Internal friction of R-phase and B19′ martensite in equiatomic TiNi shape memory alloy under isothermal conditions

S.H. Chang, S.K. Wu *
Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

Received 6 May 2006; received in revised form 19 July 2006; accepted 19 July 2006
Available online 6 September 2006

Abstract
The intrinsic internal friction IFI of R-phase and B19′ martensite are composed of static internal friction IFS and dynamic internal friction IFD. The tan δ values of IFRS and IFB19′S are both proportional to σ0/υ1/2 and are related to the stress-assisted motions of twin boundaries. The tan δ values of IFRS are higher than those of IFB19′S owing to the softer storage modulus E0 in R-phase. The tan δ values of IFB19′D are linearly proportional to T/υ1/2. The occurrence of relaxation peak at ≈−60 °C is found to come from the IFB19′S, instead of the IFB19′D.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Shape memory alloy; Thermal (dynamic mechanical) analysis; Internal friction; Martensite

1. Introduction
TiNi alloys are known as important shape memory alloys (SMAs) because of their functional properties such as shape memory effect and superelasticity [1]. Many reported studies revealed that TiNi SMAs exhibit a high internal friction peak associated with a shear modulus minimum during martensitic transformation and thus are suitable for the energy dissipation applications [2–9]. The damping characteristics of internal friction peak during martensitic transformation are associated with experimental parameters such as temperature rate T, frequency υ and amplitude σ0. It is also reported that both R-phase pre-martensite and B19′ martensite in TiNi SMAs perform a high damping property due to the easy movement of their twin boundaries in between the variants [5]. Besides, the occurrence of R-phase can strongly soften the storage modulus E0 and thus promotes the TiNi SMAs’ damping capacity [10]. In addition to the internal friction peaks in TiNi SMAs, there is also a relaxation peak appearing at temperature around 200 K. Iwasaki and Hasiguti [2] proposed that this relaxation peak is thermally activated and originates from dislocations.

It has been proposed that the internal friction of a first-order phase transformation can be decomposed into three terms: IFTr, IFPT and IFI [11–17]. The first term IFTr is the transitory internal friction which appears only at low υ and non-zero T. It depends on external parameters such as T, υ, σ0 and volume fraction transformed per unit time. The second term IFPT is the internal friction due to the phase transformation, but it does not depend on T. The third term IFI is the intrinsic internal friction of austenitic or martensitic phase measured at constant T and strongly dependent on microstructure properties such as dislocations, vacancies and twin boundaries. In the low frequency range, the internal friction peak observed during transformation is mainly ascribed to the first term IFTr. In equiatomic TiNi SMA, Chang and Wu [18] reported that the inherent internal friction (IFPT + IFI) measured under isothermal conditions during B2 → R and R → B19′ martensitic transformation are linearly proportional to σ0/υ1/2 but independent of T. The damping mechanism of the inherent internal friction (IFPT + IFI) is mainly generated from the stress-assisted martensitic transformation and stress-assisted motions of twin boundaries. However, all the reported studies focus on the damping characteristics of transitory and inherent internal friction (IFTr, IFI or IFPT + IFI) during martensitic transformation. The damping characteristics of the single phase in TiNi SMAs, such as B2 parent phase, R-phase premartensite and B19′ martensite, under isothermal conditions have not been systematically studied before. In this study, the damping capacity tan δ values of a Ti50Ni50 SMA which exhibits a two-stage B2 → R → B19′ martensitic transformation during cooling are measured by dynamic mechanical
Equiatomic Ti<sub>50</sub>Ni<sub>50</sub> alloy was prepared by conventional vacuum arc remelting. The as-melted ingot was hot-rolled at 850 °C into a 2 mm thick plate and then the plate was solution-treated at 850 °C for 2 h followed by quenching in water. Then, the plate was cold-rolled at room temperature along the hot-rolling direction and reached a final 30% thickness reduction. Subsequently, the cold-rolled plate was cut into test specimens with the dimension of 40 mm × 5 mm × 1.26 mm, sealed in an evacuated quartz tube and annealed at 650 °C for 2 min. The detailed procedure for preparing specimen is demonstrated in another paper [18].

Transformation temperatures of cold-rolled and annealed specimen were determined by differential scanning calorimetry (DSC) test using a TA Q10 DSC equipment with a constant cooling rate of 10 °C/min. Specimen for DMA experiment was cut along the rolling direction to eliminate the influence of rolling texture [19]. The tan δ and storage modulus E<sub>0</sub> were measured by a TA 2980 DMA equipment using a constant cooling rate of 3 °C/min. The isothermal damping characteristics of B2, R-phase and B19′ martensite were also investigated by DMA but tested under isothermal conditions using various amplitudes and frequencies. The detailed procedure for the isothermal DMA test was conducted as follows. The specimen was initially cooled starting from 150 °C at a constant cooling rate (1, 3 or 5 °C/min) and was kept isothermally for 30 min at the set temperature. After being isothermal for 30 min, the specimen was heated up to 150 °C to ensure it had returned to B2 parent phase. Then, the specimen was cooled to another set temperature and kept isothermally at that temperature for 30 min. During the isothermal conditions, the set temperature was chosen in between +80 °C and −80 °C in which B2, R-phase and B19′ martensite are all included.

3. Experimental results

3.1. DSC and DMA measurements at constant T

Fig. 1 shows the DSC and DMA curves of 30% cold-rolled Ti<sub>50</sub>Ni<sub>50</sub> alloy annealed at 650 °C for 2 min. As shown in Fig. 1, there are two transformation peaks, i.e. B2 → R and R → B19′ obtained in DSC cooling curve. There are also two transformation peaks appearing in the tan δ curve which correspond to B2 → R and R → B19′ transformation peaks in DSC curve. Except the aforementioned tan δ transformation peaks, an extra broad peak which is not observed in DSC curve appears at about −65 °C in tan δ curve. This extra broad peak is known as the relaxation peak [2,4]. Also from Fig. 1, the E<sub>0</sub> curve declines gently in B2 parent phase while cooling, then drops drastically and exhibits a deeper minimum during B2 → R transformation and a shallower minimum during R → B19′ transformation. After R → B19′ transformation completes, the E<sub>0</sub> value of B19′ martensite increases quickly with decreasing temperature.

3.2. DMA measurement under isothermal conditions

Fig. 2 plots the tan δ values versus isothermal interval when the specimen of Fig. 1 is tested by DMA under isothermal treatment at 60 °C (B2 parent phase), 12.5 °C (R-phase) and −60 °C (B19′ martensite) for 0–30 min. As shown in Fig. 2, the measured tan δ values of B2 parent phase are almost the same in the whole isothermal conditions. However, both the measured tan δ values of R-phase and B19′ martensite decrease with increasing isothermal intervals and reach a steady value after 10–15 min. As illustrated in Fig. 2, the tan δ values of R-phase and B19′ martensite are composed of a dynamic term IF<sub>D</sub> which diminishes during isothermal conditions and a static term IF<sub>S</sub> which is the steady value measured after 30 min of isothermal interval.

In order to investigate the damping characteristics of IF<sub>S</sub> and IF<sub>D</sub> for B2, R-phase and B19′ martensite under isothermal conditions, DMA tan δ tests under 30 min isothermal interval at different temperatures were conducted with various T, υ, σ<sub>0</sub> and the results are exhibited in Figs. 3–5, respectively. Fig. 3(a)–(c) show the tan δ curves (empty mark curves) measured after 30 min isothermal interval at different temperatures when the specimen is conducted at the cooling rate T of 1, 3 and 5 °C/min, respectively. At lower temperatures, the tan δ values of IF<sub>S</sub> are quite low and approximately same as those measured at constant T of 1, 3 and 5 °C/min, respectively.

In Figs. 4 and 5, the tan δ curves measured at constant T (solid line curves, T = 1 °C/min) are also plotted for comparison. As shown in Figs. 3–5, all the tan δ values of B2 parent phase measured after isothermal conditions, i.e. IF<sub>B2/0</sub>, are much higher than those of IF<sub>S</sub>. However, the tan δ values of B19′ martensite measured after isothermal conditions, i.e. IF<sub>B19′/S</sub>, decline quickly after R → B19′ transformation completes. With further isothermal treatment at lower temperatures, the tan δ values of IF<sub>B2/0</sub> also exhibit a relaxation peak at around −60 °C. Fig. 6 enlarges the diagram of B19′ martensite region in Fig. 3(a) and then to describe the decayed and steady tan δ values measured under isothermal conditions. As illustrated in Fig. 6, the intrinsic internal friction IF<sub>B19′/S</sub> of B19′ martensite measured at constant T is composed of IF<sub>B19′/S</sub> and IF<sub>B19′/D</sub>.
4. Discussion

4.1. IF$_S$ of B2 parent phase, R-phase and B19' martensite

From the DMA results exhibited in Figs. 3–5, all the internal friction of IF$_{B2}^S$ are very low and their tan$\delta$ values associated with $T$, $\nu$ and $\sigma_0$ are inconspicuous to investigate. Thus, only the effects of $T$, $\nu$ and $\sigma_0$ on IF$_{B2}^S$ and IF$_{B19'}^S$ are discussed in the following. Fig. 7(a) plots the tan$\delta$ values of IF$_{B2}^S$ and IF$_{B19'}^S$ as a function of $T$ measured at 20°C and $-20$°C, respectively, in Fig. 3. From Fig. 7(a), both the tan$\delta$ values of IF$_{B2}^S$ and IF$_{B19'}^S$ almost keep constant when measured at different $T$. This fea-
The intrinsic tan δ curves measured under isothermal conditions at \( \dot{T} = 1 \, ^\circ \text{C}/\text{min} \) and \( \nu = 1 \, \text{Hz} \) with different amplitudes of (a) \( \sigma_0 = 5 \, \mu \text{m} \) (empty circle curve); (b) \( \sigma_0 = 10 \, \mu \text{m} \) (empty triangle curve); and (c) \( \sigma_0 = 15 \, \mu \text{m} \) (empty diamond curve).

Fig. 5. The intrinsic tan δ curves measured under isothermal conditions at \( \dot{T} = 1 \, ^\circ \text{C}/\text{min} \) and \( \nu = 1 \, \text{Hz} \) with different amplitudes of (a) \( \sigma_0 = 5 \, \mu \text{m} \) (empty circle curve); (b) \( \sigma_0 = 10 \, \mu \text{m} \) (empty triangle curve); and (c) \( \sigma_0 = 15 \, \mu \text{m} \) (empty diamond curve).

The figure indicates that the tan δ values of IF\( _{\text{R}} \) and IF\( _{\text{B19'}} \) are both independent of \( \dot{T} \). Fig. 7(b) and (c) plot the tan δ values of IF\( _{\text{R}} \) and IF\( _{\text{B19'}} \) as a function of \( 1/\nu^{1/2} \) and \( \sigma_0 \) measured at 20 °C and \(-20\, ^\circ\text{C}\), respectively, in Figs. 4 and 5. As seen in Fig. 7, both IF\( _{\text{R}} \) and IF\( _{\text{B19'}} \) are linearly proportional to \( \sigma_0/\nu^{1/2} \) but independent of \( \dot{T} \) when the applied \( \nu \) and \( \sigma_0 \) are in between 0.1–10 Hz and 1–15 \( \mu \text{m} \), respectively. This behavior is same as the damping characteristic of the inherent internal friction IF\( _{\text{PT}} \) + IF\( _{\text{I}} \) of B\( _2 \) \( \rightarrow \) R and R \( \rightarrow \) B19’ martensitic transformations which is also linearly proportional to \( \sigma_0/\nu^{1/2} \) and independent of \( \dot{T} \) [18]. Therefore, the inherent internal friction IF\( _{\text{PT}} \) + IF\( _{\text{I}} \) of B\( _2 \) \( \rightarrow \) R and R \( \rightarrow \) B19’ martensitic transformations and IF\( _{\text{S}} \) of the single R-phase and B19’ martensite may originate from the similar damping mechanism. Since the inherent internal friction IF\( _{\text{PT}} \) + IF\( _{\text{I}} \) is mainly generated from stress-assisted martensitic transformation and stress-assisted motions of twin boundaries [18], the damping mechanism of IF\( _{\text{R}} \) and IF\( _{\text{B19'}} \) is proposed to be contributed by the stress-assisted movements of twin boundaries in between the variants of R-phase and B19’ martensite, respectively.

From Figs. 3–5, all the measured tan δ values of IF\( _{\text{B2}} \) are quite low and very close to those of IF\( _{\text{I}} \). This feature indicates that IF\( _{\text{B2}} \) is mainly contributed by the IF\( _{\text{S}} \) while IF\( _{\text{D}} \) is insignificant in B\( _2 \) parent phase. Also from Figs. 3–5, both tan δ values of IF\( _{\text{S}} \) and IF\( _{\text{B19'}} \) are much higher than those of IF\( _{\text{B2}} \). IF\( _{\text{S}} \) exhibits a rather small intrinsic internal friction because its tan δ only comes from the dynamic/static hysteresis of lattice defects [5]. On the other hand, from DMA results shown in Figs. 3–5, both IF\( _{\text{R}} \) and IF\( _{\text{B19'}} \) have higher tan δ values than those of IF\( _{\text{B2}} \) due to their abundant twin boundaries in between the variants which can be easily moved by the external stress to accommodate the applied strain. This characteristic indicates that the effect of twin boundaries on internal friction is more dominant than that of the lattice defects/dislocations introduced by cold-rolled and annealed treatment. Since the internal friction of IF\( _{\text{S}} \) and IF\( _{\text{B19'}} \) are mainly contributed by stress-assisted motions of twin boundaries, the effect of defects/dislocations due to thermal/mechanical process on damping behavior can be neglected in this study. Furthermore, Figs. 3–5 also show that the tan δ values of IF\( _{\text{S}} \) are always higher than those of IF\( _{\text{B19'}} \) measured at the same experimental parameter. This feature comes from the fact that the lower storage modulus \( E_0 \) in R-phase, as shown in Fig. 1, leads to the easier movement of twin boundaries in R-phase and hence dissipates more energy during damping than B19’ martensite.
Fig. 7. The tanδ values of IFS and IFB19′ measured in Figs. 3–5 at 20 °C and −20 °C as a function of (a) \( \dot{T} \); (b) \( 1/\sqrt{\nu} \); and (c) \( \sigma_0 \).

4.2. IFD of B19′ martensite

As illustrated in Fig. 6, when the specimen is kept isothermally at B19′ martensite, the decayed tanδ value represents the IFB19′D. The damping behavior of IFR is suggested to be similar to that of IFB19′, but IFR damping is difficult to measure due to the R-phase having a narrow existing temperature range, as shown in Fig. 1. As a result, only IFB19′D is discussed in detail in the following.

Fig. 8. The tanδ values of IFB19′ vs. temperature obtained at (a) different \( T \) in Fig. 3; (b) different \( \nu \) in Fig. 4; and (c) different \( \sigma_0 \) in Fig. 5.
Fig. 8(a) plots the tan δ values of IFD(19') versus temperature in which IFD(19') is calculated by subtracting IFB(19) from IFD(19') measured at different T in Figs. 3 and 6. The temperature deviation of IFB(19) and IFD(19') has been corrected by the peak temperature shift of $O \rightarrow 19'$ transformation to eliminate the influence of T. Fig. 8(b) and (c) show the tan δ values of IFD(19') as a function of temperature at different $\nu$ measured in Fig. 4 and at different $\sigma_0$ measured in Fig. 5, respectively. As shown in Fig. 8, the tan δ values of IFD(19') increase with T but decrease with $\nu$ and almost independent of $\sigma_0$. Fig. 9(a) and (b) plot the tan δ values of IFD(19') as a function of T and 1/$\nu^{1/2}$, respectively, in which IFD(19') is measured at different temperatures ($-20^\circ C$, $-30^\circ C$, $-40^\circ C$ and $-50^\circ C$). As shown in Figs. 8(c) and 9, all the tan δ values of IFD(19') are independent of $\nu$ and $\sigma_0$ when the applied T and $\nu$ are in between 1–5°C/min and 0.1–10 Hz, respectively. This relationship is quite similar to that of IFR and IFB(19) except that the term $\sigma_0$ is now replaced by T. This feature demonstrates that the damping mechanism of IF(19) is generated by stress-assisted movements of twin boundaries while that of IFD is contributed by thermal-assisted motions of twin boundaries. Furthermore, Fig. 8 shows that IFD(19') does not exhibit a broad peak at around $-60^\circ C$ as IFB(19) shown in Figs. 3–5. This indicates the occurrence of relaxation peak only comes from the IFD(19'), instead of the IFB(19').

5. Conclusions

The intrinsic internal friction IF of R-phase and B19' martensite measured at constant T is both composed of a static term IF(19) which keeps steady after isothermal conditions and a dynamic term IFD which diminishes during isothermal conditions. Both tan δ values of IF(19) and IFB(19) are linearly proportional to $\sigma_0\nu^{1/2}$ when the applied $\nu$ and $\sigma_0$ are in between 0.1–10 Hz and 1–15 μm, respectively. Consequently, the damping mechanism of IF(19) and IFB(19) is associated with stress-assisted movements of twin boundaries in between the variants of R-phase and B19' martensite, respectively. The tan δ value of IF(19) is higher than that of IFB(19) because the R-phase has softer storage modulus $E_0$ which leads to easier movement of twin boundaries in R-phase and dissipates more energy during damping. The tan δ value of IFD(19') increases linearly with $T/\nu^{1/2}$ and is independent of $\sigma_0$ when the applied T and $\nu$ are in between 1–5°C/min and 0.1–10 Hz, respectively. It implies that the damping mechanism of IF(19) is due to thermal-assisted motions, instead of stress-assisted movements, of twin boundaries in B19' martensite. The occurrence of relaxation peak at about $-60^\circ C$ only comes from the IFD(19'), instead of the IFB(19').

Acknowledgement

The authors gratefully acknowledge the financial support for this research provided by the National Science Council (NSC), Taiwan, Republic of China, under Grants Nos. NSC94-2216-E-002-030.

References