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Damping Properties of Shape Memory Alloys During Phase Transformation

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Abstract. A high damping capacity is considered as one of the important functional properties of shape memory alloys. Those properties are related to a thermoelastic martensitic transformation. As a consequence of this transformation, the internal friction or damping can be investigated for three different states: 1. during thermal transformation cycling, 2. during martensite induced strain cycling at constant temperature, 3. in the martensitic state.

The difficulty of formulating a unified theory to those three approaches is related to the complexity of the microstructure. Phase boundaries, dislocations, precipitates, impurities and point-defects interact strongly with each other, thereby influencing the macroscopic observation.

However, improved models have been recently formulated to describe the observed internal friction during transformation, taking into account the change in defect mobility. This has also lead to a new approach of analyzing the observed damping in an amplitude dependent and amplitude independent part.

Special attention is also given to superelastic damping with the aim of improving earthquake resistance of constructions, concentrating reversible hysteretic behaviour in detailed regions of the structure. Moreover, new relations between other functional properties and the internal friction of the martensite have been established.

This paper will describe the recent findings, the importance of the results, fundamentally and practically, concurrently pointing to some interesting topics for further research.

INTRODUCTION

The functional properties of shape memory alloys are related to a (largely) reversible (non-) thermoelastic martensitic transformation, generally in a temperature region between -100°C and $+200^{\circ}\text{C}$. A high damping capacity is considered as an important functional property of the present shape memory alloys. As a consequence a lot of research has been undertaken to quantify and optimize those damping properties as function of composition and especially the thermomechanical processing. Indeed, since the high internal friction, especially during transformation and in the martensite state, is strongly related with the mobility of martensite/martensite and parent/martensite interfaces and structural defects inherent to the martensitic phase, the distribution and concentration of several types of defects (vacancies, dislocations, grain boundaries, precipitates), controlled by the thermomechanical processing, play an important controlling role in the global internal friction spectrum. Since this internal friction spectrum is thus strongly linked to the microstructure and the presence of defects, it is not always evident to come to a unique conclusion for the explanation of the observed behaviour.

At the other side, the study of the internal friction has lead to a better understanding of the relation between the microstructure including the defects and the other functional properties of shape memory alloys such as the one- and two way memory effect and the pseudoelasticity.

A part that is hardly touched in research is using internal friction to reveal the internal structure and structural defects especially of the martensitic phase. A lot of activity related to internal friction of shape memory alloys was going on until the mid eighties, then became steadily decreasing but gained during recent years again a significant interest as well from a fundamental approach as well for application reasons.

This paper will review the latest contributions and models and discuss some interesting features of using the capacity of high energy absorption during vibrations. Earlier more detailed reviews can be found in ref.[1,2,3,4].

1. INTERNAL FRICTION DURING MARTENSITIC TRANSFORMATION

During the martensitic transformation, an internal friction peak is observed concurrently with a strong modulus minimum.

As pointed out by Bidaux et al. [5], in materials in which the two phases connected by the phase transformation can coexist over a certain temperature range, one should consider three separate contributions to the total internal friction, illustrated in Fig.1.

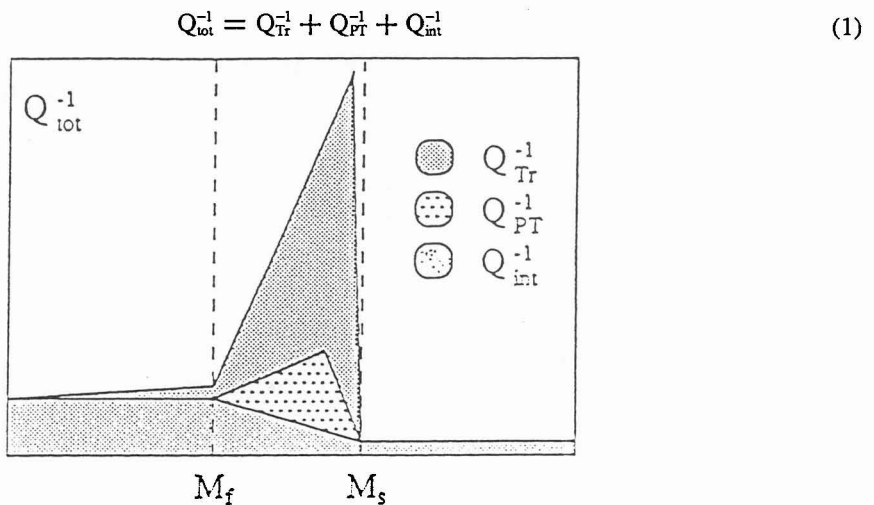


Figure 1: Schematic representation of Q^{-1} and its contributions during martensitic phase transformations.

Q_{Tr}^{-1} is the transient part of Q_{tot}^{-1} , and it exists only during cooling or heating ($\dot{T} \neq 0$). It depends on external parameters like temperature rate (\dot{T}), resonance frequency (f) and oscillation amplitude σ_0 . Q_{Tr}^{-1} depends on the transformation kinetics and is therefore proportional to the volume fraction which is transformed per unit of time. Q_{PT}^{-1} is related to mechanisms of the phase transformation (PT), which are independent of the transformation rate, such as the movement of parent/martensite and martensite/martensite interfaces. Q_{PT}^{-1} exhibits a small peak when the interface mobility is maximum. Q_{int}^{-1} is composed of the IF contributions of each phase and is strongly dependent on microstructural properties (interface density, vacancies), especially in the martensitic phase.

1.1 The Intrinsic IF Q_{int}^{-1}

This factor takes into account the intrinsic damping generated in the two coexisting phases. It can be written as:

$$Q_{int}^{-1} = VQ_{mart}^{-1} + (1 - V)Q_{beta}^{-1} \quad (2)$$

Q_{mart}^{-1} and Q_{beta}^{-1} are the intrinsic damping of the martensite and the β phase, respectively, and V is the volume fraction of the martensite phase.

1.2. The Non-transient IF peak, Q_{PT}^{-1}

For an explanation of the Q_{PT}^{-1} peak one can find different approaches in the literature [6]. The model of Dejonghe et al. [7] considers a maximum of the interface mobility in the transformation region. This maximum is expressed by a maximum amount of transformed volume fraction per stress unit ($\partial n / \partial \sigma(T)$).

When the temperature rate is zero or if the oscillation frequency is very high ($f > 50$ Hz), the transient IF goes to zero and only the amplitude dependent part remains.

Mercier and Melton [8] proposed a dislocation mechanism, which takes into account the effect of anisotropy (elastic softening) on the elastic energy of dislocations. They showed that the dislocation damping in a crystal is inversely proportional to the crystallographic anisotropy factor (A), but proportional to frequency.

Koshimizu [9] calculated the IF by using a Landau approximation of a first-order phase transition. In a thermodynamic treatment, the Gibbs free energy is developed as a function of stress (σ), temperature (T) and an internal variable (ξ), called the order parameter. Considering a relaxation type of damping, the calculations show discontinuities of Q_{PT}^{-1} and the relaxed modulus at the transition temperatures.

Existing concepts for Q_{PT}^{-1} can in fact be divided in two classes: theories in which Q_{PT}^{-1} is considered to be the result of the coexistence of macroscopic amounts of martensitic and austenitic phase [5,7] and the "pretransformational" models, where Q_{PT}^{-1} originates from the existence of submicroscopical nuclei of the martensitic phase [8,10]. Strongest contradictions between these models are related to the frequency and the amplitude dependence of Q_{PT}^{-1} .

Recently, S. Kustov et al. [11] studied Q_{PT}^{-1} in CuAlNi single crystals at ultrasonic frequencies, for the amplitude dependent (ADIF) and the amplitude independent (AIIF) part of the phase transition internal friction.

The experiments were carried out at frequencies of approximately 100 kHz by the PUCOT technique, rendering negligible, Q_{PT}^{-1} .

The internal friction spectra measurements were performed for each temperature step in the amplitude independent and amplitude dependent ranges, corresponding to respectively the strain amplitude $2 \cdot 10^{-7}$ and $8 \cdot 10^{-6} - 3 \cdot 10^{-5}$.

Several observations were made:

1. The AIIF peak lies between A_s and A_t on heating and between M_s and M_t on cooling.
2. In the range of strain amplitudes investigated no amplitude dependence is revealed in the austenite far enough from the transformation temperatures. IF is amplitude dependent both in martensite and in the transformation temperature range. ADIF exhibits peaks both on heating and on cooling.
3. The start of the increase of the resonance frequency during cooling corresponds to the M_s temperature.
4. The ADIF peak on cooling is shifted towards higher temperatures compared to the AIIF peak. The ADIF peak on cooling occurs close to M_s . The ADIF peak is accompanied by a maximum of the amplitude dependent part of the resonant frequency change, also at M_s .

5. ADIF appears about 15°C above M_s . Below M_s , when the resonant frequency begins to change rapidly, both ADIF and amplitude dependence of the resonant frequency decrease.

Based on a more detailed analysis of these observations, the hypothesis can be proposed that during direct transformation two different $AIIF_{pt}$ and $ADIF_{pt}$ mechanisms coexist which, unfortunately, are quite difficult to separate in the experimental data: the first one, purely premartensitic (IF1) and the second one, due to the coexistence of two phases (IF2). Those results appear consistent with the assumptions, that IF1 has comparatively low values for $AIIF_{pt}$ in CuAlNi single crystals, but rather pronounced amplitude dependence, and that IF2, on the contrary, has high $AIIF_{pt}$ values and much less pronounced $ADIF_{pt}$ at ultrasonic frequencies, as compared to IF1. A schematic representation of the behaviour of these two IF components is given in Fig. 2. Further experiments are needed to check the validity of the present model for polycrystalline material and for other types of alloys.

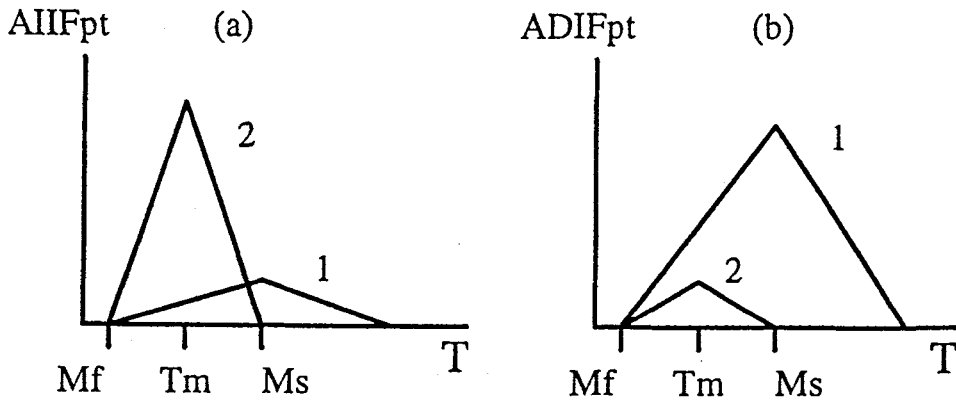


Figure 2: Schematic representation of the temperature dependence of the amplitude-independent (a) and amplitude-dependent (b) IF components due to premartensitic phenomena (1) and coexistence of two phases (2).

1.3. The Transient Part of IF, Q_{Tr}^{-1}

In the frequency range ($f \approx 1$ Hz) the transient part (Q_{Tr}^{-1}) is the most important contribution to the IF peak. The starting point for any IF modelling is the basic equation for Q^{-1} :

$$Q^{-1} = \frac{1}{\pi J \sigma_0^2} \int \sigma d\epsilon_{an}, \quad \sigma = \sigma_0 \sin \omega t \quad (3)$$

where J is the elastic compliance, σ_0 is the oscillation amplitude, ω is the angular frequency ($\omega = 2\pi f$) and $d\epsilon_{an}$ is the anelastic or irreversible part of the deformation during one oscillation cycle.

The first attempt to explain the transient character of the IF peak during martensitic transformation dates from 1956, when Scheil and Müller [12] related Q_{Tr}^{-1} to the transformation rate ($\partial n/\partial t$). The anelastic deformation ($d\epsilon_{an}$) in equation (3) arises from the lattice deformation that occurs when material is transformed during the IF measurement:

$$d\epsilon_{an} = k \cdot \frac{\partial n}{\partial t} dt \quad (4)$$

The basic idea which is expressed by a proportionality between $d\epsilon_{an}$ and $\partial n/\partial t$, has been maintained in all the following models. The crucial point for the further development of an expression for Q_{Tr}^{-1} has been defining the influence of temperature (T) and oscillation amplitude (σ_0) on the anelastic

deformation ($d\epsilon_{an}$) as well as on the transformation rate ($\partial n/\partial t$) [13]. A thermally activated type of anelastic behaviour is based on the model of Belko et al. [14]. $d\epsilon_{an}$ is due to the thermally activated formation and growth of nuclei of the new phase. The associated activation energy necessary to pass from the state of nucleation to the state of growth is modified by the oscillation stress. However, this model, which is based on a thermally activated type of anelasticity, does not seem to be appropriate for describing the IF peak found in alloys, where the transformation is strictly athermic.

The IF models that are presented in the following are based on an athermic or hysteretic type of anelastic deformation and can be applied for martensitic transformation in shape memory alloys. They are classified in Table I with respect to their suppositions for the oscillation amplitude dependence of $d\epsilon_{an}$ and $\partial n/\partial t$.

Model of Transformation "Plasticity" : $d\epsilon_{an}(\sigma, \partial n/\partial t)$

Delorme and Gobin [15] have proposed an expression for $d\epsilon_{an}$, which is based on the analysis of static "transformation plasticity" experiments. They found that the transformation deformation ($d\epsilon_p$) increases linearly with the transformed volume fraction and the applied stress,

$$d\epsilon_p = k\sigma dn \quad (5)$$

and assumed that $d\epsilon_{an}$ obeys the same law during dynamic measurements (Table I).

They derived the following expression:

$$Q_{Tr}^{-1} = \frac{k}{J} \frac{dn}{dT} \frac{\dot{T}}{\omega} \quad \frac{\Delta G}{G} = Q_{Tr}^{-1} \quad (6)$$

As an extension of Delorme's model of transformation plasticity, Dejonghe et al. [7] added a stress-dependent term of the transformation rate. Then $\partial n/\partial t$ becomes :

$$\frac{\partial n}{\partial t} = \frac{\partial n}{\partial T} \dot{T} + \frac{\partial n}{\partial \sigma} \dot{\sigma} \quad (7)$$

This equation accounts for the possibility that material transforms under the action of the applied oscillating stress. Furthermore, Dejonghe et al. [7] considered dn to include the amount of martensite which retransforms during one oscillation. Assuming that there is a critical stress (σ_c) necessary to reorientate the already existing variants or to stress-induce new variants, Q_{Tr}^{-1} becomes :

$$Q_{Tr}^{-1} = \frac{k}{J} \left\{ \frac{\partial n}{\partial T} \frac{\dot{T}}{\omega} + \frac{2}{3\pi} \sigma_0 \frac{\partial n}{\partial \sigma} \left[1 - \left(\frac{\sigma_c}{\sigma_0} \right)^3 \right] \right\} \quad (8)$$

Incorporating the possibility of stress-induced transformation, this explains the experimental observation that a small IF peak exists for $\dot{T} = 0$ and that the height of this non-transient IF peak is dependent on σ_0 .

Model of "Pure" Transformation strain : $d\epsilon_{an}(\partial n/\partial t)$

However, there is one discrepancy between the experimental results and the equations for Q_{Tr}^{-1} as presented in the model of Delorme. Experimental results showed that Q_{Tr}^{-1} does not increase linearly with \dot{T}/ω . This problem led Gremaud et al. [16] to develop a new model, which defines the role of the oscillating measuring stress for the transformation according to the Clausius-Clapeyron equation.

In the new approach of Gremaud et al. the anelastic deformation ($d\epsilon_{an}$) is related to a "pure" transformation strain, as has been proposed by Delorme in the second part of his model. The important point of the new model is that it takes into account the influence of the applied stress amplitude (σ_0) on the transformation rate ($\partial n/\partial t$). This occurs in the sense that the thermodynamic equilibrium of the material changes and the variants which are favoured by σ_0 are induced to transform. Following this idea $\partial n/\partial t$ becomes equal to:

$$\frac{\partial n}{\partial t} = \frac{\partial n}{\partial T} \cdot (\dot{T} + \alpha \cdot \dot{\sigma}) \quad (9)$$

where α is the Clausius-Clapeyron factor ($\alpha = v\epsilon'/\Delta S$), v is the molar volume and ΔS is the entropy change of the transformation.

Finally J. Stoiber [6] studied in very much detail monocrystalline and polycrystalline materials. The internal friction spectrum observed during martensitic transformation in Cu-Zn-Al alloys show significant differences when changing the microstructure of the specimen. J. Stoiber studied the effects of grain refinement and two-way shape memory training on the internal friction and found that the observed Q^{-1} peak is dependent on the microstructural properties:

- Grain refined specimens show a smaller Q^{-1} peak than specimens with a large grain size.
- Specimens with a two-way memory effect have a broad symmetric Q^{-1} peak with a relatively low Q^{-1} maximum.

From the observations a model has been developed in which the fragmentation of the martensite is taken into account [17,18]. The quantitative description of variant interactions can be conducted in terms of the model of fractal geometry [19].

The non-linear increase of the transient IF as a function of n can be explained in terms of the "fragmentation" parameter, $x(n)$, if one assumes that the additional anelastic deformation, which is due to the migration of intervariant boundaries (martensite/martensite interfaces), increases with each fragmentation.

The equation for the transient part of the IF peak (Q_{Tr}^{-1}) that is observed during martensitic phase transformations in shape memory alloys, Q_{Tr}^{-1} is now formulated as follows:

$$Q_{Tr}^{-1} = k \cdot x(n) \cdot \frac{\partial n}{\partial t} \cdot f\left(\frac{\dot{T}}{\omega \sigma_0}\right) \quad (10)$$

The new Q_{Tr}^{-1} equation accounts for the dependence of the transient IF peak on both the transformation volume fraction per cycle (Δn) and the intensity of martensite variant interactions ($x(n)$), which depends on microstructural properties of the present phase (e.g. grain size) or the transformation conditions.

The model of Stoiber can now be fitted correctly to any experimentally measured internal friction peak and can explain the differences in width or/and height of the different peaks, depending on the underlying microstructure.

1.4. The \dot{T} -effect and its consequences

The previous models describe an inherent relation between \dot{T} and Q_{Tr}^{-1} . Generally the internal friction or damping capacity of shape memory alloys are measured at a constant heating or cooling rate and thus a significant damping peak appears during transformation. However, at $\dot{T}=0$, thus at constant temperature, Q_{Tr}^{-1} becomes zero. This is also actually seen during the experiment and the remaining damping capacity remains a summation of Q_{Tr}^{-1} and Q_{PT}^{-1} . As a consequence, the damping capacity becomes a function of the volume fraction of the martensite, and the very high damping capacity *during* transformation is lost.

Table 1: Existing models of the big damping peak during martensite transformations

$\frac{\partial n}{\partial t} = \frac{\partial n}{\partial T} \dot{T}$ <p>Delorme</p> $Q_{Tr}^{-1} = \frac{k}{J} \frac{\partial n}{\partial T} \dot{T}$ $\frac{\partial n}{\partial t} = \frac{\partial n}{\partial T} \dot{T}$ <p>Delorme</p> $Q_{Tr}^{-1} = \frac{4k}{\pi J} \frac{\partial n}{\partial T} \frac{\dot{T}}{\omega \sigma_0}$	$Q^{-1} = \frac{1}{\pi J \sigma_0^2} \int \sigma d\epsilon_{an}, \quad \sigma = \sigma_0 \sin \omega t$ <p>Approach I: $d\epsilon_{an} = k \cdot \sigma \frac{\partial n}{\partial t} dt$ (transformation "plasticity")</p> <p>Approach II: $d\epsilon_{an} = k \cdot \sigma \frac{\partial n}{\partial t} dt$ ("pure" transformation strain)</p> <p>Gremaud-Bidaux</p> $Q_I^{-1} = \frac{2K}{J} \frac{\partial n}{\partial T} \frac{1 - \frac{\pi}{2\alpha} \frac{\dot{T}}{\omega \sigma_0}}{1 + \frac{\pi}{2\alpha} \frac{\dot{T}}{\omega \sigma_0}} \frac{\dot{T}}{\omega \sigma_0}, \quad \frac{\dot{T}}{\omega \sigma_0} < \frac{2\alpha}{3\pi}$ $Q_{II}^{-1} = \frac{k}{4J} \frac{\partial n}{\partial T} \left(\frac{\dot{T}}{\omega \sigma_0} + \frac{2\alpha}{\pi} \right), \quad \frac{2\alpha}{3\pi} < \frac{\dot{T}}{\omega \sigma_0} < \frac{2\alpha}{\pi}$ $Q_{III}^{-1} = \frac{k}{2J} \frac{\partial n}{\partial T} \frac{\dot{T}}{\omega \sigma_0}, \quad \frac{\dot{T}}{\omega \sigma_0} > \frac{2\alpha}{\pi}$	$\frac{\partial n}{\partial t} = \frac{\partial n}{\partial T} \dot{T} + \frac{\partial n}{\partial \sigma} \dot{\sigma}$ <p>Dejonghe</p> $Q_{Tr}^{-1} = \frac{k}{J} \left[\frac{\partial n}{\partial T} \dot{T} + \frac{2}{3\pi} \sigma_0 \frac{\partial n}{\partial \sigma} \left[1 - \left(\frac{\sigma_c}{\sigma_0} \right)^3 \right] \right]$ $\frac{\partial n}{\partial t} = \frac{\partial n}{\partial T} (\dot{T} + \alpha \dot{\sigma})$ <p>Stoiber</p> $Q_{Tr}^{-1} = k \cdot x(n) \cdot \frac{\partial n}{\partial T} \cdot f \left(\frac{\dot{T}}{\omega \sigma_0} \right)$ <p>$x(n) =$ fragmentation parameter</p>
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For applications where a continuous vibration is applied at constant temperature a 100 % martensite condition offers a more stable damping.

In the case of impact loadings with very low frequency, the two-phase region can be interesting since the martensite will be now stress-induced concurrent with an exothermic heat effect.

2. RELAXATION PEAKS IN MARTENSITE

Several types of relaxation peaks have been reported. For Ni-Ti, Hasiguti and Iwasaki [20] and Postnikow et al. [21] report a peak at 203 K with an activation energy of 0.38 eV and a frequency factor of $6 \times 10^9 \text{ s}^{-1}$. This peak might be due to a movement of dislocations or a movement of point-defect-pinned dislocations.

Tirbonod and Koshimizu [22] report a Bordoni type peak in an equiatomic Ni-Ti alloy. The presence of this peak should be due to the motion of imperfect dislocations with a Burgers vector smaller than the lattice parameter. These can be twinning dislocations but the dislocations situated at the interface between the different variants can not be ruled out. Experiments on monovariant specimens could make this matter clearer.

Cu-Al-Ni alloys with γ -martensite exhibit a twin relaxation peak as observed by Suzuki et al. [23]. The intensity of this peak is even higher than the one of the transformation peak. It is also strain-amplitude-dependent in a range from 5×10^{-5} to 3×10^{-3} . From the peak shift method an activation energy of $7.8 \times 10^4 \text{ J/mol}$ was calculated.

A similar twin relaxation peak with an activation energy at $5.15 \times 10^4 \text{ J/mol}$ has also been derived in Cu-Mn [24].

Recently a broad peak in the Au-Cd system has been presented by Y. Murakami et al. [25]. This peak is also related with the twin boundaries motion and could be a relaxational effect. It appears that the twin boundaries became less mobile with ageing, leading to changes in the internal friction spectrum.

Finally, the existence of an amplitude-dependent relaxational internal friction peak due to a competition between depinning and dragging interactions between dislocations and pinning points has been revealed by S. Kustov in β_1 Cu-Al-Ni martensite [26].

3. APPLICATION ORIENTED RESEARCH BASED ON THE MARTENSITIC TRANSFORMATION

3.1 Damping by pseudoelastic loading

When shape memory alloys are loaded above the A_f -temperature, martensite will be induced at a critical stress (Fig. 3). This stress remains almost constant during further straining, until the sample is completely martensite. Further straining will lead again to a stress increase, due to elastic loading of the martensite.

Unloading leads to the reverse transformation ending at the initial shape of the sample. The unloading stress-plateau however is below the loading stress-plateau, creating a hysteresis loop.

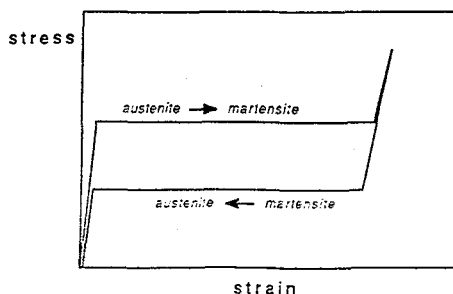


Figure 3: A pseudoelastic loop showing the hysteresis after loading and unloading.

The area enclosed by the hysteresis loop is proportional to the energy absorbed and thus to the damping capacity during this type of transformation.

Since large superelastic strains can be obtained up to 8% in polycrystalline Ni-Ti, this property is now very much under investigation for applications in large structures such as buildings in seismic active regions [27] or to damp low frequency vibrations in space structures [28].

For those applications a high loading and low unloading plateau is optimal. This is reached by alloys with a large transformation hysteresis such as Ni-Ti-Nb alloys. However the system shows two disadvantages:

1. The stresses at which the transformation occurs, increase linearly with temperature which can be explained by the Clausius-Clapeyron equation:

$$\frac{\Delta \sigma^{p-m}}{\Delta T} = \frac{\Delta S}{\epsilon_{\max}}$$

where σ^{p-m} is the critical stress during loading, T the absolute temperature, ΔS the entropy change and ϵ_{\max} the total transformation strain.

2. The damping is frequency dependent. The reason is that during the forward transformation (beta→martensite, loading) the transformation occurs exothermic. During unloading, the transformation occurs endothermic. The combination of the hysteresis and the heat effects influence the total damping capacity that goes through a maximum as function of temperature [29].

3.2 Smart materials

Shape memory alloys can be used as actuators in so-called smart materials. One of the envisaged application is the damping of resonance vibrations of panels. For this purpose, strained shape memory wires are embedded in the composite structure. In case of resonance vibration, the wires can be externally heated to transform. Since the wire is constrained in the panel it cannot exhibit the memory effect, thereby creating high internal stresses during transformation. Those stresses change the internal energy of the plate leading to a shift of the resonance frequency so that the actual vibration will stop.

For the same type of purpose also the significant modulus-defect or modulus change during the martensitic transformation has interesting possibilities. Depending on material type, texture orientation and microstructure, large modulus changes can be obtained [30] leading to significant changes in resonance frequencies in a small temperature range.

Conclusion

During recent years significant progress has been made in identifying the influencing parameters and the modellisation of the internal friction behaviour during the martensitic transformation of shape memory alloys.

The complexity of the microstructure, the concentration, distribution and interaction of different types of defects however must be taken into account when results are compared for identical and different systems.

The explosive growth of shape memory alloy applications has also raised the question of transformation and phase stability, the influence of frequency and temperature and the influence of the thermomechanical processing leading to different microstructures.

Observations of relaxational effects during the transformation and in the martensitic state can help in the further understanding of these fascinating structures.

This paper has paid mainly attention to the internal friction during transformation. But it should be stated that internal friction is still an underestimated tool for the study of the martensitic phase itself. As an example, Y. Liu et al. [31] have recently shown that a linear relation exists between the reorientation stress level in Ni-Ti alloys at strains between 2 and 6%, stresses between 150 and 200 MPa, and the

damping capacity of the martensitic phase at room temperatures where strains of only 10^{-5} are applied [28].

So there is an appeal to internal friction to become a handsome tool for the investigation of other functional properties of shape memory alloys and the understanding of the role of the microstructure on those properties.

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