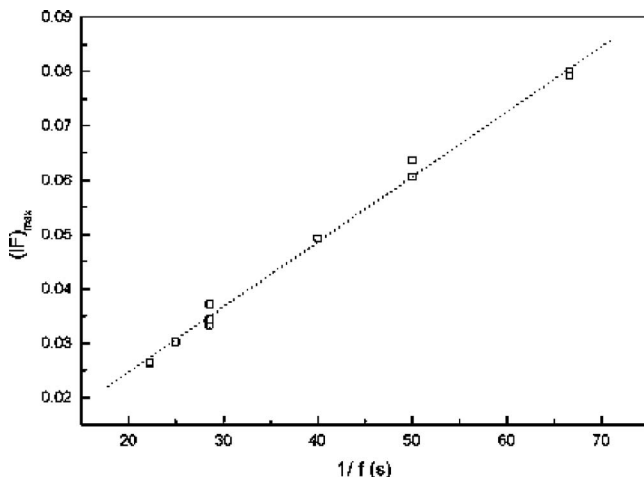


FIG. 7. The height of P_H peak as a function of measuring frequency, in which the open square and the dot line are the measured and fitted results, respectively.

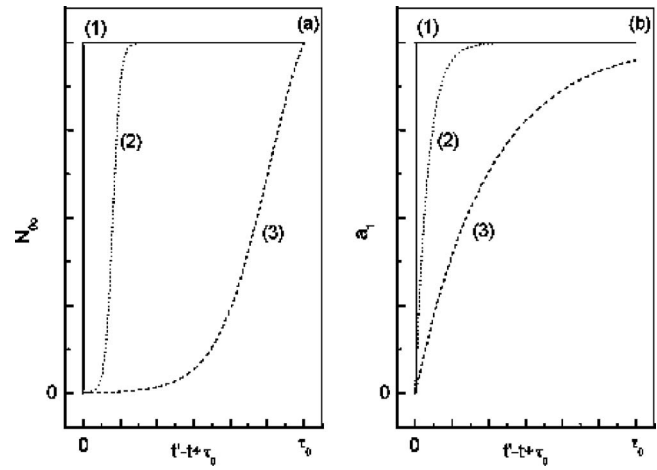


FIG. 8. Schematic representation of the critical nucleus density N_{0c} (a) and the real part a_1 of mean nonelastic strain (b) as functions of $t'-t+\tau_0$, where (1), (2), and (3) represent the time independent (ideal), roughly time independent, and time dependent conditions, respectively.

According to the aforementioned analysis and curve (2) in Fig. 8(a), the following right boundary conditions exist:

$$N_{0c}^{(n)}(T, t' - t + \tau_0)|_{t'=t} = N_{0c}^{(n)}(T, \tau_0) = 0, \quad n = 1, 2, 3, \dots \quad (4.15)$$

Based on these conditions Eq. (4.13) becomes

$$a_1^{(n)}(\omega \tau_0) = \omega a_2^{(n-1)}(\omega \tau_0), \quad n = 1, 2, 3, \dots \quad (4.16)$$

Obviously, when $a_2(\omega \tau_0) = 0$, $a_1^{(1)}(\omega \tau_0) = 0$, thus $a_1(\omega \tau_0) = \text{const}$.

Since both a_1 and a_2 are functions of $\omega \tau_0$, it is difficult to obtain the precisely analytical form of the functions. To solve this problem, the Voigt solid model was employed to approximately describe the behavior of phase interfaces. As is known, the nonelastic strain in a single nucleus under a constant stress can be written as $\varepsilon(t' - t + \tau_0) = a_{\text{max}} [1 - \exp\{-(t' - t + \tau_0)/\tau'\}]$, where $t' - t + \tau_0$ is the time used for the formation of quasistable nuclei during $0 \sim \tau_0$ and τ' is a time factor used to meet the need of dimensionless exponential. When $t' = t$, $\varepsilon(\tau_0) = a_{\text{max}} [1 - \exp(\tau_0/\tau')]$ where τ_0 is the relaxation time of nucleation, being the characteristics of a material.

In terms of the fundamentals of IF, τ' roughly equals $1/\omega$. Inserting $\tau' = 1/\omega$ into $\varepsilon(\tau_0) = a_{\text{max}} [1 - \exp(\tau_0/\tau')]$ we get an approximate expression of the real part $a_1(\omega \tau_0)$ of the nonelastic strain

$$a_1(\omega \tau_0) \approx a_{\text{max}} [1 - \exp(-\omega \tau_0)], \quad (4.17)$$

which is just case shown by curve (3) in Fig. 8(b). The imaginary part of the nonelastic strain can be directly obtained from (4.16), i.e.,

$$a_2(\omega \tau_0) \approx a_{\text{max}} \exp(-\omega \tau_0). \quad (4.18)$$

Comparing $\varepsilon(\tau_0)$ with $a_1(\omega \tau_0)$ and noting the meanings of the constants in Voigt model, we get $a_{\text{max}} = \sigma_0/G_i$, and $\eta_i = G_i/\omega$, where σ_0 is the stress amplitude, and G_i and η_i are the shear modulus and viscosity coefficient of phase interfaces, respectively. From (4.17), when $\omega \rightarrow \infty$, $a_1(\omega \tau_0) \rightarrow a_{\text{max}}$, so that a_{max} is intrinsic characteristics of material,

i.e., it is the maximum nonelastic strain in a single nucleus induced by phase transformation itself. For a given material, a_{\max} is a constant and thus the following relations hold:

$$G_i \propto \sigma_0, \quad \eta_i \propto \sigma_0/\omega. \quad (4.19)$$

It is interesting that the dynamic properties G_i and η_i of phase interfaces (rather than material itself) are closely related to applied stress σ_0 or ω . When ω is constant, both G_i and η_i are proportional to σ_0 . Based on the parallel relation of spring with dashpot in the Voigt model, it is certain that σ_0 has no influence over the viscoelasticity of phase interfaces. When σ_0 is fixed, the following conclusions can be drawn.

- (1) When $\omega \rightarrow 0$, $\eta_i \rightarrow \infty$. From (4.17) and (4.18), $a_1(\omega\tau_0) \rightarrow 0$ and $a_2(\omega\tau_0) \rightarrow a_{\max}$, showing that the phase interface is viscous.
- (2) When $\omega \rightarrow \infty$, $\eta_i \rightarrow 0$, and thus $a_1(\omega\tau_0) \rightarrow a_{\max}$, $a_2(\omega\tau_0) \rightarrow 0$, showing that the phase interface is elastic.

Substituting (4.17) into (4.14), we get the nonelastic strain of material

$$\varepsilon'' = a_{\max} \delta f = -i \frac{\alpha \beta a_{\max}^2 N_{0c} T, \tau_0 \sigma [1 - \exp(-\omega\tau_0)]}{kT \omega \tau_0}, \quad (4.20)$$

and substituting the elastic strain $\varepsilon' = J_U \sigma$ and (4.20) into the total strain $\varepsilon = \varepsilon' + \varepsilon''$, we can obtain the storage and loss compliances as well as IF,

$$J_1 = J_U, \quad J_2 = \frac{\delta J [1 - \exp(-\omega\tau_0)]}{\omega \tau_0}, \quad (4.21)$$

$$\tan \varphi = \frac{J_2}{J_1} = \frac{\Delta [1 - \exp(-\omega\tau_0)]}{\omega \tau_0}, \quad (4.22)$$

where J_U is the unrelaxed compliance. The relaxed compliance and relaxation strength are

$$\delta J = \frac{\alpha \beta a_{\max}^2 N_{0c}(T, \tau_0)}{kT} \quad \text{and} \quad \Delta = \frac{\delta J}{J_U}, \quad (4.23)$$

respectively. The other useful parameters included in (4.21) and (4.22) can be derived from (4.1)–(4.3) and (4.23), i.e.,

$$\tau_0 = A^{1/(1+l)} \left[\dot{T} \frac{dN_0(T)}{dT} \right]^{-1/(1+l)}, \quad (4.24)$$

$$\bar{N}_{0c}(T, \tau_0) = \frac{A}{\tau_0^l} = A^{1/(1+l)} \left[\dot{T} \frac{dN_0(T)}{dT} \right]^{l/(1+l)}, \quad (4.25)$$

$$\delta J = \frac{A \alpha \beta a_{\max}^2}{kT} \frac{1}{\tau_0^l} = A^{1/(1+l)} \frac{\alpha \beta a_{\max}^2}{kT} \left[\dot{T} \frac{dN_0(T)}{dT} \right]^{l/(1+l)}, \quad (4.26)$$

where $N_0(T, \dot{T}) = N_0(T)$ is independent of time. Replacing the τ_0 and δJ in (4.21) with (4.24) and (4.26), respectively, we finally obtain the following expression describing the first order phase transformation without soft mode effect:

$$J_2 = \frac{\alpha \beta a_{\max}^2}{kT} \frac{dN_0(T)}{dT} \frac{\dot{T}}{\omega} \times \left(1 - \exp \left\{ -A^{1/(1+l)} \omega \left[\dot{T} \frac{dN_0(T)}{dT} \right]^{-1/(1+l)} \right\} \right). \quad (4.27)$$

Since the relaxation time only has a very narrow distribution during the phase transformation in the condition of no soft mode effect, it is reasonable to make $l \approx 1$ in the equation.

As mentioned above, although the normal motion of phase interfaces does not cause soft mode effect during phase transformation, a physical nonlinear effect can be expected in the IF, as shown by the exponent terms in (4.27). This nonlinear effect is dependent on the change of nonelastic strain $a(\omega\tau_0)$ with time induced by σ , as shown by curve (3) in Fig. 8(b), and thus what Eq. (4.27) describes is a relaxation peak caused by both the normal motion of phase interfaces irrelevant to soft mode effect and the relaxation process of nonelastic strain. Figure 9 shows the normalized theoretical curve of J_2 as a function of $\omega\tau_0$ and that obtained by Belko and Delorme models. It is seen from the figure that the two curves are separated from each other only when $\omega\tau_0 < 4$

From Eq. (4.27), the following conclusions can also be drawn.

- (1) When $\omega\tau_0$ is relatively great, i.e., ω is high while \dot{T} is low, e.g., $\omega\tau_0 \geq 4$, we have

$$J_2 \approx \frac{\delta J}{\omega \tau_0} = \frac{\alpha \beta a_{\max}^2}{kT} \frac{dN_0(T)}{dT} \frac{\dot{T}}{\omega}, \quad (4.28)$$

which is in agreement with Belko and Delorme models in the case as shown in Refs. 10 and 11.

- (2) The smaller the $\omega\tau_0$ is, i.e., ω is lower while \dot{T} is higher, e.g., $\omega\tau_0 \leq 4$, the more evident the nonlinear effect of J_2 is.
- (3) When $0 \leq \omega < \infty$, $dJ_2/d\omega = \delta J [(1 + \omega\tau_0) \exp(-\omega\tau_0) - 1] / \omega^2 \tau_0 < 0$, and thus J_2 is a monotonous decaying

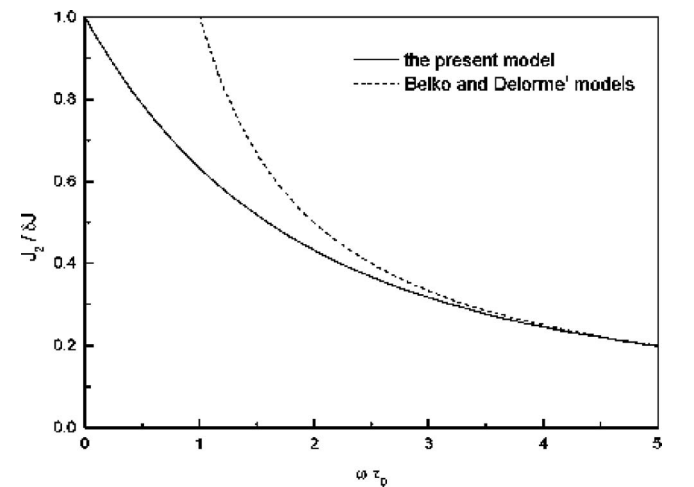


FIG. 9. The normalized theoretical curve of J_2 by the present model (solid line) and that by Belko and Delorme' models (dash line) as functions of $\omega\tau_0$.

function of ω . Specially, when $\omega \rightarrow 0$, $J_2 \rightarrow \delta J$ (the maximum value of J_2) and only when $\dot{T} \rightarrow \infty$, $J_2 \rightarrow \infty$, as shown by Eqs. (4.24) and (4.26).

- (4) When $0 \leq \tau_0 < \infty$, $dJ_2/d\tau_0 = \delta J[(1+l+\omega\tau_0)\exp(-\omega\tau_0) - (1+l)]/\omega\tau_0^2 < 0$, showing that J_2 is also a monotonous decaying function of τ_0 and when $\tau_0 \rightarrow 0$ (i.e., $\dot{T} \rightarrow \infty$), $J_2 \rightarrow \infty$.
- (5) It is clear from Eq. (4.24) and the above conclusion (4) that the larger the nucleation rate $dN_0(T)/dT$, the smaller the τ_0 and the larger the J_2 . As a result, the J_2 peak just corresponds to the maximum of $dN_0(T)/dT$, i.e., to the inflection point of $N_0(T)$ or the fastest volume transition rate. If there is no viscous movement between the old and new phases, the volume transition rate should be proportional to the modulus of the mixture of the two phases. It follows that the J_2 peak corresponds to the inflection point of the modulus curve, being consistent with the experimental results, as shown in Fig. 3(a).
- (6) From Eq. (4.27) and the above conclusion (4), the temperature T_{pH} of J_2 peak is independent of ω , being in agreement with the experimental results, as seen in Fig. 3(a).

V. DISCUSSION

According to the general law of thermoelastic MT, the nucleation and growth of the new phase are accompanied with interaction of elastic stress fields. If the growth direction is perpendicular to the interface, i.e., the normal growth, it is thermodynamically irreversible and only causes the volume change of each phase without soft mode effect. It follows that the IF resulted from the motion should be proportional to the volume change in a vibration cycle and has a linear relation with heating/cooling rate or reciprocal of frequency, as described by Belko and Delorme models. The results shown in Figs. 3(a) and 7 demonstrate that the P_H peak is consistent with these features.

Different from Belko and Delorme models, the present model takes account of the dependences of the nucleation and nonelastic strain on time. It is known that MT meets the Arrhenius relation because the nucleation in the MT is thermally activated, and thus Eq. (4.12) is suitable for describing a first order transformation because the nucleus density and relaxation time follow Arrhenius relation. For the normal movement of interfaces during the MT, the nucleus density is mainly dependent on temperature and independent of time due to the interface irreversibility. Compared with the rapid change of nucleus density with time, however, the nonelastic strain produced around the martensite plates is necessarily time dependent because the release of nonelastic stress is time relevant. Equation (4.27) was proposed just on this analysis and is only a special case irrelevant to soft mode effect. The physical nonlinear effect of IF involved in the equation is different from the traditional nonlinear effect that resulted from the soft mode effect rather than the time dependence of nonelastic strain. The predictions from Eq. (4.27) can be well proved by the results in Fig. 3(a), i.e., the

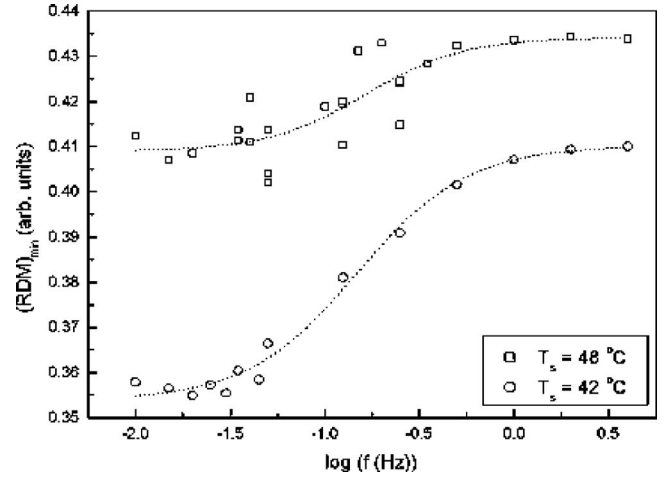


FIG. 10. Comparison of the minima of RDM as functions of measuring frequency between the partial MT temperature $T_s=48$ °C and $T_s=42$ °C.

P_H peak corresponds to the inflection of RDM curves and the peak temperature is independent of the measuring frequency.

As mentioned above, when $\omega \rightarrow 0$, $J_2 \rightarrow \delta J$, i.e., J_2 tends to a finite value, different from the traditional IF theories of first order transformation. For instance, Belko and Delorme models show that the transitory IF is proportional to the transformed volume fraction in a vibration cycle. This necessarily leads to a conclusion that J_2 tends to an infinity when $\omega \rightarrow 0$, implying that the sample will go through an infinitely broad temperature range in a cycle, which is obviously unmeaningful.

For the M -type dynamic response functions, the storage and loss modulus M_1 and M_2 can be obtained by substituting the common expressions of $M_1=1/J_1(1+\tan^2 \varphi)$, $M_2=1/J_2(1+\cot^2 \varphi)$ into Eqs. (4.21) and (4.22), i.e.,

$$M_1 = \frac{J_U(\omega\tau_0)^2}{J_U^2(\omega\tau_0)^2 + \delta J^2[1 - \exp(-\omega\tau_0)]^2}, \quad (5.1)$$

$$M_2 = \frac{\delta J(\omega\tau_0)[1 - \exp(-\omega\tau_0)]}{J_U^2(\omega\tau_0)^2 + \delta J^2[1 - \exp(-\omega\tau_0)]^2}. \quad (5.2)$$

From Eqs. (4.21), (5.1), and (5.2), the following two group data of dynamic response functions can be obtained at the extreme conditions of ω :

$$J_1(0) = J_1(\infty) = J_U, \quad J_2(0) = \delta J, \quad J_2(\infty) = 0, \quad (5.3)$$

$$M_1(0) = J_U/(J_U^2 + \delta J^2) \approx 1/J_U = M_U (\because J_U \gg \delta J),$$

$$M_1(\infty) = 1/J_U = M_U, \quad (5.4)$$

$$M_2(0) = \delta J/(J_U^2 + \delta J^2) \approx \delta J/J_U^2 = \delta M (\because J_U \gg \delta J),$$

$$M_2(\infty) = 0.$$

These data clearly show that the J -type and M -type response functions have precise correspondence at both $\omega \rightarrow 0$ and $\omega \rightarrow \infty$, and moreover, there does not exist soft mode effect according to $J_1(0)=J_1(\infty)=J_U$, or $M_1(0) \approx M_1(\infty) = M_U$. This is in good agreement with the present experimental results, as shown in Fig. 10.

However, if the nonlinear parts in the square bracket of (4.21) and (4.22) are neglected, like the situation in Belko and Delorme models, the following relations are yielded that are completely different from the results yielded by (5.3) and (5.4), i.e.,

$$J_1(0) = J_1(\infty) = J_U, \quad J_2(0) = \infty, \quad J_2(\infty) = 0, \quad (5.5)$$

$$M_1(0) = 0, \quad M_1(\infty) = 1/J_U = M_U, \quad M_2(0) = M_2(\infty) = 0. \quad (5.6)$$

Equations (5.5) and (5.6) indicate that Belko and Delorme models would be incapable of describing the first order transformation irrelevant to soft mode effect particularly at low frequencies because the contradictory conclusions may be drawn from the response functions. Firstly, the values $J_1(0)=J_1(\infty)=J_U$ in (5.5) show that the soft mode will not appear, whereas the values $M_1(0)=0$ and $M_1(\infty)=M_U$ in (5.6) just show the opposite. Secondly, the value $M_1(0)=0$ suggests that the material will flow like a liquid when $\omega \rightarrow 0$, which is, however, impossible for a solid, as demonstrated by Fig. 10, in which each RDM curve reaches a stable nonzero value as $\omega \rightarrow 0$. Finally, when $\omega \rightarrow 0$, $J_2(0)=\infty$ and $M_2(0)=0$, suggesting that the IF and modulus tend to change towards the same direction. This is contrary to the real case.

VI. CONCLUSIONS

The high-temperature IF peak P_H , found in the MT of a CuAlNiMnTi polycrystalline shape memory alloy, was experimentally and theoretically studied in the present study. An IF model related to the P_H peak was derived based on the nucleation and growth of the new phase during the MT. Different from Belko and Delorme models, the present model takes account of the dependences of the nucleation and mean nonelastic strain upon time so that the model would be suitable for any first order transformation and the IF irrelevant to soft mode effect is only a special case. Furthermore, the following conclusions can be summarized.

- (1) The P_H peak always corresponds to the inflection point of RDM curves in temperature spectra, or in other words, the peak is only related to the phase transformation rate.
- (2) The height of P_H peak decreases with increasing frequency in frequency spectra. When the frequency is relatively high, generally $\omega\tau_0 \geq 4$, the peak roughly meets the linear relation shown by Belko and Delorme models.
- (3) There exist nonlinear relations between IF and ω and between IF and \dot{T} particularly at low frequencies. This nonlinear effect is physically different from that in traditional IF theories, in which the IF has also nonlinear relations with frequency and heating/cooling rate.
- (4) The P_H peak is such a phase transformation peak that originates from the normal motion of phase interfaces without soft mode effect as well as the relaxation process of nonelastic strain.

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- ¹Z. L. Song, J. S. Zhu, Y. S. Qian, A. S. Aruna, Y. N. Wang, and C. Xie, *Solid State Commun.* **118**, 257 (2001).
- ²S. K. Wu and H. C. Lin, *J. Alloys Compd.* **355**, 72 (2003).
- ³B. Coluzzi, A. Biscarini, R. Campanella, G. Mazzolai, L. Trotta, and F. M. Mazzolai, *J. Alloys Compd.* **310**, 300 (2000).
- ⁴R. B. Pérez-Sáez, V. Recarte, M. L. Nó, and J. San Juan, *J. Alloys Compd.* **310**, 334 (2000).
- ⁵J. X. Zhang, Z. H. Yang, and P. C. W. Fung, *Phys. Rev. B* **52**, 278 (1995).
- ⁶O. Mercier, K. N. Melton, and Y. De Préville, *Acta Metall.* **27**, 1467 (1979).
- ⁷C. L. Gong, F. S. Han, Z. Li, and M. P. Wang, *Phys. Rev. B* **70**, 094103 (2004).
- ⁸C. L. Gong, F. S. Han, Z. Li, and M. P. Wang, *Philos. Mag.* **87**, 2281 (2007).
- ⁹A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).
- ¹⁰V. N. Belko, B. M. Darinsky, V. S. Postnikov, and I. M. Sharshakov, *Phys. Met. Metallogr.* **27**, 140 (1969).
- ¹¹J. F. Delorme and P. F. Gobin, *Met.: Corros.-Ind.* **573**, 185 (1973).
- ¹²T. Xiao, *Metall. Trans. A* **24A**, 1067 (1993).
- ¹³W. Dejonghe, R. De Batist, and L. Delaey, *Scr. Metall.* **10**, 1125 (1976).
- ¹⁴G. Gremaud, J. E. Bidaux, and W. Benoit, *Helv. Phys. Acta* **60**, 947 (1987).
- ¹⁵J. X. Zhang, P. C. W. Fung, and W. G. Zeng, *Phys. Rev. B* **52**, 268 (1995).
- ¹⁶F. S. Han, Z. G. Zhu, and J. C. Gao, *Metall. Mater. Trans. A* **30A**, 771 (1999).
- ¹⁷W. H. Zou, H. Y. Peng, R. Wang, J. Gui, and D. Z. Yang, *Acta Metall. Mater.* **43**, 3009 (1995).
- ¹⁸I. Hurtado, D. Segers, J. Van Humbeeck, L. Dorikens-Vanpraet, and C. Dauwe, *Scr. Metall. Mater.* **33**, 741 (1995).